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THERMODYNAMIC LIMITATION OF SELF-DESICCATION

O. Mejlhede Jensen
Building Materials Laboratory
The Technical University of Denmark
DK-2800 Lyngby, Denmark

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ABSTRACT

Hydration reactions of sealed portland cement paste may lower the relative humidity within the hardening cement paste. Powers called this phenomenon self-desiccation and stated that self-desiccation gives rise to a bulk shrinkage, so-called autogenous shrinkage (1,2). This paper presents a thermodynamic analysis of self-desiccation in hardening cement paste. The thermodynamic calculations are carried out on the basis of fundamental equations of reaction for the clinker minerals. According to the calculations C_2S hydration seems not to be thermodynamically feasible at low relative humidities. The presence of C_2S in the cement may contribute to limit self-desiccation of portland cement paste.

Introduction

Due to low water-cement-ratios some cement pastes may not contain enough water to permit full unrestricted hydration of the cement. This causes a lowering of the relative humidity within the hardening cement paste even under sealed conditions. Powers called this phenomenon self-desiccation and stated that self-desiccation gives rise to a bulk shrinkage, so-called autogenous shrinkage (1,2). Self-desiccation and thereby autogenous shrinkage is widely considered to be an important cause of crack formation in concrete at early ages.

Several factors influence the course of self-desiccation in hardening cement paste, for example w/c-ratio, cement type, and silica-fume addition. However, many published data in the literature indicate that self-desiccation is not able to lower the relative humidity (RH) in a cement paste to more than approximately 75%. This observation is also made by Powers (2) for pure portland cement paste and later by Paillère et al. (4) for pastes containing silica fume. Figure 1 from (4) demonstrates this trend.

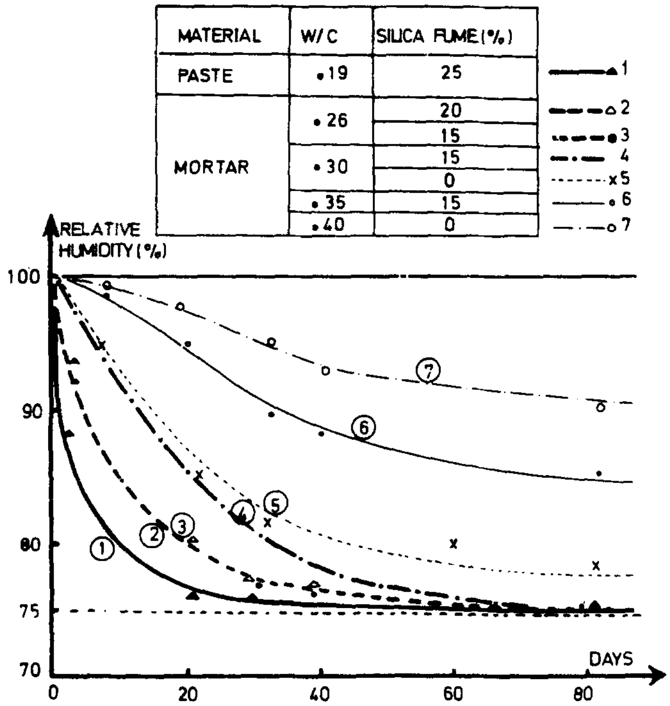

FIG. 1.

Relative humidity within various cement paste and mortar specimens during sealed curing (4).

Measurements reported by Powers (2) support the suggestion that the above mentioned relative humidity level of 75% RH in some way is fundamental to cement hydration.

Powers stored portions of unhydrated cement in atmospheres of controlled relative humidity. The amounts of water taken up by the cement after 6 months of storage are presented in Figure 2.

Powers' experiment shows that cement hydration is generally hampered at lower relative humidities but markedly detained at relative humidity levels lower than approximately 75%.

Similar results indicating the same tendency have been published by Rodt (3).

As pointed out by Powers (2), some physical factors must play an important role in the retardation of cement hydration at lower relative humidities. This will be mentioned further on. But the fact that the cement hydration is distinctly retarded at a certain relative humidity level indicates that chemical factors could be important, too. Therefore, a thermodynamic analysis of the observed phenomenon seems appropriate.

Thermodynamic analysis

Seen from a chemical point of view, the hydration reaction of cement is very complicated:

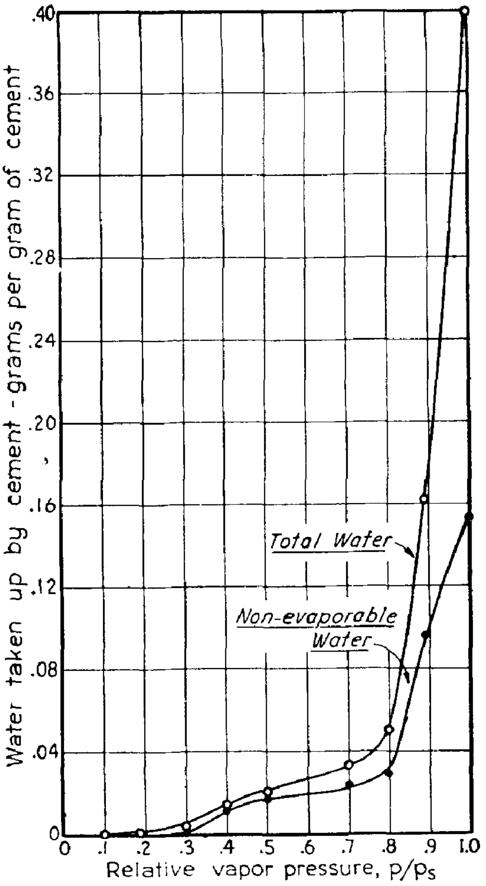

FIG. 2.

Amounts of water taken up by dry cement exposed to water vapor of different relative humidities for 6 months (2). (p/p_s=RH).

- the hydration reaction involves both liquid and solid substances

- the involved substances are generally not in thermodynamic equilibrium

- depending upon the conditions under which the reactions take place, several different products can be produced.

A classical thermodynamic analysis can therefore only be approximate.

Mchedlov-Petrossyan et al. (6) have published a comprehensive exposition of silicate thermodynamics. Mchedlov-Petrossyan presents basic equations of reaction for important cement clinker minerals as shown in Table 1. He also presents tables of thermodynamic constants for the constituent substances, see Table 2. This enables thermodynamic calculations to be carried out.

At constant temperature and pressure Gibbs free energy indicates the direction of spontaneous chemical change. Only chemical reactions that minimize Gibbs free energy are spontaneous.

Based on this concept the lowest relative humidities that allow hydration to proceed are calculated in the following.

TABLE 1.
Equations of reaction for C_3S, C_2S, and C_3A according to Mchedlov-Petrossyan et al. (6).

Eq. no.	Equation of reaction	CSH mineral name
C_3S:		
1	$C_3S + 2.17H \rightarrow C_2SH_{1.17} + CH$	Hillebrandite
2	$C_3S + 3H \rightarrow \frac{1}{2}C_3S_2H_3 + \frac{3}{2}CH$	Afwillite
3	$C_3S + \frac{13}{6}H \rightarrow \frac{1}{3}C_4S_3H_{1.5} + \frac{5}{3}CH$	Foshagite
4	$C_3S + \frac{13}{6}H \rightarrow \frac{1}{6}C_6S_6H + 2CH$	Xonolite
5	$C_3S + \frac{8}{3}H \rightarrow \frac{1}{6}C_5S_6H_3 + \frac{13}{6}CH$	Riversideite
6	$C_3S + \frac{37}{12}H \rightarrow \frac{1}{6}C_5S_6H_{5.5} + \frac{13}{6}CH$	Tobermorite
7	$C_3S + \frac{47}{12}H \rightarrow \frac{1}{6}C_5S_6H_{10.5} + \frac{13}{6}CH$	Plombierite
8	$C_3S + \frac{19}{6}H \rightarrow \frac{1}{3}C_2S_3H_{2.5} + \frac{7}{3}CH$	Gyrolite
9	$C_3S + \frac{7}{2}H \rightarrow \frac{1}{2}CS_2H_2 + \frac{5}{2}CH$	Okenite
C_2S:		
1	$C_2S + 1.17H \rightarrow C_2SH_{1.17}$	Hillebrandite
2	$C_2S + 2H \rightarrow \frac{1}{2}C_3S_2H_3 + \frac{1}{2}CH$	Afwillite
3	$C_2S + \frac{7}{6}H \rightarrow \frac{1}{3}C_4S_3H_{1.5} + \frac{2}{3}CH$	Foshagite
4	$C_2S + \frac{7}{6}H \rightarrow \frac{1}{6}C_6S_6H + CH$	Xonolite
5	$C_2S + \frac{5}{3}H \rightarrow \frac{1}{6}C_5S_6H_3 + \frac{7}{6}CH$	Riversideite
6	$C_2S + \frac{25}{12}H \rightarrow \frac{1}{6}C_5S_6H_{5.5} + \frac{7}{6}CH$	Tobermorite
7	$C_2S + \frac{35}{12}H \rightarrow \frac{1}{6}C_5S_6H_{10.5} + \frac{7}{6}CH$	Plombierite
8	$C_2S + \frac{13}{6}H \rightarrow \frac{1}{3}C_2S_3H_{2.5} + \frac{4}{3}CH$	Gyrolite
9	$C_2S + \frac{5}{2}H \rightarrow \frac{1}{2}CS_2H_2 + \frac{3}{2}CH$	Okenite
C_3A:		
1	$C_3A + 15H \rightarrow \frac{3}{4}C_4AH_{19} + \frac{1}{2}A_{0.5}H_{1.5}$	-
2	$C_3A + \frac{21}{2}H \rightarrow \frac{3}{4}C_4AH_{13} + \frac{1}{2}A_{0.5}H_{1.5}$	Hydrocalumite
3	$C_3A + 6H \rightarrow C_3AH_6$	-
4	$C_3A + 9H \rightarrow C_2AH_8 + CH$	-
5	$C_3A + 12H \rightarrow CAH_{10} + 2CH$	-

Substance	$G^{\ominus}_{298}$ (kJ/mol)
$C_2SH_{1.17}$	-2481.88
$C_3S_2H_3$	-4407.65
$C_4S_3H_{1.5}$	-5642.31
C_6S_6H	-9457.85
$C_5S_6H_3$	-9271.99
$C_5S_6H_{5.5}$	-9885.03
$C_5S_6H_{10.5}$	-11081.6
$C_2S_3H_{2.5}$	-4544.53
CS_2H_2	-2873.27
C_4AH_{19}	-8775.24
C_4AH_{13}	-7351.33
C_3AH_6	-5016.50
C_2AH_8	-4820.35
CAH_{10}	-4620.09
$A_{0.5}H_{1.5}$	-1154.50
C_3S	-2785.66
C_2S (ß)	-2194.26
C_3A	-3383.96
CH	-897.437
H	-228.698

TABLE 2.
Standard molar Gibbs free energy, $G^{\ominus}_{298}$, of substances in Table 1 (6). The given figures apply to the solid state except for H which is for the gaseous state.

At non-standard conditions the Gibbs free energy of a substance, G, can be written as shown in Equation (1).

$$G = G^{\ominus} + RT \cdot \ln(a) \qquad \text{Eq. (1)}$$

R denotes the gas constant ($R=8.314\ J \cdot (mol \cdot K)^{-1}$), T the temperature [K], and a the activity [ ] of the substance. $\ominus$ denotes "standard conditions" - that is, at a pressure of 1 atmosphere (=101325 Pa).

a=1 for pure solids, whereby Equation (1) is reduced to:

$$G = G^{\ominus} \quad \text{(pure solids)} \qquad \text{Eq. (2)}$$

$a = \frac{p}{p^{\ominus}}$ for water vapor, because water vapor can be considered a good approximation for an ideal gas. p denotes the partial pressure of the water vapor [Pa], and $p^{\ominus}$ the standard pressure ($p^{\ominus}=101325$ Pa). For water vapor, Equation (1) thereby is transformed into Equation (3).

$$G_H = G_H^{\ominus} + RT \cdot \ln(\frac{p}{p^{\ominus}}) = G_H^{\ominus} + RT \cdot \ln(\frac{p_s}{p^{\ominus}}) + RT \cdot \ln(\frac{p}{p_s})$$
$$= G_H^{\ominus} + RT \cdot \ln(\frac{p_s}{p^{\ominus}}) + RT \cdot \ln(RH) \quad \text{(water vapor)} \qquad \text{Eq. (3)}$$

Where p_s denotes the saturation pressure of water vapor (p_s=3167 Pa at 25°C).

As an example numerical calculations based on equation no. 6 for C_2S hydration as shown in Table 1 are presented in the following. At 25°C (298 K) numerical values from Table 2 are inserted in Equation (2) and Equation (3) as follows:

$$G_{CH} = G_{CH}^{\ominus} = -897.437 \ \frac{KJ}{mol}$$
$$G_{C_2S} = G_{C_2S}^{\ominus} = -2194.26 \ \frac{KJ}{mol}$$
$$G_{C_5S_6H_{5.5}} = G_{C_5S_6H_{5.5}}^{\ominus} = -9885.03 \ \frac{KJ}{mol}$$
$$G_H = G_H^{\ominus} + RT \cdot \ln(\frac{p_s}{p^{\ominus}}) + RT \cdot \ln(RH) = -237.29 + 2.48 \ln(RH) \ \frac{KJ}{mol}$$

The change in Gibbs free energy per mole of reaction, $\Delta_r G$, then becomes:

$$\Delta_r G = \sum G_{products} - \sum G_{reactants} = \frac{1}{6} G_{C_5S_6H_{5.5}} + \frac{7}{6} G_{CH} - \left(G_{C_2S} + \frac{25}{12} G_H\right)$$
$$= -5.90 - 5.16 \cdot \ln(RH) \ \frac{KJ}{mol}$$

For RH=100% it will be seen that $\Delta_r G$ is negative. This indicates that the Gibbs free energy of the products is lower than the Gibbs free energy of the reactants. At 100% RH C_2S hydration according to equation 6 in Table 1 is therefore able to proceed spontaneously.

Solving the equation for $\Delta_r G=0$ gives a relative humidity of 32%. This is the limiting relative humidity of this particular reaction equation. At lower relative humidities $\Delta_r G$ is positive and C_2S hydration according to equation 6 in Table 1 can not proceed spontaneously.

Numerical calculations for the other equations of reaction in Table 1 have been carried out in the same way. Table 3 lists the results.

The calculated values in Table 3 should not be considered as being exact values. Due to uncertainty in the thermodynamic data the values only indicate approximate levels. Actually, the calculated limiting relative humidity of equation 6 could be anywhere between 14 and 72% RH, according to uncertainties stated in (6).

Furthermore, the thermodynamic data given in Table 2 apply to the crystalline state. Calcium silicate hydrates produced in cement pastes are normally ill-crystallized. The Gibbs free energy of the calcium silicate hydrates produced in cement pastes, therefore, may be slightly higher than the values in Table 2. Taking this into account, the limiting relative humidities should be higher than indicated in Table 3.

Eq. no.	Relative humidity (%)		
	C_3S	C_2S	C_3A
1	0.000044	3.2	0.30
2	0.086	2700	0.026
3	0.000063	6.4	0.000080
4	0.00017	40	0.014
5	0.0021	53	0.21
6	0.0057	32	
7	0.038	35	
8	0.011	57	
9	0.062	210	

TABLE 3.
Lowest relative humidities that allow hydration to proceed, according to the equations of reaction in Table 1. The values are far more uncertain than indicated by the number of significant digits - cf. the remarks in the text.

Discussion

Limiting relative humidities in Table 3 larger than 100% indicate reactions which are thermodynamically not feasible. C_2S hydration according to equation of reaction no. 2 and 9, therefore, can not proceed at the given temperature and pressure (25°C and 1 atm).

Classical thermodynamics is not able to predict which reaction of the others will proceed. This is determined by kinetic factors.

In principle C_2S hydration is possible at a RH-level close to 3% if hillebrandite is produced (according to equation 1 in Table 3). This might however be irrelevant if hillebrandite is a kinetically less favourable product. If some of the equations of reaction no. 4, 5, 6, 7, or 8 are kinetically dominating a substantial reduction of the hydration rate of C_2S should be expected at a much higher RH-level.

The general trend of Table 3 is clear no matter which of the products that is produced during the hydration of the clinker minerals. Theoretically, hydration of C_3S and C_3A is possible at RH-levels close to 0%, while C_2S hydration contrary to this is expected to stop at a substantially higher RH-level.

Both physical and chemical factors lead to a retardation of cement hydration at lower relative humidities:

The lower the relative humidity the smaller will be the amount of physically held water in the cement paste. Lower relative humidities thus reduce the amount of unhydrated cement which is exposed to water and the space available for hydration products - the cement gel can be produced only in water-filled space. In order to nucleate the hydrate and form hydration products a minimum size of the water-filled spaces is in addition probably required. Furthermore, a decrease in the relative humidity leads to a lower Gibbs free energy of water and thereby reduces the chemical motive power of the hydration.

The experimental data presented in Figures 1 and 2 show that cement hydration is generally hampered at lower relative humidities but markedly detained at RH-levels lower than approximately 75%. This value is not inconsistent with the calculated limiting relative humidities of C_2S hydration presented in Table 3 (note the uncertainties). The discontinuation of self-desiccation at approximately 75% RH therefore might be partly due to thermodynamic factors.

The results of the thermodynamic calculations are supported by experimental evidence of Patel et al. (7). Patel stored a two days old Portland cement paste at different relative humidities and measured the fractions of the C_3S, C_2S, C_3A, and C_4AF phases hydrated after 14 and 90 days. The experiments show that the hydration rate of the C_2S appears to be especially sensitive to relative humidity.

Conclusions

Thermodynamic calculations indicate that especially C_2S hydration is markedly hampered at low relative humidities.

From a practical point of view the presence of C_2S in the cement may contribute to restrict self-desiccation of cement paste.

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