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SURFACE CHARGES OF WOLLASTONITE AND XONOTLITE IN AQUEOUS SOLUTIONS

A.J.G. van Diemen and H.N.Stein

Adsorption data for wollastonite and xonotlite in aqueous solutions show, that there exist marked differences between these interfaces: the xonotlite surface may be ordered, but the surface of the wollastonite investigated must exhibit some disorder. A surface gel layer is not formed.

Adsorptionsexperimente an Wollastonit und Xonotlit in wässrigen Lösungen zeigen, dass es deutliche Unterschiede gibt zwischen diesen Grenzflächen: die Xonotlitoberfläche kann geordnet sein, doch die Oberfläche des untersuchten Wollastonits muss eine gewisse Unordnung vorweisen. Ein oberflächlicher Gelfilm wird nicht gebildet.

Des expériences d'adsorption sur wollastonite et xonotlite dans des solutions aqueuses montrent, qu'il y a des différences prononcées entre ces surfaces: celle du xonotlite peut être réglée, mais celle du wollastonite étudié doit avoir un certain désordre. Un film gélatineux superficiel n'est pas formé.

INTRODUCTION

Interfaces between calcium silicate hydrates and aqueous electrolyte solution determine the behaviour of hydrated Portland cement and of sand lime bricks. At these interfaces, surface charges arise which may be either positive or negative depending on the electrolyte concentrations (1,2). The present investigation is concerned with the question, what processes are involved in originating these surface charges, and whether there are significant differences between an anhydrous calcium silicate (wollastonite, β -CaSiO₃) and a calcium hydrate of equal Ca/Si atomic ratio (xonotlite, Ca₆Si₆O₁₇(OH)₂). The latter point is of importance with a view to the question, whether the adsorption characteristics can be correlated with the bulk crystal structure of the solids, or whether a surface gel layer is formed which has only a remote relationship with the bulk crystal structure of the solids.

EXPERIMENTAL

Materials

Xonotlite and wollastonite were prepared as previously described (3), from CaCO₃ ex Merck "zur Analyse" or CaCO₃ ex Merck "supra pur". If CaCO₃ "Zur Analyse" is used (β CaSiO₃III, xonotlite III) the samples contain about 500 p.p.m. Na. Using CaCO₃ "supra pur" (wollastonite I and II, xonotlite I and II) the content is about 25 p.p.m. After sun-thesis the compounds were ground in a porcelain mortar until the solid particles were smaller than 250 μ . Before and after grinding the xonotlite was stored in a desiccator, above a saturated CaCl₂ solution in water. Wollastonite was prepared by heating xonotlite for 20 hrs at 950°C (3). X-ray diffraction diagrams were in agreement with literature data (4). The surface areas as determined by means of an areameter (Ströhlein) were: wollastonite I: 9.6m²g⁻¹, wollastonite II: 11.7m²g⁻¹, wollastonite III: 10.3m²g⁻¹, xonotlite I: 19.6m²g⁻¹, xonotlite II: 20.2m²g⁻¹, xonotlite III: 22.5m²g⁻¹. The sodium content in the solid was determined by means of neutron activation analysis. Neither in xonotlite nor in wollastonite samples separate (e.g. Na⁺ rich) solid phases could be detected by SEM.

Methods

Adsorption measurements were carried out in 100 ml polyethylene vessels at constant NaOH concentrations in a nitrogen atmosphere. 2 g xonotlite or 4 g wollastonite were suspended in 50 ml NaOH solution (0.01 M or 0.002 M). CaCl₂ solution (1M) and NaOH solution were added, the latter in the amount necessary to keep the pH constant during the adsorption as determined by a preceding "dummy" experiment with an automatic titrator (TTT2 Radiometer). The vessel was shaken during 150 min. After shaking the greater part of the suspension was centrifuged (16000 r/min) during 1½ hour. The clear liquid was decanted. In this liquid the concentration of all ions, possibly involved in originating the surface charge, were determined. The concentrations of these ions were also determined in an equal experiment but without the solid. The adsorption or desorption was calculated from the difference between both concentrations. Ca²⁺ was determined spectrophotometrically (5). Na⁺ and OH⁻ were determined with a specific ion electrode (ORION); the equivalence point was calculated by the method of Gran (6); OH⁻ titration was performed until a pH of 3. Silicate was determined spectrophotometrically (7). With the rest of the suspension ζ -potential measurements were performed using an electroosmosis apparatus (2).

RESULTS

Fig. 1 shows adsorption isotherms for xonotlite II, for those ions which play a role in the origin of the surface charge. Negative adsorption = desorption. "OH⁻ adsorption" consists of the OH⁻ adsorption proper, dissociation of surface silanol groups and silicate adsorption, since the titration of OH⁻ was continued to a pH = 3. σ_{silicate} was calculated from the silicate concentration in the solution after solid/liquid contact, awarding a charge $-2e_0$ to every silicate ion.

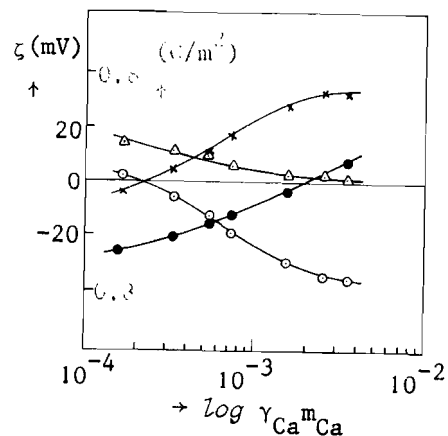


Figure 1

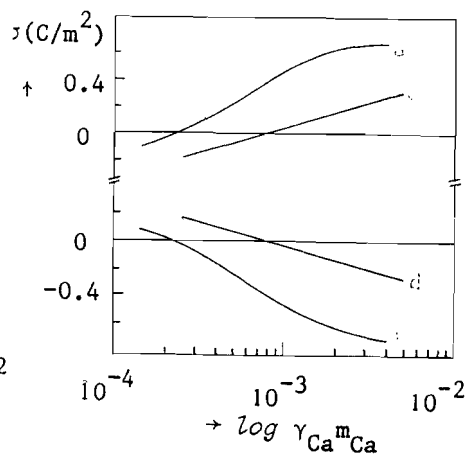


Figure 2

Typical adsorption and electrokinetic data for xonotlite II.

x: σ_{Ca} , Δ : σ_{silicate}
o: σ_{OH} , •: ζ -potential

σ_{Ca} and σ_{OH} for different NaOH concentrations.

a: σ_{Ca} , 0.01-M NaOH

b: σ_{OH} , 0.01 M NaOH

c: σ_{Ca} , 0.002 M NaOH

d: σ_{OH} , 0.002 M NaOH

Adsorption was calculated as "surface charge": σ_i (in coulomb- m^{-2}) = $z_i F V \Delta c_i / (n \cdot s)$ with F = Faraday ($\text{C} \cdot \text{mol}^{-1}$), V = volume of the solution (l), Δc_i = difference in concentrations of species i before and after solid/liquid contact ($\text{mol} \cdot \text{l}^{-1}$), n = amount of solid (g), s = surface area of the solid ($\text{m}^2 \cdot \text{g}^{-1}$). The surface charges for calcium and hydroxyl ions were corrected for the electrostatic charge in the diffuse double layer, according to: (8)

$$\sigma_i = z_i e_0 \int_{\phi=0}^{\zeta} \frac{N_i^{\infty} [\exp(-z_i e_0 \phi / (kT)) - 1]}{d\phi/dx} d\phi \quad (I)$$

where N_i^{∞} = concentration of species i in the bulk liquid

e_0 = elementary charge

z_i = valence of ion i including sign

On the horizontal axis in fig. 1, $\log \gamma_{\text{Ca}} m_{\text{Ca}}$ is plotted. Here m_{Ca} is the concentration of free calcium ions (corrected for CaOH^+ formation) and the activity coefficient γ_{Ca} is calculated from (9):

$$-\log \gamma_{\text{Ca}} = 4 A \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0,2 I \right] \quad (I = \text{ionic strength}) \quad (II)$$

The correction for CaOH^+ formation was carried out by an iterative procedure; first m_{CaOH^+} was calculated from:

$$K = \frac{m_{\text{Ca}} m_{\text{Ca}} \gamma_{\text{OH}} m_{\text{OH}}}{\gamma_{\text{CaOH}^+} m_{\text{CaOH}^+}} \quad \text{with } -\log K = 1.221 + 2.802 I^{10} \quad (III)$$

using uncorrected values for m_{Ca} and m_{OH} ; this was employed to calculate a corrected I etc.

In fig. 1 the adsorption isotherm for Na^+ is omitted since σ_{Na^+} was very small. With increasing CaCl_2 concentration, both Ca^{2+} and OH-adsorption increase simultaneously in nearly stoichiometric ratio as observed previously by Siskens c.s. (11) for $\alpha\text{-CaSiO}_3$. At large $[\text{CaCl}_2]$, σ_{Ca} and σ_{OH} both level off at

$|\sigma| \approx 0.7 \text{ C} \cdot \text{m}^{-2}$. Essentially the same is found for xonotlite I.

With wollastonite I and II, a similar picture is found. However, both σ_{Ca} and σ_{OH} increase less with increasing

$[\text{CaCl}_2]$; the maximum adsorption is not reached within the concentration range investigated. For samples containing considerable amounts of Na (wollastonite III, xonotlite III) σ_{Ca} and σ_{OH} increase stronger with increasing $[\text{CaCl}_2]$ than with samples poor in Na. A Na^+ desorption is found increasing with $[\text{CaCl}_2]$. This indicates exchange of Ca^{2+} against 2Na^+ .

Desorption of silicate is more pronounced than for samples poor in Na^+ . Desorption Na^+ amounts to about 50% of all Na^+

present in the solid. These facts indicate a surface layer enriched in Na^+ .

Fig. 2 shows that, for increasing NaOH concentrations at constant $[\text{CaCl}_2]$, both σ_{Ca} and σ_{OH} increase. This agrees with the "stimulated adsorption" described by Siskens c.s. (11) for $\alpha\text{-CaSiO}_3$.

DISCUSSION

The levelling of σ_{Ca} and σ_{OH} at large $[\text{CaCl}_2]$ seen in fig. 1, contradicts a "surface precipitation" as postulated by James and Healy (12). Thus, the model of stimulated adsorption of Ca^{2+} and OH^- (11) appears to be more appropriate in the present case.

Siskens c.s. derived the relation:

$$\frac{\delta(X/N_s)}{\delta \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}} = \left[1 - \frac{2F}{RT} \cdot \frac{\delta \bar{\phi}}{\delta \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}} \right] \cdot \sum \frac{N_i \theta_i (1-\theta_i)}{N_s} \quad (\text{IV})$$

Here, X = total amount of Ca^{2+} ions adsorbed,

N_s = total number of Ca^{2+} adsorption sites, per m^2 of surface area,

N_i = number of Ca^{2+} adsorption sites of type i,

θ_i = degree of occupation of sites of type i,

ϕ_i = potential at a site of type i,

$$\frac{\delta \bar{\phi}}{\delta \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}} = \frac{\delta \phi_i}{\delta \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}} \text{ averaged in a certain way over the calcium sites.}$$

This formula is based on :

$$\mu_{\text{Ca(ads)}} = \mu_{\text{Ca(ads)}}^* + RT \ln(\theta_i/(1-\theta_i)) + 2F\theta_i \quad (\text{V})$$

If we assume, that for both $\beta\text{-CaSiO}_3$ and xonotlite the surface charge can vary between the limits -0.7 and $+0.7 \text{ C.m}^{-2}$ (see crystal structure data (13)), then:

$$\sum N_i \theta_i / N_s = (\sigma_{\text{ads}} + 0.7) / 1.4 \quad (\text{VI})$$

can be calculated for all adsorption points. From this,

$\sum N_i \theta_i (1-\theta_i) / N_s$ in (IV) can be calculated if a model for the

distribution of the number of sites as a function of $\Delta G_i^0 / RT = (\mu_{\text{Ca}}^*(\text{solution}) - \mu_{\text{Ca}}^*(\text{ads}) - 2F\theta_i) / RT$ is assumed. Thus, for a certain concentration ($\gamma_{\text{Ca}^{m_{\text{Ca}}}} = 0.001 \text{ M}$), $\sum N_i \theta_i / N_s$ is calculated from σ_{Ca} . For a Gauss distribution of the sites:

$$\frac{dN_i}{du} = \frac{N_s}{w\sqrt{2\pi}} \exp(-(u-f)^2 / (2w^2)) \quad (\text{VII})$$

where $u = \Delta G_i^0 / RT$,

f = the mean value of u

w = its standard deviation,

$\sum N_i \theta_i / N_s$ as calculated from σ_{Ca} must be equal to:

$$\frac{1}{w\sqrt{2\pi}} \int_{-\infty}^{+\infty} \frac{\gamma_{\text{Ca}^{m_{\text{Ca}}}} \exp.u}{(1 + \gamma_{\text{Ca}^{m_{\text{Ca}}}} \exp.u)} \exp(-(u-f)^2 / (2w^2)) du \quad (\text{VIII})$$

since $\theta_i = (\gamma_{\text{Ca}^{m_{\text{Ca}}}} \exp.u) / (1 + \gamma_{\text{Ca}^{m_{\text{Ca}}}} \exp.u)$.

For any particular value of w , f was adjusted such as to make $\sum \theta_i N_i / N_s$ calculated from (VIII) agree with that calculated

from (VI). The value of f was then used, to calculate

$$\sum \frac{N_i \theta_i (1-\theta_i)}{N_s} = \frac{1}{w\sqrt{2\pi}} \int_{-\infty}^{+\infty} \frac{\gamma_{\text{Ca}^{m_{\text{Ca}}}} \exp.u}{(1 + \gamma_{\text{Ca}^{m_{\text{Ca}}}} \exp.u)^2} \exp(-(u-f)^2 / (2w^2)) du \quad (\text{IX})$$

Then $\delta \bar{\phi} / \delta \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}$ can be calculated from (IV). This was performed both for calcium and for hydroxyl sites.

Fig. 3 shows the results for wollastonite II; wollastonite I gave similar results. It is seen, that at $w = 0$ (a so-called single type site adsorption model) $|\partial \bar{\phi} / \partial \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}|$ for both Ca^{2+} and OH^- sites is smaller than $|\partial \zeta / \partial \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}|$; the same

obtains for any kind of average value. Similar results are calculated with the square distribution. The electrokinetic slipping plane, however, cannot be situated closer to the phase boundary than the plane of the adsorption sites. Therefore $|\partial \zeta / \partial \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}|$ must be $< |\delta \bar{\phi} / \delta \ln \gamma_{\text{Ca}^{m_{\text{Ca}}}}|$ averaged over the plane of the adsorption sites.

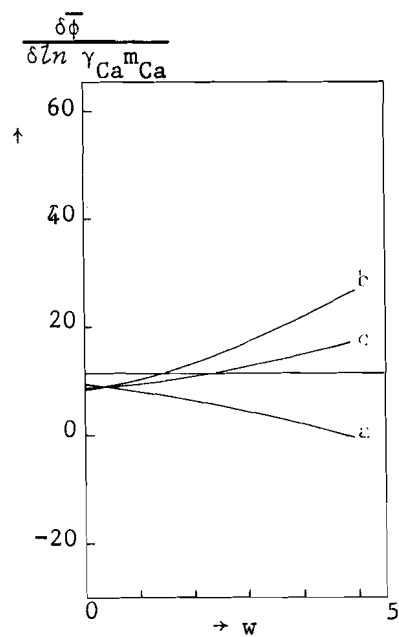


Figure 3

$\delta\phi/\delta\ln\gamma_{Ca^{m}Ca}$ for wollastonite II.

Gauss distribution for adsorption sites assumed. w as independent variable.

- a : for Ca^{++} sites,
- b : for OH^{-} sites,
- c : $1/3 a + 2/3 b$.

Again, a distinct difference is found between the situations at interfaces β - $CaSiO_3$ / electrolyte solution and

$Ca_6Si_6O_{17}(OH)_2$ / electrolyte solution, respectively. This indicates that a surface gel layer is not formed under the conditions of our experiments.

CONCLUSIONS

A marked difference exists between interfaces wollastonite/ electrolyte solution and xonotlite/electrolyte solution. At wollastonite surfaces as prepared in the present investigation some disorder must exist.

If the solid contains Na, then the surface layer is enriched in Na towards the bulk.

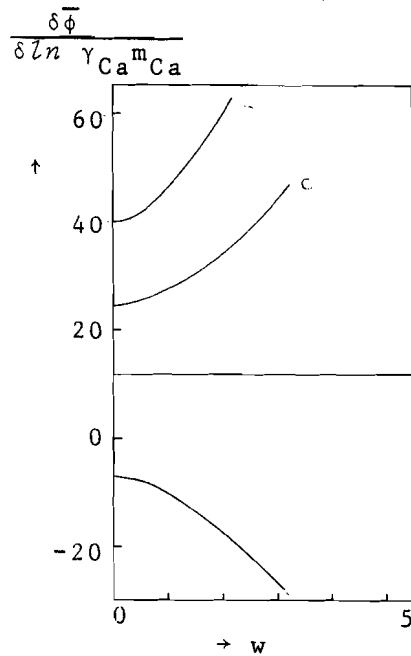


Figure 4

As figure 3, for xonotlite II

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