Use of thermodynamic chemical potential diagrams (μCaO, μCO_2) to understand the weathering of cement by a slightly carbonated water

(Uso de diagramas de potencial químico termodinâmico (μCaO, μCO_2) para o entendimento da resistência do cimento à água levemente carbonatada)

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Abstract

Cement is a ubiquitous material that may suffer hazardous weathering. The chemical weathering of cement in natural environment is mostly characterized by the leaching of CaO and the addition of CO_2. The different weathering zones that develop at the expense of the cement may be predicted by the help of chemical potential phase diagrams; these diagrams simulate the behaviour of systems open to some chemical elements. Some components have a so-called *inert* status, that is to say the system is closed for these components, their amount in the system remains constant; some other components have a *mobile* status, that is to say these components can be exchanged with the outside of the system, their amount can vary from one sample zone to another. The mobile components are represented in the model by their chemical potentials (linked to their concentrations) that are variable in the external environment. The main features of the weathering of a cement system open to CaO and CO_2 are predicted in a phase diagram with μCaO et μCO_2 as diagram axes. From core to rim, one observes the disappearance of portlandite, ettringite and calcium monosulfoaluminate, the precipitation of calcite and amorphous silica, the modification of the composition of the CSH minerals (hydrated calcium silicates) that see a decrease of their c/s ratio (CaO/SiO_2) from the core to the rim of the sample. For the CSH minerals, we have separated their continuous solid solution into three compositions defined by different CaO/SiO_2 ratios and called phases 1, 2 and 3: CaO = 0.8, 1.1, 1.8 respectively for one mole of SiO_2 knowing that H_2O varies in the three compositions.

Keywords: thermodynamic chemical potential, cement weathering.

Resumo

Cimento é um material de ampla utilização que pode ser sujeito a modificação pelo tempo. A modificação química do cimento em meio natural é principalmente caracterizada por lixiviação de CaO e adição de CO_2. As diferentes zonas de resistência que se desenvolvem às custas do cimento podem ser previstas com os diagramas de fase do potencial químico; estes diagramas simulam o comportamento de sistemas abertos a alguns elementos químicos. Alguns componentes têm o chamado status inerte, significando que o sistema é fechado para estes componentes, seu teor no sistema permanece constante; alguns outros componentes tem um status móvel, significando que estes componentes podem ser trocados com o meio exterior, seu teor podendo variar de uma região da amostra para outra. Os componentes móveis são representados no modelo pelos potenciais químicos (ligados às suas concentrações) que variam no meio exterior. Os principais aspectos da resistência ao tempo de um sistema cementício aberto a CaO e CO_2 são previstos em um diagrama de fases com μCaO e μCO_2 como eixos do diagrama. Do centro para a extremidade observa-se o desaparecimento de portlandita, ettringita e monosulfoaluminato de cálcio, a precipitação de calcita e sílica amorfa, a modificação da composição de minerais CSH (silicatos de cálcio hidratados) que tem o decréscimo da razão c/s (CaO/SiO_2) do centro para a extremidade da amostra. Para os minerais CSH, forma separadas as soluções sólidas contínuas em três composições definidas por diferentes razões CaO/SiO_2, denominadas fases 1, 2 e 3: CaO = 0,8, 1,1, 1,8, respectivamente para 1 mol SiO_2 sabendo que H_2O varia nas três composições.

***Palavras-chave**: potencial químico termodinâmico, cimento.*

INTRODUCTION

Cement is an ubiquitous material that may often suffer weathering from rain and various superficial waters. In order to better assess the risk and the possible cure of accompanying damage, it is important to understand the chemical weathering process with some detail. The objective of this work is to illustrate how a thermodynamic approach can allow one to understand the weathering of cement in natural conditions. In particular, we will show the predictive character of phase diagrams to simulate an open environment where chemical

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Table I - The different zones formed by the weathering of the cement M40; the mineralogy of each zone is determined by X-ray diffraction [1].
[Tabela I - As diferentes zonas formadas pela resistência do cimento M40; a mineralogia de cada zona é determinada por difração de raios X .]

M40	M40 weathered			
	Core	Zone 1	Zone 2	Zone 3 (rim)
portlandite	portlandite	CSH	calcite	calcite
monosulfoaluminate	monosulfoaluminate	($0.9<C/S<1.9$)	CSH	CSH
CSH	CSH		$0.2<C/S<1.3$	($C/S = 0.7$)
($1.2<C/S<2.3$)	($1.2<C/S<2.3$)	ettringite	amorphous silica	amorphous silica
ettringite	ettringite	(primary and secondary)	ettringite	

elements are exchanged (in our case principally CaO and CO_2) between the cement and the external aqueous fluid. In a preceding work [1], we studied in detail the weathering of a standard concrete, M40, by naturally carbonated distilled water. The paste of this concrete is very similar to that of the cement studied in [2] and equally weathered by slightly carbonated water. The different weathering zones observable on this type of sample were analysed in detail and are described in Table I. The important features of the zoning, when one progresses from the core to the rim of the sample are the following: disappearance of portlandite, ettringite and calcium monosulfoaluminate, precipitation of calcite and amorphous silica at the rim of the sample, modification of the composition of the CSH minerals (hydrated calcium silicates) that see a decrease of their c/s ratio (CaO/SiO_2) from the core to the rim of the sample; that is to say, the content in calcium as compared with that of silicon diminishes from the core to the rim. The aluminium rich phases hydrogarnet and hydrotalcite are ubiquitous and do not present any modification. vaterite, the polymorph of $CaCO_3$, precipitates. The chemical analysis of the fluid shows that there is an enrichment of the fluid in CaO; so there is a washing out of CaO from the sample; carbonate precipitation shows that there is also a CO_2 addition.

METHODS

We will use here a thermodynamic approach in order to understand the main features described above concerning the weathering of cement by water. Our approach will be semi-quantitative, that is to say it will not take into account the time, nor the depth of the weathered zone in the samples. We chose to construct phase diagrams. A phase diagram is the representation of the thermodynamic stability regions of one or several phases as a function of at least two thermodynamic variables. In our case, temperature and pressure are constant and we will take the chemical potentials of the components as diagram axes. These variables (in energy units: kilojoules, or kJ) are directly linked up to the concentrations of the elements that may exchange from one zone to another between the sample and the fluid. More precisely, the relation $\mu = \mu_0 + RT.\ln a_i$ holds; μ is the chemical potential, μ_0 a constant, R the constant of perfect gases, T the temperature, ln the Neperian logarithm and a_i the activity of component i; the activity is more or less close to the concentration depending on the dilution of the solution. Provided a change in units and a shift in the origin are taken into account, the chemical potentials are therefore equivalent to logarithms of the concentrations. The interest of the use of chemical potentials is to provide linear relations and to give a direct access to the topology of the phase diagrams, even when ignoring the relations between activities and concentrations. We used a phase diagram software developed at Ecole Nationale Supérieure des Mines de Saint-Etienne, named “Zen+k”. One will find in [3, 4] indications on the thermodynamic basis of this software.

In order to use this software, it is necessary to define a chemical system by: - the number and the nature of the independent chemical components, - the composition of the phases, - the choice of the reference temperature and the reference pressure (we will choose 25 °C and 1 bar respectively). For each phase, it is necessary to specify its molar formation Gibbs free energy. It is then necessary to specify the status of the components: - so-called *inert* status, that is to say the system is closed for this component, its amount in the system remains constant; or - *mobile* status, that is to say this component can be exchanged with the outside of the system, its amount can vary from one sample zone to another. The mobile components are represented in the model by their chemical potentials (linked to their concentrations) that are variable in the external environment. Some components may be said to be *in excess*: their chemical potential is fixed to a constant value for the whole sample, from the outside of the system. The software calculates the assemblage of stable phases, according to the values of the chemical potentials of the mobile components (that will be able to vary from one place of the system to another), and represents these assemblages in a phase diagram. The software can indicate the metastable associations. One can also represent the part of a phase diagram that pertains to

Table II - Matrix defining the composition of the studied phases in the system SiO_2, CaO, CO_2, Al_2O_3 SO_3 H_2O. The different symbols used are defined in the matrix.
[Tabela II - Matriz contendo a composição das fases estudadas no sistema SiO_2, CaO, CO_2, Al_2O_3 SO_3 H_2O. Os diferentes símbolos estão definidos na matriz.]

	P Portlandite	1 $C_{0.8}SH$	2 $C_{1.1}SH$	3 $C_{1.8}SH$	E Ettringite	M Monosulfo-aluminate	S amor-phous Silica	H Hydro-garnet	C Calcite
c CaO	1	0.8	1.1	1.8	6	4	0	3	1
s SiO_2	0	1	1	1	0	0	1	0	0
o CO_2	0	0	0	0	0	0	0	0	1
g SO_3	0	0	0	0	3	1	0	0	0
a Al_2O_3	0	0	0	0	1	1	0	1	0
h H_2O	1	1.8	2.1	2.8	32	12	0	6	0

a chemical system of a special composition, defined by its content in inert elements (so-called restricted diagrams).

The chemical system envisaged here is described by the matrix given in Table II. The chemical components are CaO, SiO_2, Al_2O_3, SO_3 , H_2O and CO_2 and the envisaged phases are: portlandite, amorphous silica, ettringite, calcium monosulfoaluminate, hydrogarnet, calcite and the CSH minerals; for the CSH minerals, we have discretized their continuous solid solution into three compositions defined by different CaO/SiO_2 ratios and called phases 1, 2 and 3: CaO = 0.8, 1.1, 1.8 respectively for one mole of SiO_2 knowing that H_2O varies in the three compositions (see composition matrix). We did not take Hydrotalcite nor Vaterite (described in Table I) into account. The useful thermodynamic data were found in various bibliographical sources: [5] for the CSH minerals, [6] for portlandite, amorphous silica, ettringite, and calcium monosulfoaluminate, [7] for calcite. The choice of thermodynamic data is discussed in [2]. Mobile components must then be chosen. We will start to choose CaO and CO_2 as mobile; we saw indeed that the weathering of cement involved an exchange of CaO and CO_2. We will keep SiO_2, Al_2O_3 and SO_3 as inert, knowing that there is no exchange, or a more restricted exchange for these three components. And we will take H_2O as in excess, with its chemical potential fixed. We will take first $\mu_{H2O} = g^{\circ}_{f\,H2O}$, that is to say the system is at water saturation.

RESULTS AND DISCUSSION

Fig. 1 displays the phase relations in the composition space of the inert components (chemography). Fig. 2 displays a phase diagram with μCaO and μCO_2 as diagram axes. The chemical potential of H_2O is equal to its molar free energy (-237.14 kJ), that is to say the system is just at water saturation. The saturation lines of calcite and portlandite are observable in the figure so as a series of domains marked by the change in the composition of the CSH minerals. The following sequence is observed:

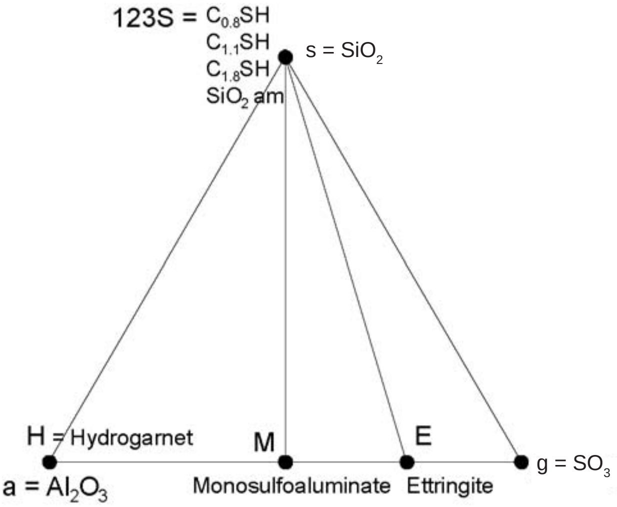

Figure 1: Representation of the phases H, M, E, 1, 2, 3, S (see symbols in Table II) in chemical space Al_2O_3, SiO_2, SO_3.
[Figura 1: Representação das fases H, M, E, 1, 2, 3, S (ver símbolos na Tabela II) no espaço químico Al_2O_3, SiO_2, SO_3.]

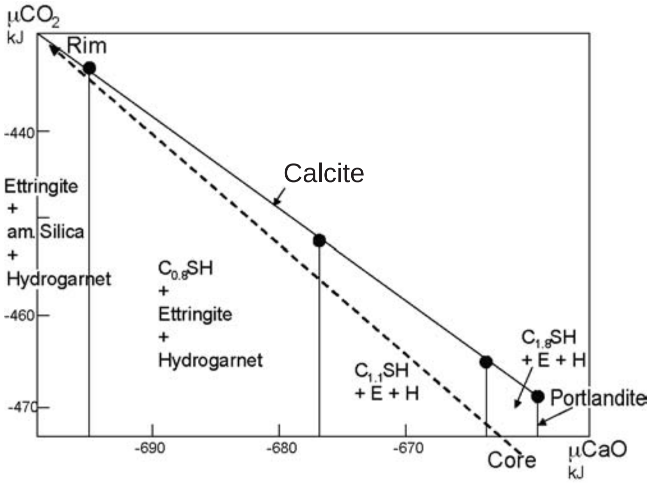

Figure 2: Phase diagram (μCaO, μCO_2), with $\mu H_2O = g_{f0}\ H_2O$ representing the phases of interest in the system of inert components SiO_2, Al_2O_3, SO_3. The arrow indicates the chemical path observed in the sample and in the interstitial aqueous solution from the core to the rim.

[Figura 2: Diagrama de fases (μCaO, μCO$_2$), com $\mu H_2O = g_{f0}\ H_2O$ representando as fases de interesse no sistema de componentes inertes SiO_2, Al_2O_3, SO_3. A seta indica a trajetória química observada na amostra e na solução aquosa intersticial do centro para a extremidade.]

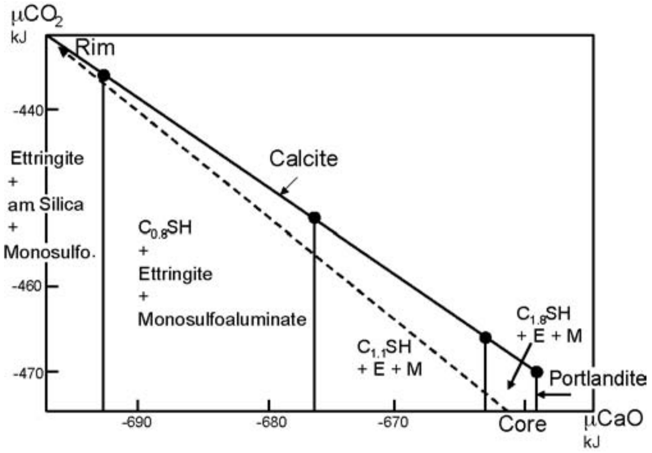

Figure 3: Phase diagram (μCaO, μCO_2) with $\mu H_2O \leq g_{f0}\ H_2O$ = -238.123 kJ/mole. Owing to the lower water activity than in Fig. 1, the monosulfoaluminate M is stabilized.

[Figura 3: Diagrama de fases (μCaO, μCO$_2$) com $\mu H_2O \leq g_{f0}\ H_2O$ = -238.123 kJ/mol. Devido à menor atividade da água que na Fig. 1, o monosulfoaluminato é estabilizado.]

1EH, 2EH, 3EH, always accompanied by ettringite and hydrogarnet; this is necessarily so because these are the only phases that contain aluminium and SO_3. One retrieves the main features that have been observed on the natural samples accompanying a decrease in CaO and an increase in CO_2 content according to the trend represented in the figure by the arrow: disappearance of portlandite, appearance of calcite and amorphous silica (in the last zone), change in the composition of the CSH minerals. Some phases are not retrieved, in particular monosulfoaluminate is absent. A detailed discussion of this question is given [2, 8]: one shows in particular that a lowering of water activity, what can be expected for solutions concentrated in cations of Ca, Na, K…, can stabilize monosulfoaluminate. This is represented in the following figure (Fig. 3), where the chemical potential of H_2O has been taken at -238 kJ, a lower value than water saturation; presence of monosulfoaluminate (phase M) is retrieved. One finds the sequence of phases represented by the arrow: disappearance of portlandite, appearance of calcite and amorphous silica, change in the composition of the CSH minerals. The diagram was drawn for a specific cement composition with Al_2O_3 and SO_3 contents typical for the chosen cement ($SiO_2 = 0.328$; $Al_2O_3 = 0.036$; $SO_3 = 0.003$). One thus retrieves in a simple manner the main features of what was observed. The model may of course be complicated, taking for example SO_3 as mobile (SO_3 can vary and be washed out) as studied in detail in [2].

CONCLUSIONS

The interest of a thermodynamic approach in the study of cement weathering has been shown. An important contribution of the method is the prediction of the different possible weathering zones of cement, as due to the influence of external water; in our case it was an acid carbonated water washing out the alkaline elements. In particular, we showed that the zoning could be explained by a decrease of CaO and an increase in CO_2. The thermodynamic tool presented allows one to vary the composition of the starting rock (nature of the phases, envisaged chemical elements), that of the external fluid (one can for example study the influence of sulphated waters as in [2]) and allows to understand the mineralogy of the weathered zones. The proposed method can help put some order in the observations and provide a better understanding of the chemistry of the weathering process intervening in the degradation of cements.

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