Study of mineralogy and leaching behavior of stabilized/solidified sludge using differential acid neutralization analysis
Part II: Use of numerical simulation as an aid tool for cementitious hydrates identification

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ABSTRACT

In this work, we propose a methodology coupling differential acid neutralization analysis, chemical analysis of selected leachates and numerical simulation to identify the minerals controlling the leaching behavior of stabilized hydroxide sludge. This second part deals with the use of numerical simulation as an aid tool for the identification of the minerals. The framework for minerals identification is based on the study of minerals stability in function of the geochemical context using numerical simulation. A mineral assemblage permitting the simulation of a pH dependence leaching test (acid neutralization and release of elements) has been identified for the four studied cement pastes. Therefore, the proposed methodology is a pertinent tool for the modeling of the leaching behavior of inorganic wastes.

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1. Introduction

To control the risk for environment of the disposal of stabilized/solidified wastes, legislations impose to assess their leaching behavior. In the last decade, behavioral modeling became a useful tool in ecological risk assessment to estimate the release of pollutants in disposal conditions [1,2]. Due to the complexity of the reactions controlling the mobilizations of the pollutants, geochemical modeling is more and more used to represent the leaching behavior of inorganic wastes. Therefore, the development of a behavioral model to describe the leaching of stabilized/solidified wastes requires a minimal knowledge of their mineralogy [3].

Links between mineralogy and leaching behavior can be approached through saturation index calculations, that permits to identify the minerals possibly in equilibrium (or close to equilibrium) with the leachates coming from leaching tests [4–6]. However, saturation indexes can be calculated only for the phases containing the analyzed elements. Therefore, the resulting list of minerals close to equilibrium with leachates is not exhaustive. For example, carbonated phases are often forgotten by such calculations.

The differential analysis of acid neutralization data proposed by Glass and Buenfeld [7] permits a mineralogical interpretation of the leaching behavior of cementitious pastes. However, the identification of hydrates remains fairly complex because of the influences of the geochemical context on the stability of cementitious phases [7–9].

Based on the thermodynamic equilibrium laws [3], geochemical models are designed to simulate chemical reactions in water systems in contact with solid and gas phases. These models are able to predict the theoretical response to an acid attack of minerals in various geochemical contexts. Therefore, geochemical modeling could be an interesting tool to study the stability of hydrated cement phase.

In this two parts paper, we propose to characterize and to model the leaching behavior of stabilized/solidified sludge doped in zinc and chromium. The part I [10] deals with the experiments (difference acid neutralization analysis, chemical analysis of selected leachates, SEM-EDS observations and XRD) implemented to establish the links between leaching and mineralogy. In this second part, we propose to use numerical simulation as an aid tool to interpret experimental results, in particular those of the differential acid neutralization analysis test. In this paper, our attention is focused on the implementation of a model (mineral assemblage) able to represent the behavior of the main hydrates because they are controlling the evolution of pH and, thus, the release of pollutants. Nevertheless, some hypotheses about the behavior of zinc and chromium were tested.

Numerous hypotheses can be formulated from experimental results to explain the leaching behavior. Nevertheless they can hardly be confirmed. In this work, a framework is proposed to use geochemical

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calculations as an aid tool to identify and quantify the minerals controlling the leaching behavior of stabilized hydroxide sludge. Numerical simulation were performed using USGS's software PHREEQC [11], that has been successfully used to model the leaching behavior of cement stabilized/solidified wastes [12–14].

2. Experimental data [10]

Experiments were performed on synthetic hydroxide sludge, containing iron, zinc and hexavalent chromium. Sludge was stabilized/solidified by ordinary Portland cement (OPC, CEM I) or a mix of 50% of Portland cement and 50% of class F coal fly ashes (OPC-PFA). Four pastes were studied:

– two blanks containing only binders: OPC and OPC-PFA;
– two stabilized/solidified sludge: OPC-S and OPC-PFA-S.

Links between mineralogy and leaching behavior were investigated by differential acid neutralization analysis, chemical analysis of selected leachates, SEM-EDS observations and XRD. All the details on experimental conditions and the obtained results are presented in the part I of this paper [10].

3. Methodological framework for the identification of minerals

The identification of reactive minerals within cementitious composites using a numerical simulator is based on the assumption that numerical simulation permits to calculate the pH of dissolution of various hydrated phases in various environments. Thus, the comparison between simulated and experimental results should help for the identification of the cementitious hydrates. This comparison also inform on the reaction path and the possible precipitations occurring during the acid attack.

A five step framework was followed to identify the mineral assemblages (mix of pure phases and solid solutions) representing the tested materials:

1. Estimation of the mineral phases potentially present or which could precipitate based on:
   – the knowledge of the studied material (bibliographic study, previous works…);
   – a mineralogical study by direct methods: XRD, SEM-EDS. Other methods like FTIR or thermal analysis can also be used;
   – the identification of phases potentially at equilibrium with the analyzed leachates by calculations of saturation index [4].
2. Simulation of the acid attack on simplified mineral assemblages issued from the previous step. These simulations permit the compilation of a bank of spectra adapted to the studied case. For cementitious materials like cement stabilized wastes, it is interesting to simulate the behaviors of cementitious composite considering the presence of portlandite and/or C-S-H.
3. Minerals identification and quantification:
   – identification of the cementitious hydrates by comparison of the simulated and experimental spectra;
   – quantification from the area below peaks, the leachable fraction or the total content of elements.
4. Simulation of the behavior of the mineral assemblage determined at the previous step and comparison with experimental results. This comparison is made on the differential analysis spectra, the titration curves and the release of elements. Step 3 and 4 are reiterated until the obtaining of an acceptable simulation.

Table 1
Reactions and equilibrium constants for minerals considered in the minerals assemblages representing the four studied materials.

Mineral	Reaction	Log K_1 [ref]	Log K_2 [ref]
Portlandite	$Ca(OH)_2 + 2H^+ \leftrightarrow Ca^{2+} + 2H_2O$	22.8 [15]	22.555 [16] 22.9 [20]
Brucite	$Mg(OH)_2 + 2H^+ \leftrightarrow Mg^{2+} + 2H_2O$	16.84 [15]	
$Zn(OH)_2$	$Zn(OH)_2 + 2H^+ \leftrightarrow Zn^{2+} + 2H_2O$	11.9 [16]	
Ca-hydroxizincate	$CaZn_2(OH)_6 : 2H_2O + 6H^+ \leftrightarrow Ca^{2+} + 2Zn^{2+} + 8H_2O$	43.9 [17]	
Gypsum	$CaSO_4 : 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$	−4.581 [15]	−4.48 [16]
$Al(OH)_3(am)$	$Al(OH)_3 + OH^- \leftrightarrow Al(OH)_4^-$	0.24 [18]	
$Fe(OH)_3(am)$	$Fe(OH)_3 + 3H^+ \leftrightarrow Fe^{3+} + 3H_2O$	5 [15]	
$SiO_2(am)$	$SiO_2 + 2H_2O \leftrightarrow Si(OH)_4$	−2.714 [15–17]	
C_2ASH_8	$Ca_2Al_2O_5SiO_2 : 8H_2O \leftrightarrow 2Ca^{2+} + 2Al(OH)_4^- + SiO(OH)_3^- + OH^- + 2H_2O$	−20.49 [19]	
C-S-H			
C-S-H1.8	$(CaO)_{1.8}SiO_2 : 1.8H_2O + 3.6H^+ \leftrightarrow 1.8Ca^{2+} + Si(OH)_4 + 1.6H_2O$	32.6 [13]	
	$Ca_{1.8}SiO_{3.8} : H_2O + 3.6H^+ \leftrightarrow 1.8Ca^{2+} + Si(OH)_4 + 0.8H_2O$		32.7 [20]
C-S-H1.1	$(CaO)_{1.1}SiO_2 : 1.1H_2O + 2.2H^+ \leftrightarrow 1.1Ca^{2+} + Si(OH)_4 + 0.2H_2O$	16.7 [13]	
	$Ca_{1.1}SiO_{3.1} : H_2O + 2.2H^+ \leftrightarrow 1.1Ca^{2+} + Si(OH)_4 + 0.1H_2O$		16.72 [20]
C-S-H0.8	$(CaO)_{0.8}SiO_2 : 0.8H_2O + 1.6H^+ + 0.4H_2O \leftrightarrow 0.8Ca^{2+} + Si(OH)_4$	11.1 [13]	
	$Ca_{0.8}SiO_{2.8} : H_2O + 1.6H^+ + 0.2H_2O \leftrightarrow 0.8Ca^{2+} + Si(OH)_4$		11.08 [20]
AFm			
Al-monosulfate	$(CaO)_3Al_2O_3CaSO_4 : 12H_2O \leftrightarrow 4Ca^{2+} + 2Al(OH)_4^- + SO_4^{2-} + 4OH^- + 6H_2O$	−29.43 [21]	−27.62 [22]
Fe-monosulfate	$(CaO)_3Fe_2O_3CaSO_4 : 12H_2O \leftrightarrow 4Ca^{2+} + 2Fe(OH)_4^- + SO_4^{2-} + 4OH^- + 6H_2O$	−32.02 [19]	
Cr-monophase	$(CaO)_3Al_2O_3CaCrO_4 : 15H_2O \leftrightarrow 4Ca^{2+} + 2Al(OH)_4^- + CrO_4^{2-} + 4OH^- + 9H_2O$	−30.38 [23]	
Al-monocarbonate	$(CaO)_3Al_2O_3CaCO_3 : 11H_2O \leftrightarrow 4Ca^{2+} + 2Al(OH)_4^- + CO_3^{2-} + 4OH^- + 5H_2O$	−31.47 [19]	
Fe-monocarbonate	$(CaO)_3Fe_2O_3CaCO_3 : 11H_2O \leftrightarrow 4Ca^{2+} + 2Fe(OH)_4^- + CO_3^{2-} + 4OH^- + 5H_2O$	−35.79 [19]	
Friedel's salt	$(CaO)_3Al_2O_3CaCl_2 : 10H2O \leftrightarrow 4Ca^{2+} + 2Al(OH)_4^- + 2Cl^- + 4OH^- + 4H_2O$	−28.8 [14]	
C_4AH_{13}	$(CaO)_4Al_2O_3 : 13H_2O \leftrightarrow 4Ca^{2+} + 2Al(OH)_4^- + 6OH^- + 6H_2O$	−27.49 [22]	
	$(CaO)_4Al_2O_3 : 13H_2O + 14H^+ \leftrightarrow 4Ca^{2+} + 2Al^{3+} + 20H_2O$		107.25 [16]
C_4FH_{13}	$(CaO)_4Fe_2O_3 : 13H_2O \leftrightarrow 4Ca^{2+} + 2Fe(OH)_4^- + 6OH^- + 6H_2O$	−29.88 [19]	
Aft			
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} : 26H_2O \leftrightarrow 6Ca^{2+} + 2Al(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O$	−45.09 [19]	
	$Ca_6Al_2(SO_4)_3(OH)_{12} : 26H_2O + 12H^+ \leftrightarrow 6Ca^{2+} + 2Al^{3+} + 3SO_4^{2-} + 38H_2O$		62.536 [16]
Fe-ettringite	$Ca_6Fe_2(SO_4)_3(OH)_{12} : 26H_2O \leftrightarrow 6Ca^{2+} + 2Fe(OH)_4^- + 3SO_4^{2-} + 4OH^- + 26H_2O$	−49.49 [19]	
Cr-ettringite	$Ca_6Al_2(CrO_4)_3(OH)_{12} : 26H_2O \leftrightarrow 6Ca^{2+} + 2Al(OH)_4^- + 3CrO_4^{2-} + 4OH^- + 26H_2O$	−41.46 [23]	
Al-tricarbonate	$Ca_6Al_2(CO_3)_3(OH)_{12} : 26H_2O \leftrightarrow 6Ca^{2+} + 2Al(OH)_4^- + 3CO_3^{2-} + 4OH^- + 26H_2O$	−41.3 [19]	

Log K_1 correspond to the solubility product used during minerals identification; log K_2 was used to study the influence of thermodynamic data on simulation results. Values are given for a temperature of 25 °C.