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Prediction of chemical speciation in stabilized/solidified wastes using a general chemical equilibrium model

Part I. Chemical representation of cementitious binders

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Abstract

Chemical equilibrium models are useful to evaluate stabilized/solidified waste. A general equilibrium model, SOLTEQ, a modified version of MINTEQA2 for S/S, was applied to predict the chemical speciations in the stabilized/solidified waste form. A method was developed to prepare SOLTEQ input data that can chemically represent various stabilized/solidified binders. Taylor's empirical model was used to describe partitioning of alkali ions. As a result, SOLTEQ could represent chemical speciation in pure binder systems such as ordinary Portland cement and ordinary Portland cement + fly ash. Moreover, SOLTEQ could reasonably describe the effects on the chemical speciation due to variations in water-to-cement, fly ash contents, and hydration times of various binder systems. However, this application of SOLTEQ was not accurate in predicting concentrations of Ca, Si, and SO_4 ions, due to uncertainties in the CSH solubility model and K_{sp} values of cement hydrates at high pH values.

Keywords: Modeling; Waste management; Calcium-silicate-hydrate; Alkalis

Stabilization/solidification (s/s) is the technology that uses binding materials such as cement, fly ash, lime, or organic polymers to transform a waste into a more manageable form and/or into a less toxic form by physically and/or chemically immobilizing the waste contaminants [1]. Stabilization/solidification is a widely used technology for hazardous waste management, and it is the most commonly used technology at Superfund sites [2]. The goal of s/s for hazardous wastes is the safe, ultimate disposal of the wastes through landfilling or other alternatives by containing waste contaminants and preventing or minimizing the release of the contaminants into the environment [1,3].

An approach for evaluating the stabilized/solidified wastes involves the combination of a leach model and a chemical equilibrium model. Batchelor [4,5] developed simple leaching models that, when combined with a chemical equilibrium model or laboratory leaching test, could be applied to simulate laboratory leaching conditions or long-term leaching behavior. Based on MINTEQA2 [6], Batchelor and Wu [7] developed the generic chemical equilibrium model, SOLTEQ, which can calculate activity coefficients for high ionic strength solutions occurring in the s/s waste forms and can describe the variable stoichiometry and incongruent solubility of calcium-silicate-hydrate (CSH). Activity coefficients are calculated with the Pitzer ion interaction model [8] using interaction parameters suggested by Reardon [9]. CSH solubility is described by an empirical model developed by Reardon [9]. Batchelor and Wu [7] illustrated how SOLTEQ containing a thermodynamic database of compounds in various waste/binder systems can be linked to the simple leaching model to predict leaching. They emphasized that such a model could serve as a flexible framework to coordinate knowledge on the chemistry of contaminants and binders and that it could be applied to predict chemical speciation in various binder/waste systems, even when it was not used to predict leaching.

To apply a general chemical equilibrium model like SOLTEQ to predict the chemical speciation of compound in various waste/binder systems, two steps must be taken. First, an appropriate thermodynamic database must be prepared. Second, techniques for describing initial characteristics of the s/s binders and waste in terms of the chemical components used by the model must be developed. Developing such techniques requires sufficient knowledge of the true phase composition (clinker phases) of raw binders, their hydration chemistry, and thermodynamic properties of their hydration products. Such knowledge allows various s/s

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binders to be chemically represented using basic and readily available pieces of information such as oxide composition of cement and/or fly ash, water-to-cement (w/c) ratio, and types of doped waste contaminants. If a chemical equilibrium model can have well-represented input data for various s/s binders, it will be very useful in designing s/s binder systems because it can predict the chemical speciation in the various s/s wastes and it can be linked to leaching models to predict long-term leaching behavior of such s/s wastes.

Successful chemical representation of a waste/binder system requires collection of accurate thermodynamic properties for individual s/s hydration products as well as for combinations of such products. Although the solubility properties of some s/s hydration products such as portlandite and brucite are well known, those of others are still uncertain, especially at the high pH values that normally occur in cement porewater.

Another requirement for good chemical representation is the ability to describe the uptake of alkali ions by cement hydrates [7,10–12]. Upon hydration of cement, alkali ions become the principal cations that affect the pH of the porewater. Because the pH greatly influences the chemical speciation in the s/s wastes, this ability is indispensable. Taylor [13] offered an empirical model to describe partitioning of alkali ions.

The purpose of this paper is to expand the usefulness of SOLTEQ by developing procedures that can provide SOLTEQ with input data that chemically represents various s/s binder systems. Such procedures were evaluated by simulating the pore solutions of various s/s binder systems and by comparing the results with published experimental data. Solubilities of s/s hydration products also were evaluated.

1. Hydration chemistry of cement-based binders

The calcined product of the cement consists mainly of four mineral phases: alite (C_3S), belite (C_2S), aluminate (C_3A), and ferrite (C_4AF). Other phases are free lime (CaO) and gypsum ($CaSO_4 \cdot 2H_2O$). Hydration of cement has been studied extensively. Alite and belite are hydrated to CSH and portlandite. When lime and gypsum are present, aluminate is hydrated into calcium aluminate hydrate (C_4AH_{13}) [14]. This reaction is immediately followed by the formation of ettringite from gypsum. Hydration chemistry of fly ash is poorly understood because detailed information on the composition of hydration products is insufficient [13]. However, siliceous glass in fly ash is known to react with free $Ca(OH)_2$ from cement to form CSH [15]. The provision of silica, aluminum, alkalies, and other components from the fly ash results in a decrease in the Ca/Si ratio of CSH and in the formation of a product especially high in Si and Al that replaces the fly ash particles [13]. Aitcin et al. [16] reported that major hydrates from fly ash reacting with lime were CSH, C_4AH_{13}, ettringite, and Ca-carboaluminate.

Gypsum, portlandite, and brucite are crystalline phases that have well-defined solubilities [17]. CSH is an amorphous gel phase of variable Ca and Si composition whose solubility behavior is still the subject of many studies. Ettringite, monosulfate, and C_4AH_{13} are aluminum-bearing and calcium sulfate phases in which ferric iron often substitutes for aluminum. Table 1 shows the solubility properties of principal cement hydrates. As shown in Table 1, Reardon [9] introduced two quadratic expressions to represent the incongruent solubility of CSH as a function of the activity ratio (r) of Ca^{2+} to $H_4SiO_4^0$. These expressions were used in developing SOLTEQ [7]. In Reardon's recent study [10], this CSH model was revised with the adoption of different values for the dissociation constants of silicic acids. The maximum pH of the CSH solubility data that had been used in the regressions for both models was 12.5, the limit of portlandite saturation. Accordingly, the limitation of those CSH models was also imposed at pH 12.5. However, Reardon [10] reported that the extrapolation of the new model had a good representation for the CSH solubility in the experiments at the higher solution pH up to 14.

Berry et al. [18] reported that more K^+ than Na^+ was taken up from various pore solutions in the Portland cement system. By monitoring the pore solutions of silica fume-blended cement pastes, Larbi et al. [12] suggested that Na^+ and K^+ as well as OH^- and Ca^{2+} became chemisorbed on the negatively charged silicon groups after the silica had been attacked by the OH^- ions in the liquid phase to form alkali-rich silicates. Taylor [13] proposed an empirical model for predicting the concentrations of the alkali ions in the cement porewater. He set up mass–balance relationships assuming that the amount of alkali ions taken up by the amorphous hydration products, such as CSH and monosulfate, is linearly proportional to the concentration of alkali ions in the pore solution. Taylor determined the empirical constants for the partitioning of Na^+ and K^+ using a wide range of experimental data.

2. Model development and evaluation procedure

A method was developed to provide SOLTEQ with input data by representing various binder systems as a composition of minerals of which the solubility properties are known. This method requires information about the oxide compositions of binder materials and the hydration time of the binder paste as input. It converts the oxide compositions into the liquid and solid phase compositions of the hydrated binder materials whose solubility properties are available in the SOLTEQ database. This method was programmed using a popular spreadsheet software for binder systems of ordinary Portland cement (OPC), OPC + fly ash (FA) or lime, and lime + fly ash, which is available upon request. A summary of the method is given in the following.

In the method for OPC, the oxide composition of OPC is converted by the Bogue calculation [19] into the mineralogical phase compositions of alite, belite, aluminate, and ferrite. Then, the available mineralogical phase compositions at the given hydration time are determined using Taylor's

Table 1
Solubility properties of principal cement hydrates at 25°C

Hydrate	Reaction	log K_{sp}	
		Reardon [10]	SOLTEQ database*
Portlandite	$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$	-5.19	-5.321
Ettringite	$Ca_6Al_2O_6(SO_4)_3 \cdot 32H_2O \rightarrow 6Ca^{2+} + 2Al\ (OH)_4^-\ 1\ 3SO_4^{-2} + 4OH^- + 6H_2O$	-43.94 ± 0.36	-43.13
Monosulfate	$Ca_4Al_2O_6SO_4 \cdot 12H_2O \rightarrow 4Ca^{2+} + 2Al(OH)_4^- + SO_4^{-2} + 4OH^- + 6H_2O$	-29.25 ± 0.5	-27.62
C_4AH_{13}	$4CaO \cdot Al_2O_3 \cdot 13H_2O \rightarrow 4Ca^{2+} + 2Al(OH)_4^- + 6OH^- + 6H_2O$	—	-27.49
CSH[†]	$xCaO \cdot SiO_2 \cdot xH_2O + H_2O \rightarrow xCa^{2+} + H_3SiO_4^- + (2x - 1)OH^-$	$-4.507 - 1.3306r - 0.019172r^{2‡}$	$-9.044 + 0.568r - 0.193r^{2§}$

* Based on reference [9] except for portlandite.

[†] x = Ca/Si ratio in CSH, $r = \log(\{Ca^{2+}\}/\{H_4SiO_4^0\})$.

[‡] r is determined by the equation: $x = 0.48548 + 0.11563r + 0.0104536r^2$.

[§] r is determined by the equation: $x = 0.88 + 0.03\exp(0.513r)$.

empirical equations [13] for the hydrated fraction of each mineralogical phase. The available mineralogical phases are converted to the hydrate compositions using the hydration stoichiometry given in Table 2. Finally, the concentrations of aqueous species and finite solids as input data for SOLTEQ are obtained by using the porewater volume calculated according to Taylor [13].

There is no established procedure to convert the oxide compositions of fly ash to the mineralogical phase composition, because fly ash is an extremely variable material. Therefore, the SOLTEQ input preparation method for OPC + FA requires input of the mineralogical phase compositions as well as the oxide compositions of the blended fly ash. However, a set of default values for type F fly ash was obtained from the literature [16,20]. The method was designed to calculate the oxide composition of the glass phase in fly ash by the mass–balance relationship between the two compositions. Another important input for this method is the percentage replacement of the fly ash to the total weight of binder materials.

Using empirical equations for hydration rate of fly ash [13], the available amounts of glass, carbon, and alkalies at the given hydration time were calculated with a similar manner described in the method for OPC. Based on observations [13,15,16] for hydration of fly ash, the following mass–balance relations were derived: 1) only the glass phase in fly ash participates in the hydration; 2) CaO in fly ash is hydrated to portlandite; 2) free carbon forms Ca-carboaluminate with the portlandite that is produced by hydration of cement and fly ash [Eq. (1)]; 4) sulfate reacts with portlandite and aluminate to form ettringite; 5) portlandite consumes remaining aluminate to form C_4AH_{13}; and, 6) CSH is produced from the reaction of silicate and remaining portlandite.

$$2Ca(OH)_2 + CO_2 + Al_2O_3 + 9H_2O \rightarrow CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O. \tag{1}$$

Table 2
Hydration stoichiometry used in SOLTEQ input preparation method

Clinker phase	Hydration stoichiometry	Hydration product
Alite, belite	$C_xS + (x + 1)H \rightarrow C_gSH_{(1+g)} + (x - g)CH$	CSH, portlandite
Aluminate	$C_3A + CH + 12H \rightarrow C_4AH_{13}$	C_4AH_{13}
Ferrite	$C_4AF + 2CH \rightarrow 2C_3A_{0.5}F_{0.5} + 2H$	Incorporated into C_3A
With Gypsum	$C_4AH_{13} + 3C\overline{S}H_2 + 14H \rightarrow C_3A3C\overline{S}H_{32} + CH$	Ettringite, portandite
Free MgO	$MgO + H_2O \rightarrow Mg(OH)_2$	Brucite

These mass–balance relations were used to obtain the hydrate compositions of the blended fly ash. Then, the hydrate compositions were added to the separate hydrate compositions of OPC to provide the total hydrate compositions of OPC + FA. Finally, the SOLTEQ input data were prepared using the total hydrate compositions and the calculated porewater volume.

In summary, the method used for stoichiometric calculation of OPC was modified to allow the contributions of SiO_2, Al_2O_3, alkalies, and other components from the fly ash. Empirical equations were used to consider the changed hydration rates of the mineralogical phases and the decrease of portlandite formation due to fly ash addition. Similarly, the SOLTEQ input preparation methods of OPC + lime and lime + fly ash were developed by modifying those of OPC and OPC + FA considering the contributions of lime. The added lime was assumed to be hydrated into portlandite.

The pore solution compositions was simulated to evaluate the SOLTEQ input preparation method. Taylor's empirical model [13] was used to predict the amount of alkali ions in the cement porewater after partitioning. Table 3 shows the porewater analyses from four references [12,18,21,22] that were used in this work. The SOLTEQ input preparation method calculated the compositions of aqueous species and finite solids at the given conditions using the oxide compositions of the raw binder materials used for the porewater analyses. These compositions were input to SOLTEQ to provide the equilibrium speciations of all soluble and solid species for each porewater analysis in Table 3. Pitzer − $B^{\bullet}$ option in SOLTEQ was selected to calculate activity coeffi-

Table 3
Pore solution analyses for SOLTEQ simulations

Reference	Berry et al. [18]	Larbi [12]	Diamond [21]	Trussell and Batchelor [22]
Binder system	OPC, OPC + FA	OPC	OPC, OPC + FA	OPC
W/C ratio	0.475 ∼ 0.484	0.4, 0.45, 0.56	0.4	0.4, 0.7, 1.0
Hydration time (days)	28	28	10, 30, 174	28
Doped wastes	None	None	None	Cd*, Cr(VI), Pb, Hg

* Heavy metal ions had been added in the forms of $Cd(NO_3)_2$, Na_2CrO_4, $Pb(NO_3)_2$, and $Hg(NO_3)_2$.

cients with Pitzer ion interaction model for primary components combined with the B$^{\bullet}$ method for contaminants [7].

3. Results and discussion

Table 4 illustrates some of the SOLTEQ input data that were obtained by applying the input preparation method to three analyses [12,18,21]. The outcome of this method is the compositions of soluble components and finite solids [6].

In Fig. 1, the measured porewater concentrations of experiments by Berry et al. [18] were compared with the predictions made by SOLTEQ using Taylor's model for alkali partitioning. The predicted concentrations of alkali ions were very close to the measured concentrations despite variations of fly ash contents from 0% to 30%. This implies that using Taylor's model in the SOLTEQ input preparation methods for OPC and OPC + FA can effectively describe the change of alkali ion concentrations due to the dilution effect of the blended fly ash. The OH^- concentrations also were predicted well.

The simulation results using data from Larbi [12] are presented in Fig. 2a and shows the effect of w/c ratio on predicted and measured concentration of Na^+, K^+, and OH^-. The trend of measured values agreed well with that of predicted values with respect to the variation of w/c ratio from 0.4 to 0.56. This indicates that the input preparation method for OPC can effectively describe the effect of the w/c ratio increase on chemical compositions of the porewater. Fig. 2b shows the simulation result of data from Diamond [21] and shows the effects of hydration time. The SOLTEQ prediction with Taylor's model could accurately represent the changes of chemical compositions due to the change of hydration time. The trend of measured values was well maintained in the predicted values older than 30 days. Measured values show peaks at 10 day unlike predicted values. Both Diamond [21] and Larbi et al. [12] reported these temporary peaks, which may be related to the kinetics of sorption of alkali ions onto cement hydrates. SOLTEQ predictions do not follow this temporary trend at the early stage of hydration.

Table 4
Typical SOLTEQ input data for porewater simulation prepared by the input preparation method

Reference	Berry et al. [18]	Larbi [12]	Diamond [21]
Binder system	OPC + FA	OPC	OPC + FA
FA content (%)	30	0	30
Hydration time (days)	28	28	174
W/C ratio	0.475	0.4	0.4
Total soluble component (mole/L)			
T-NA$^+$	0.055	0.150	0.115
T-K$^+$	0.336	0.522	0.243
T-H$^+$	−0.391	−0.672	−0.358
Finite solid (mole/L)			
CSH (Ca/Si = 1.2))	5.980	13.83	15.95
Portlandite	3.674	16.47	5.042
C_4AH_{13}	1.468	3.412	3.017
Ettringite	0.254	0.636	0.307
Ca-carboaluminate	0.212	—	0.545
Brucite	0.272	0.851	0.701

Although this application of SOLTEQ could successfully describe the behavior of alkali ions as well as hydroxide ion, it shows some limitations in predicting porewater concentrations of Ca, Si, and SO_4 (Fig. 1). Si was overestimated whereas Ca was underestimated by an order of magnitude. Aluminum was fairly well predicted by SOLTEQ, and predictions improve as pH goes down. The concentrations of SO_4 and Si were overestimated most, and those of Ca were underestimated most at the highest pH porewater (0% fly ash content). Such overestimations or underestimations gradually are reduced as the predicted pH decreases. Fig. 1 shows that Si and SO_4 predictions may be strongly pH dependent, although they are for different fly ash contents.

To identify factors affecting inaccurate predictions of Ca, SO_4, Al, and Si, the solubility properties of cement hydrates containing these components were evaluated. Using three sets of data from Berry et al. [18] and nine sets from Trussell and Batchelor [22], the ion activity products (IAPs) with respect to formation of such hydrates were calculated on the basis of the reaction stoichiometry as given in Table 1. To calculate the activities of the given species by the Pitzer ion interaction model [8], measured values were input to SOLTEQ without allowing any solid to precipitate. The calculated IAP values for cement hydrates except CSH are given in Table 5. Another experimental data set [23], which had been corrected for the presence of portlandite by Reardon [10], was used to provide Ca/Si ratios (x in Table 1) to calculate the IAPs of CSH based on the 12 experimental data sets. The K_{sp} values of CSH were calculated for these Ca/Si ratios using Reardon's two CSH models [9,10] as presented in Table 1. These values are plotted and compared with the IAP values in Fig. 3.

The comparison given in Table 5 shows that the reported K_{sp} values of ettringite and monosulfate are within 95%

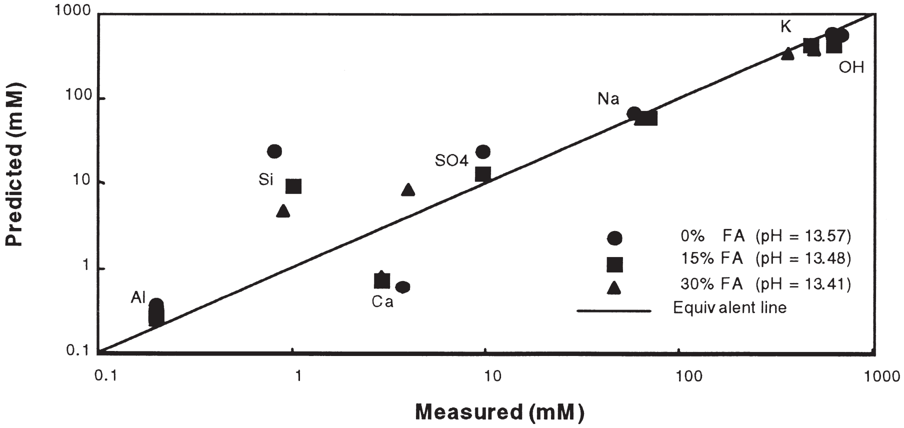


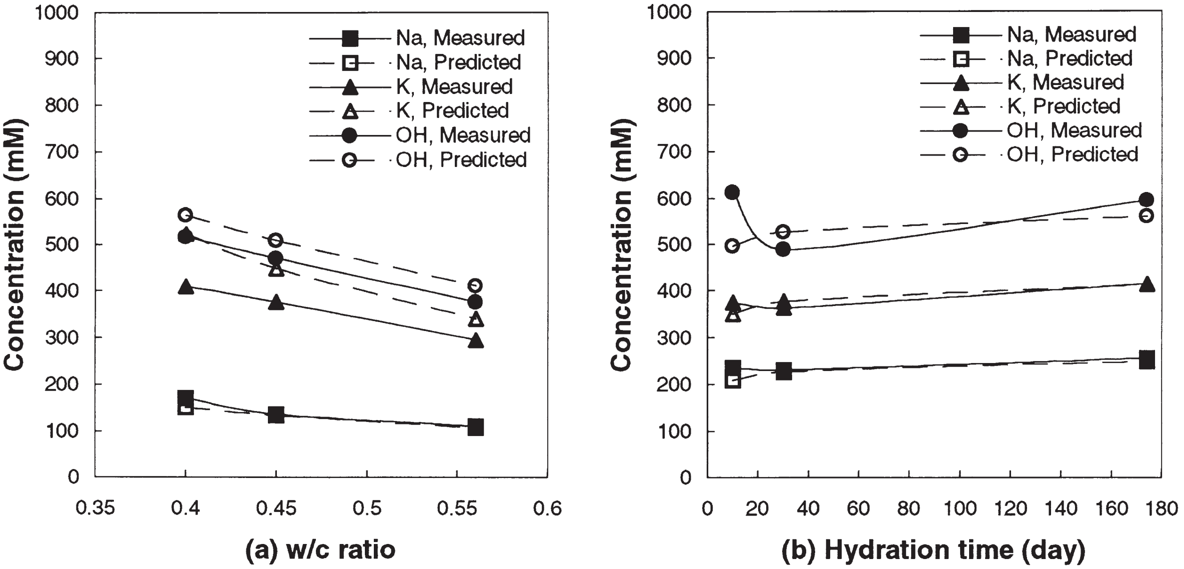
Fig. 1. Porewater simulation by SOLTEQ with Taylor's model for alkali partitioning using data from Berry et al. [18].

confidence intervals of their IAP values. This indicates that both solids can be controlling solids for their components. However, the K_{sp} values of portlandite and C_4AH_{13} exceed the higher limit of 95% confidence, indicating that the systems are oversaturated or that the K_{sp} values are inadequate at the high pH range of the cement porewater. It also indicates that solids other than those in Table 5 might be present.

Comparison for CSH in Fig. 3 reveals shortcomings of both CSH models, especially at higher pH values. Both CSH models were developed using solubility data with pH values <12.5. Fig. 3 shows some limitations in extrapolating these CSH models toward higher pH values, especially beyond pH 13.4. Although there could be some errors involved from borrowing Ca/Si ratios from different experiment, the old CSH model [9] showed better performance in describing CSH's solubility at higher pH values ($pH > 13.4$) in OPC porewaters.

The effect of using different values of K_{sp} on predicted concentrations of four components (Ca, SO_4, Al, Si) was investigated by substituting average IAP values for K_{sp} values in SOLTEQ. SOLTEQ simulations were conducted with different formation constants for four minerals (portlandite, ettringite or monosulfate, C_4AH_{13}, CSH). Table 6 describes each SOLTEQ simulation.

Fig. 4 shows the results of these simulations and compares them with the experimental data [18,22]. In Fig. 4, the CH lines are different from the C lines in predictions of all components. This indicates that SOLTEQ predictions of all components are sensitive to the variation in K_{sp} value of portlandite. The Ett and Mon lines are different from the C line in only SO_4 predictions. This means that K_{sp} changes of ettringite and monosulfate affect the prediction of sulfate concentration, whereas they have little effect on Ca, Al, and Si predictions. Because the C4 lines show their differences from the C line in both SO_4 and Al predictions, C_4AH_{13} af-



(a) w/c ratio

(b) Hydration time (day)

Fig. 2. Porewater simulation results by SOLTEQ with Taylor's model using data from *(a)* Larbi [12] and *(b)* Diamond [21].

Table 5
Ion activity product of hydrates based on experimental data [18,22] by SOLTEQ

	Portlandite	Ettringite	Monosulfate	C_4AH_{13}
Log IAP (average ± 2 SD*)	−4.67 ± 0.44	−42.47 ± 2.28	−28.31 ± 1.44	−25.91 ± 1.52
Log K_{sp} from Reardon [10]	−5.19†	−43.94	−29.25	—
Log K_{sp} in SOLTEQ database	−5.321†	−43.13	−27.62	−27.49†

IAP: ion activity product.
* For 95% confidence interval.
† Over 95% confidence limits.

fects both SO_4 and Al predictions. The CSH models influences only Si predictions, because the CSH lines do not show any differences from C lines in all components except Si. These results indicate the significance of portlandite on the chemical speciation in high pH cement porewaters. The presence of portlandite determines the concentration of Ca at a given pH. The concentrations of other components are determined by equilibrating relevant Ca-containing solids (e.g., CSH for Si) with the Ca concentration determined by equilibrium with portlandite. Thus, portlandite affects equilibrium concentrations of all other components, even though it does not contain the other components.

The comparisons with experimental data in Fig. 4 well illustrate inaccuracy in predictions using default set of K_{sp} values (C lines in Fig. 4), Ca is underestimated and SO_4 and Si are overestimated. Simulation using all IAP values (AE lines in Fig. 4) seems to correct these over- and underprediction problems so that predicted values are very close to the measured values, but Si was considerably underestimated. The underestimation of Si in this simulation is due to the characteristics of the adopted CSH models in SOLTEQ. As shown in the Table 1, the K_{sp} and Ca/Si ratio (x) are expressed as functions of the activity ratio (r) of Ca^{2+} and $H_4SiO_2^0$. Increased Ca caused by using higher K_{sp} value of portlandite reduces the predicted Si concentration according to the concept of the solubility product. Moreover, according to these CSH models, the increased Ca and decreased Si increases the r value, which makes K_{sp} even smaller. This makes Si much smaller, because Ca is determined only by hydroxide concentrations and equilibrium with portlandite.

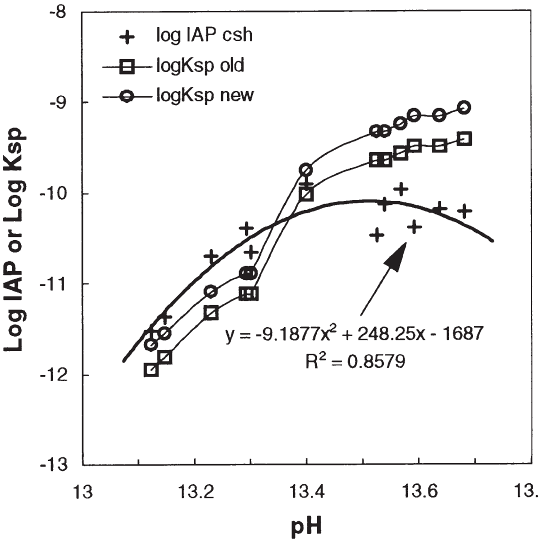


Fig. 3. Comparison between IAP and K_{sp} values of CSH. $K_{sp\,old}$ is by the CSH model [9] in SOLTEQ, whereas $K_{sp\,new}$ is by the CSH model from reference [10].

Because portlandite equilibrium affects the predicted Ca concentration, the predictions of all the other components are influenced by the value of the solubility product for portlandite. A small error in K_{sp} of portlandite could greatly affect the whole speciation problem. Published values of its K_{sp} exceed 95% confidence limit of the calculated IAP as shown in Table 5. Using this IAP value could not improve the predictions and makes Si significantly underpredicted, even though CSH models performs relatively well under pH 13.4 as shown in Fig. 3. This implies that the published value of portlandite K_{sp} probably is correct. However, Ca may be influenced by solids other than portlandite, by inaccurate calculations of activity coefficients, or by formation of unknown soluble complexes.

If portlandite is present and solid–liquid equilibrium occurs, then only $\{OH^-\}$ and K_{sp} of portlandite can affect $\{Ca^{2+}\}$. Inaccurate estimations of $\{OH^-\}$ could be important reasons for the inaccurate prediction of Ca, because reactions of OH^-, such as sorption and formation of soluble complexes, are not described in the SOLTEQ predictions. Moreover, the activity coefficient of OH^- could be incorrect, because the Pitzer method considers ion–ion interactions in calculating the activity coefficient rather than calculating soluble complexes. Inaccurate K_{sp} could be a good reason for the inaccurate Ca prediction. The reported K_{sp} should be good for pure $Ca(OH)_2$ of reasonable size, but actual K_{sp} could vary if the actual solid phase is not pure $Ca(OH)_2$, but has substitutions, or if portlandite crystals are so small that surface energy becomes important. Duchesne and Reardon [24] indicated that $Ca(OH)_2$ solubility depends on crystal size due to high surface energy of portlandite particles in water. The high surface energy of fine particles increases the change of Gibb's free energy (ΔG), increases solubility product (K_{sp}), and enhances their solubilities [25].

Considering these possible reasons for the discrepancy of Ca prediction, a modest set of K_{sp} values that can perform best at the given CSH model was established for further research on the chemical speciation of doped waste contaminant in cement porewaters. The K_{sp} values were obtained from recent literature [9,10,24]. This set is given as Mod in

Table 6
Descriptions of SOLTEQ simulations for Fig. 4

		Input K_{sp} values				
Code	Description	Portlandite	Ettringite	Monosulfate	C_4AH_{13}	CSH
C	Default in SOLTEQ	−5.321	−43.13	—	−27.49	Old
CH	Only portlandite change	−4.67	−43.13	—	−27.49	Old
Ett	Only ettringite change	−5.321	−42.47	—	−27.49	Old
Mon	With IAP of monosulfate	−5.321	—	−28.37	−27.49	Old
C4	Only C_4AH_{13} change	−5.321	−43.13	—	−25.91	Old
AE	All change with ettringite	−4.67	−42.47	—	−25.91	Old
CSH	Only CSH change	−5.321	−43.13	—	−27.49	New
ACSH	All change including CSH	−4.67	−42.47	—	−25.91	New
Mod	From references	−5.19*	−44.91†	—	−27.49‡	Old

* References [9,10]; † reference [24]; ‡ reference [9].

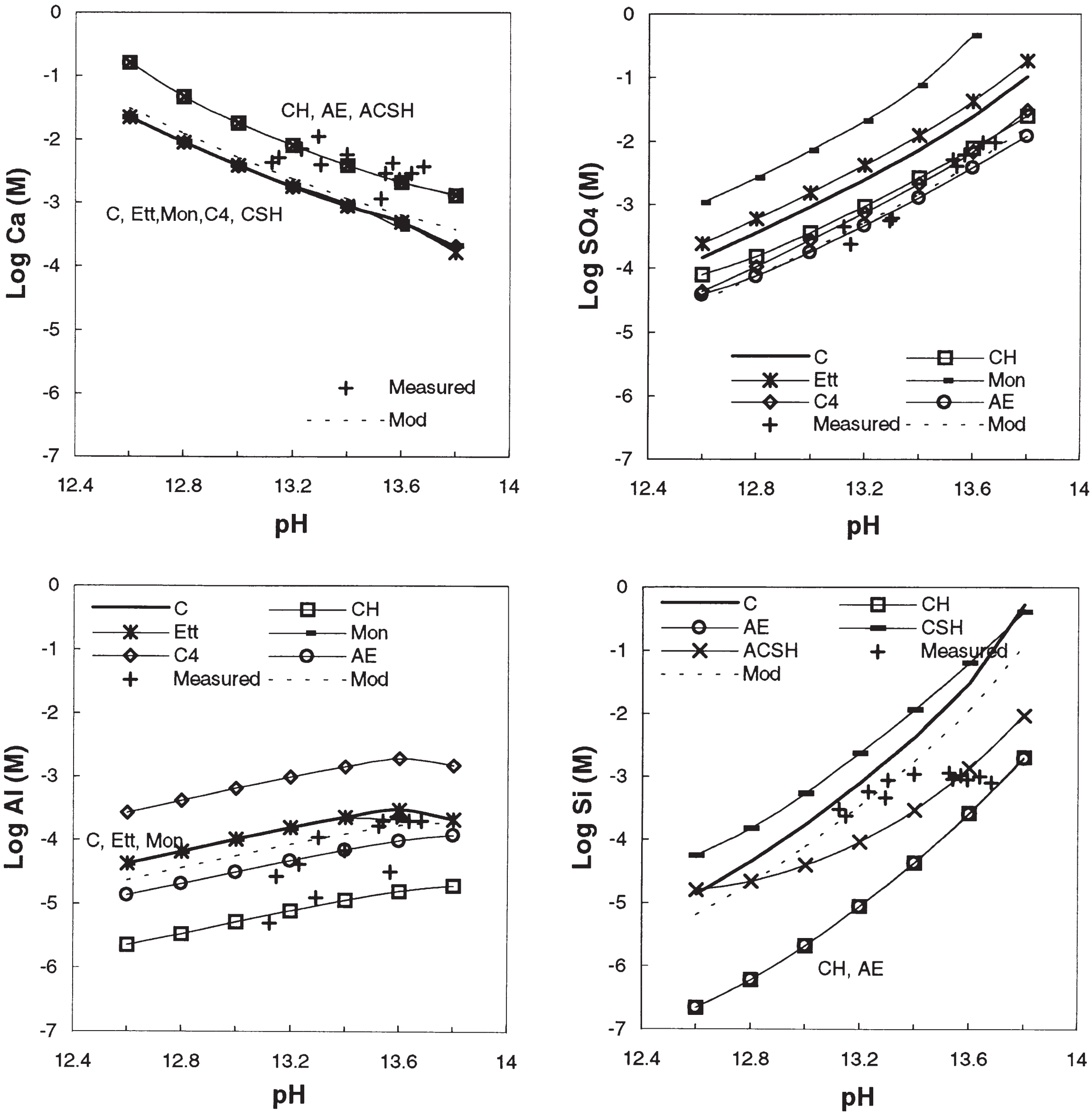


Fig. 4. Results of SOLTEQ simulations for sensitivity analyses of solubilities of major cement hydration products. Measured data come from two experimental data sets [18,22]. Descriptions for codes of simulations are given in Table 6.

Table 6 and its performance is illustrated in Fig. 4. In the simulation using this set, SO_4, Al, and Si were reasonably predicted for pH $<$13.4, although Ca was slightly underestimated. This indicates that the earlier overestimation can be corrected partially in the Si predictions or completely in the SO_4 predictions.

4. Conclusions

SOLTEQ was applied to predict the chemical speciations of the s/s waste form. A method was developed to prepare SOLTEQ input data for various s/s binders. Taylor's empirical model was used to describe the partitioning of alkali ions. As a result, SOLTEQ could represent the chemical speciations in pure binder systems such as OPC and OPC + FA. Moreover, SOLTEQ could reasonably describe the effects on the chemical speciations due to variations in the w/c ratios, the fly ash contents, and the hydration times of various binder systems. However, this application of SOLTEQ showed inaccuracy in predicting the concentrations of Ca, Si, and SO_4 ions.

Comparison between calculated IAP values and published K_{sp} values showed that the systems are mostly oversaturated with respect to formations of selected solids. The comparison using CSH models revealed their shortcoming in representing the chemical speciation at the higher pH values. Sensitivity analyses for K_{sp} values showed that the Ca concentration is controlled only by portlandite so that portlandite affects speciation of other components that form solid phases with calcium by determining Ca concentrations. Considering possible reasons for Ca underprediction, an improved set of K_{sp} values was obtained using published K_{sp} values. SOLTEQ simulation using this set could improve the overall prediction of chemical speciations in cement porewaters.

References

[1] C.C. Wiles, in: R. Abboud (Ed.), Hazardous Waste: Detection, Control, Treatment, Elsevier Science Publishers B.V., Amsterdam, 1988, p. 1525.
[2] W.W. Kovalick, Water Sci Tech 26 (1992) 99.
[3] M.E. Tittlebaum, F.K. Cartledge, S. Engels, CRC Crit Rev Environ Contr 15 (1985) 179.
[4] B. Batchelor, J Hazard Mater 24 (1990) 255.
[5] B. Batchelor, Water Sci Tech 26 (1992) 107.
[6] J.D. Allison, D.S. Brown, K.J. Novo-Gradac, MINTEQ2/PRODEFA2—A geochemical assessment model for environmental systems, Version 3.0, EPA/600/3-91/021, 1991.
[7] B. Batchelor, K. Wu, in: R.D. Spence (Ed.), Chemistry and Microstructure of Solidified Waste Forms, Lewis Publishers, Boca Raton, FL, 1993, p. 243.
[8] K.S. Pitzer, Theory: ion interaction approach, in: R.M. Pytkowicz (Ed.), Activity Coefficients in Electrolyte Solutions, CRC Press, Boca Raton, FL, 1979, p. 157.
[9] E.J. Reardon, Cem Concr Res 20 (1990) 175.
[10] E.J. Reardon, Waste Management 12 (1992) 221.
[11] M. Atkins, F.P. Glasser, Waste Management 12 (1992) 105.
[12] J.A. Larbi, A.L.A. Fraay, J.M.J.M. Bijen, Cem Concr Res 20 (1990) 506.
[13] H.F.W. Taylor, Adv Cem Res1 (1987) 5.
[14] J. Bensted, in: S.N. Ghosh (Ed.), Advances in Cement Technology, Pergamon Press, Oxford, 1983, p. 307.
[15] U.S. EPA, Stabilization/Solidification of CERCLA and RCRA Wastes, Physical Tests, Chemical Testing Procedures, Technology Screening, and Field Activities. EPA/625/6-89/022, U.S. EPA, Washington, DC, 1989.
[16] P.C. Aitcin, F. Autefage, A. Carles-Gibergues, in: Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, American Concrete Institute, Madrid, Spain, 1986, p. 91.
[17] M. Atkins, D.G. Bennett, A.C. Dawes, F.P. Glasser, A. Kindness, D. Read, Cem Concr Res 22 (1992) 497.
[18] E.E. Berry, R.T. Hemmings, W.S. Langley, C.G. Carette, in: Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, American Concrete Institute, Detroit, Michigan, 1989, p. 241.
[19] R.H. Bogue, Ind Engnrg Chem Anal 1 (1929) 192.
[20] H.F.W. Taylor, Cement Chemistry, Academic Press, San Diego, CA, 1990.
[21] S. Diamond, Cem Concr Res 11 (1981) 383.
[22] S. Trussell, B. Batchelor, Chemical characterization of pore water of a solidified hazardous waste, in: T.M. Gilliam and C.C. Wiles (Eds.), Stabilization and Solidification of Hazardous, Radioactive, and Mixed Wastes, ASTM STP 1240, American Society for Testing and Materials, Philadelphia, PA. 1994.
[23] G.L. Kalousek, J Res US Natl Bur Stand 32 (1944) 285.
[24] J. Duchesne, E.J. Reardon, Cem Concr Res 25 (1995) 1043.
[25] W. Stumm, J.J. Morgan, Aquatic Chemistry, second edition, John Wiley & Sons, Inc., New York, 1981.