

CHEMICAL REACTION OF FLY ASH

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ABSTRACT

In a previous paper, Brouwers and Van Eijk [1] presented a theoretical study on the dissolution (reaction) of pulverised powder coal fly ash. This fly ash was modelled as hollow spheres, and a shrinking core model was derived for these hollow spheres that contain two regions (an outer hull and an inner region). The obtained analytical equations were applied to the dissolution experiments by Pietersen [2, 3], yielding reaction rates at various temperatures and pH for two class F fly ashes. Based on the observed trends, in the present paper a reaction mechanism is proposed for the glass phase which accounts for the oxide composition of the fly ash (and that is applicable to slags as well). Finally, using the reaction product, the following thermodynamic properties of the studied fly ashes are derived: the free energy, enthalpy and entropy of reaction. The values obtained are in line with those of known substances: silica and an aluminosilicate ($2\text{SiO}_2\cdot\text{Al}_2\text{O}_3$).

1. INTRODUCTION

The ability of fly ash and ground granulated blast furnace slag to react depends strongly on the alkali content and temperature of the ambient solution (Fraay et al. [4], Xu and Sarkar [5], Taylor [6], Hewlett [7], Song and Jennings [8], Song et al. [9]). To investigate the reactivity of fly ash, Pietersen [2, 3] performed dissolution experiments with two pulverised coal fly ashes. They were dissolved in sodium hydroxide (NaOH) solutions of pOH 0.3, 0.6 and 1, and at various temperatures. The two fly ashes originate from two different power plants and have broad and mutually different particle size distributions. One power plant was a “wet-bottom” type plant that operates at 1800 °C (“EFA”); the other FA originates from a low NO_x furnace plant (“LM”). For the dissolution experiments the particles were separated into a fraction of low density (“cenospheres”) with a density smaller than 1400 kg/m³ and in a fraction of high density (“solid spheres”) with a density of 2300-2600 kg/m³. SEM images of polished sections of these fractions revealed that the cenospheres were hollow thin-walled spheres. The dissolution experiments were executed with the hollow cenospheres and the solid spheres, which differ in density about a factor of two.

All dissolution experiments were executed with a sieved part of the fly ashes, the diameter lying between 38 µm and 50 µm. The fly ashes have also been ultrasonically vibrated to prevent agglomeration of small particles to large ones. As expected, dissolution rates (and related reaction rates as well) increased significantly with decreasing pOH (increasing pH) and temperature. The experiments revealed that for EFA and LM, Si, Al and K all congruently dissolve, implying bulk dissolution. Accordingly, the dissolution of one component, Si, represents an adequate measure for the dissolution of the entire glass mass.

In a previous paper [1], the fly ash particles were considered to be spherical, and a shrinking core model was derived and applied to aforesaid experiments of Pietersen [2, 3]. Based on this application, the dependence of the reactivity on the hydroxide content of the solution was obtained, indicating a dissolution rate proportional to $[\text{OH}^-]^{0.9-1}$ for the outer region and to $[\text{OH}^-]^{1.4}$ in the inner region of the fly ash particle. Furthermore, it seemed that the outer region (outer hull) of solid spheres and cenospheres are having the same thickness, about 2 μm .

In this paper a chemical reaction equation for the fly ash is put forward that accounts for the silica, aluminium oxide, alkali, alkaline earth, iron oxide and titanium oxide contents. From this application and proposed reaction mechanism, the solubility of the fly ashes as a function of pH is obtained. Finally, thermodynamic properties (such as the equilibrium constant and free energy of reaction) are determined of the considered fly ashes, and compared with similar substances.

2. CHEMICAL REACTION MECHANISM

In Table 1 the mass fraction of all glass phases in the studied fly ashes are listed, based on the data of Brouwers and Van Eijk [1]. A part of the fly ash is crystalline (quartz and mullite) which is non-reactive. Assuming the same mass density for glass and crystalline phase, the volume fraction of crystalline material corresponds to $1 - \phi$ (ϕ is the glass volume fraction, i.e. the porosity of the leached shell). The vitreous SiO_2 and Al_2O_3 follow from the total mass fraction of each substance minus the crystalline SiO_2 (in quartz and in mullite) and crystalline Al_2O_3 (in mullite only), see Brouwers and Van Eijk [1], respectively. Using the mass fractions of all oxides in the glass, the mean mole fraction of all components in the glass can be computed using the molecular mass of each component, which are included in Table 1 for the EFA and LM solid spheres only (between the brackets). From the composition of the fly ashes as presented in Table 1 it is clear that the glass phases of both fly ashes consist of SiO_2 , as well as the network formers Al_2O_3 , Fe_2O_3 , TiO_2 and P_2O_5 , and the network modifiers CaO , MgO , Na_2O and K_2O (Hemmings and Berry [10]).

Table 1. Mass and mole fraction (between brackets) of the glass phases in LM and EFA solid and cenospheres. Mass fraction is based on total fly ash mass, mole fraction is based on glass phase only.

	EFA		LM		M
	solid (\bar{x})	ceno	solid (\bar{x})	ceno	(g/mole)
crystalline					
$\text{SiO}_2 + \text{Al}_2\text{O}_3 (= 1 - \phi)$	5.1%	8.4%	33.3%	37.8%	
glass					
SiO_2 (S)	51.96% (0.648)	47.05%	38.79% (0.695)	40.41%	60
Al_2O_3 (A)	25.89% (0.190)	28.06%	16.48% (0.174)	13.54%	102
Fe_2O_3 (F)	4.65% (0.022)	2.96%	3.50% (0.024)	2.02%	160
P_2O_5 (P)	n.d.	n.d.	0.54% (0.004)	n.d.	142
TiO_2 (T)	1.20% (0.011)	0.91%	1.90% (0.026)	1.43%	80
CaO (C)	2.83% (0.038)	0.80%	2.75% (0.053)	1.15%	56
MgO (M)	1.82% (0.034)	1.41%	0.28% (0.008)	0.24%	40
Na_2O (N)	1.84% (0.022)	1.94%	0.37% (0.006)	0.38%	62
K_2O (K)	4.40% (0.035)	5.68%	1.00% (0.011)	1.02%	94
$\alpha = x_A/x_S$	0.293		0.250		
$\beta = (x_A + x_C)/x_S$	0.111		0.087		
$\gamma = (x_N + x_K)/x_S$	0.088		0.026		
$\delta = x_F/x_S$	0.034		0.034		
$\varepsilon = x_T/x_S$	0.017		0.037		
a (eq. (10))	1.022		1.208		
\bar{M}	71		72		

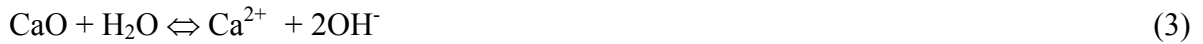
In Pourbaix [11] the prevailing equilibria of the various substances can be found for $\text{pH} > 12$ and an electric potential ranging from -0.3 to 0.2 V, values that are found in ordinary Portland and slag cement systems (MacPhee and Glasser [12]). Paul [13, 14] also presented hydration reactions for vitreous SiO_2 , Al_2O_3 , Na_2O and K_2O . Accordingly, from all this literature it follows that for $\text{pH} > 12$ vitreous silica is hydrated as



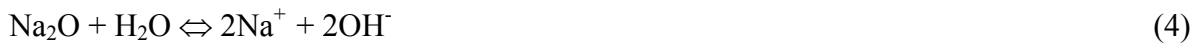
and that Al_2O_3 is hydrated according to



that CaO (and MgO) reacts as follows



that Na_2O (and K_2O) reacts as follows



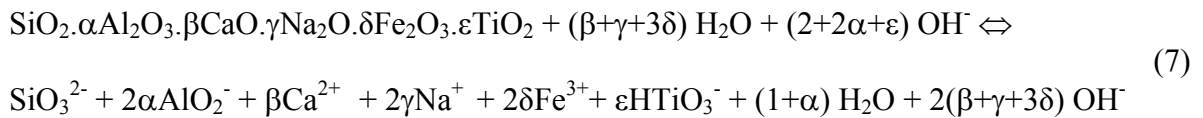
that Fe_2O_3 reacts as follows



and that TiO_2 hydrates as follows



Accordingly, the following reaction of the fly ash glass is proposed as



Note that silica, aluminium oxide and titanium oxide consume hydroxides, whereas the earth alkalis (CaO , MgO), alkalis (Na_2O , K_2O) and iron oxide produce them. As slag contain the same components as fly ashes, it is believed that the model might be applicable to the dissolution of this material as well. In case a fly ash or a slag also contains MnO and SO_3 , the former reacts as CaO/MgO (to Mn^{2+}), and the latter likewise SiO_2 (to SO_4^{2-}).

As the activity of pure liquids and solids are unity, the equilibrium constant is defined as

$$K = \frac{[\text{AlO}_2^-]^{2\alpha} [\text{Ca}^{2+}]^\beta [\text{Na}^+]^{2\gamma} [\text{Fe}^{3+}]^{2\delta} [\text{HTiO}_3^-]^\varepsilon [\text{SiO}_3^{2-}]}{[\text{OH}^-]^{2+2\alpha-2\beta-2\gamma-6\delta+\varepsilon}} \quad (8)$$

Invoking $[\text{AlO}_2^-] = 2\alpha [\text{SiO}_3^{2-}]$, $[\text{Ca}^{2+}] = \beta [\text{SiO}_3^{2-}]$, $[\text{Na}^+] = 2\gamma [\text{SiO}_3^{2-}]$, $[\text{Fe}^{3+}] = 2\delta [\text{SiO}_3^{2-}]$ and $[\text{HTiO}_3^-] = \varepsilon [\text{SiO}_3^{2-}]$ yields

$$[\text{SiO}_3^{2-}] = \left(\frac{K}{(2\alpha)^{2\alpha} \beta^\beta (2\gamma)^{2\gamma} (2\delta)^{2\delta} \varepsilon^\varepsilon} \right)^{\frac{1}{1+2\alpha+\beta+2\gamma+2\delta+\varepsilon}} [\text{OH}^-]^a \quad (9)$$

with

$$a = \frac{2 + 2\alpha - 2\beta - 2\gamma - 6\delta + \varepsilon}{1 + 2\alpha + \beta + 2\gamma + 2\delta + \varepsilon} \quad (10)$$

Note that the powers appearing in the denominator of the first factor of equation (9), $(2\alpha)^{2\alpha}$ etc., are of order unity. The function x^x namely attains a value of 1 at $x = 0$ and $x = 1$, and has a minimum of $(1/e)^{(1/e)} (\approx 0.69)$ at $x = e^{-1}$. From Table 1 it can be seen that the values of α etc. are such that 2α etc. all fall in the range 0 to 1, so that $(2\alpha)^{2\alpha}$ etc. all have a value between 0.69 and 1. Furthermore, it will be demonstrated that K is (much) smaller than unity. So, with increasing α etc. (i.e. less silica) the power of the first factor decreases, and hence, the factor increases. Accordingly, when the silica content diminishes, the solubility (reactivity) is enhanced. This trend is also supported by the second factor on the right-hand side of equation (9). The power a decreases with increasing α , β etc., see equation (10). For β , γ and δ this effect is obvious. But this trend also holds for α and ε : the function $(2+x)/(1+x)$ attains a value of 2 at $x = 0$, and monotonically decreases towards the asymptotic value of 1 for large x . Considering that $[\text{OH}^-]$ is usually smaller than 1 mole/l, increasing α , β etc. imply a smaller a and also a larger second factor in equation (9), i.e. the same trend as the first factor.

Considering the equilibrium product it follows that the hydration of pure silica is quadratically dependent on $[\text{OH}^-]$ ($\alpha = \beta = \gamma = \delta = \varepsilon = 0$). In case of a pure aluminosilicate glass ($\beta = \gamma = \delta = \varepsilon = 0$), the power a is located between unity and 2, but depending weakly on changes in α . E.g., for α ranging from $\frac{1}{4}$ to 1, this power ranges from 1.66 to 1.33 (it equals 1.5 for $\alpha = 0.5$). For alkali silicate glasses ($\alpha = \beta = \delta = \varepsilon = 0$), it follows from equation (10) that the power a is smaller than unity when $\gamma > 0.25$.

With the mole fractions listed in Table 1, subsequently the mean α , β , γ , δ and ε and a can be computed for solid EFA and LM, which are included in this table as well. For this calculation it is assumed MgO to react as CaO and K₂O as Na₂O. P₂O₅ can be neglected, as its presence is minor (Table 1).

One can readily see that the power a takes a value of 1.022 (EFA) and 1.208 (LM), which is reasonably in line with the power obtained by Brouwers and Van Eijk [1]: 1.4 in LM inner region, 0.9 and 1 in EFA and LM outer region, respectively. This deviation can probably be attributed to the inhomogeneity of the fly ash. Inner and outer region may have different composition, which would result in each region having its own value for a . Experiments by Dudas and Warren [15] confirm that the glass components K₂O, Na₂O, CaO, MgO, and Fe₂O₃ are concentrated in the exterior (outer) hull. Smith [16] found a similar enrichment in the outer layer, and explained this inhomogeneity by the fact that the boiling point of silica and aluminiumoxide are practically the same (2950 °C and 2980 °C, respectively), and higher than the boiling points of all other components. This will result in a concentration of more volatile components (i.e. the other oxides) in the outer layer. Considering equation (10), one can see indeed that the power a is smaller/larger for larger/smaller values of β , γ etc. This confirms the hypothesis of K₂O, Na₂O, CaO, MgO, and Fe₂O₃ concentrated in the outer region.

3. THERMODYNAMIC ANALYSIS

On the basis of the reaction times determined by Brouwers and Van Eijk [1] and the proposed reaction mechanism in the previous section, thermodynamic data for the fly ash can be determined. The first step in this analysis is the determination of $[\text{SiO}_3^{2-}]$ that appears in equations (8) and (9). This property follows from the scaled reaction time that reads:

$$\tau = \frac{x_s \rho_g R^2}{6\phi D_s C_{Sc}} \quad (11)$$

The values of τ for EFA and LM followed from the application (fitting) of a shrinking core model to the experiments of Pietersen [2,3] by Brouwers and Van Eijk [1]. In equation (11) ρ_g is the molar density of the glass, x_s the mole fraction of silica in the glass, D_s the bulk diffusion coefficient of the SiO_3^{2-} ion, R the outer radius of the fly ash particle, and C_{Sc} the SiO_3^{2-} concentration at the glass core (i.e. on the reacting surface) and ϕ the glass volume fraction (porosity of leached shell).

It is expected that the dissolution process will be governed by the ion that diffuses the slowest through the leached shell. Here, only the diffusion coefficients of $[\text{AlO}_2^-]$ and $[\text{SiO}_3^{2-}]$ are compared, which are not both directly available. Accordingly, D_A^0 was estimated using the diffusion coefficients of the similar ions NO_2^- ($1.912 \cdot 10^{-9} \text{ m}^2/\text{s}$) and ClO_2^- ($1.385 \cdot 10^{-9} \text{ m}^2/\text{s}$), yielding $D_A^0 = 1.7 \cdot 10^{-9} \text{ m}^2/\text{s}$ at $T = 298 \text{ K}$ (Lide [17]). Similarly, D_S^0 was estimated using the diffusion coefficients of CO_3^{2-} ($0.912 \cdot 10^{-9} \text{ m}^2/\text{s}$) and SO_3^{2-} ($1.064 \cdot 10^{-9} \text{ m}^2/\text{s}$), yielding $D_S^0 = 1.0 \cdot 10^{-9} \text{ m}^2/\text{s}$ at $T = 298 \text{ K}$ (Lide [17]). Note that the molecular mass of aluminium lies between the molecular masses of nitrogen and chloride, and silicon between carbon and sulphur, so that the estimation is expected to a yield reasonable result. As D_A (but also the diffusion coefficients of Ca^{2+} , Na^+ , K^+ and Fe^{3+} [17]) is larger than D_s , it is believed henceforth that the process is governed by the diffusion of SiO_3^{2-} and hence, $D_s C_{Sc}$ appearing in equation (11) to correspond to $D_s [\text{SiO}_3^{2-}]$. For deviating temperatures, D_s is determined via

$$D_s = \frac{T}{298K} D_s^0 \quad (12)$$

whereby T is in Kelvin. Combining equations (11), (9) and (12) yields

$$K = (2\alpha)^\alpha (\beta)^\beta (2\gamma)^{2\gamma} (2\delta)^{2\delta} (\varepsilon)^\varepsilon \left[\frac{x_s \rho_g R^2}{6\phi D_s^0 \tau} \frac{298K}{T} \right]^{1+2\alpha+\beta+2\gamma+2\delta+\varepsilon} [\text{OH}^-]^{-2-2\alpha+2\beta+2\gamma+6\delta-\varepsilon} \quad (13)$$

The physical properties that appear in this equation are known: R ($22 \mu\text{m}$), ϕ (Table 1), while ρ_g follows from the mass density of the glass (about 2450 kg/m^3) divided by the mean molar mass. The mean molar mass of the glass follows from the sum of the molar fraction of each constituent times its molar mass ($\bar{M} = \sum x_k M_k$), which are included in Table 1 as well.

Table 2. Reaction time τ for EFA solid spheres for various temperatures (pOH = 0.3).

T (K)	τ_o (days)	τ_i (days)	$t_{i-o}(1-\tau_i/\tau_o)$ (days)	K_o (l/mole)	ΔG_o (J/mole)
293	8000			$4.46 \cdot 10^{-17}$	$9.1717 \cdot 10^4$
303	3000			$2.84 \cdot 10^{-16}$	$9.0179 \cdot 10^4$
313	750	275	1.6	$4.02 \cdot 10^{-15}$	$8.6264 \cdot 10^4$
ΔH (J/mole)					$1.80 \cdot 10^5$
ΔS (J/moleK)					298
ΔG_{298} (J/mole)					$9.120 \cdot 10^4$

The τ at various temperature have been determined by Brouwers and Van Eijk [1] and are listed in Tables 2 and 3, as well as $[\text{OH}^-]$ and the temperature. The reaction time has been determined both for inner and outer region (denoted by τ_i and τ_o , respectively).

Using the data of Tables 2 and 3, the K of EFA and LM solid spheres, respectively, are computed using equation (13) and the result is included in both tables as well. For inner and outer region, K is denoted by K_i and K_o , respectively. For these computations the mean values α , β etc. and x_S have been used. Note that t_{i-o} is that the time when the outer region has fully reacted and the inner region starts to react (the outer region starts to react at $t = 0$ s. [1]).

Table 3. Reaction time τ for LM solid spheres for various temperatures (pOH = 0.3)

T (K)	τ_o (days)	τ_i (days)	$t_{i-o}(1-\tau_i/\tau_o)$ (days)	K_o (l/mole)	ΔG_o (J/mole)	K_i (l/mole)	ΔG_i (J/mole)
293	2000			$8.99 \cdot 10^{-14}$	$7.3181 \cdot 10^4$		
303	1500	900	1.0	$1.40 \cdot 10^{-13}$	$7.4563 \cdot 10^4$	$3.41 \cdot 10^{-13}$	$7.2322 \cdot 10^4$
313	700	190	1.0	$4.99 \cdot 10^{-13}$	$7.3716 \cdot 10^4$	$4.84 \cdot 10^{-12}$	$6.7805 \cdot 10^4$
ΔH (J/mole)					$8.00 \cdot 10^4$	$1.90 \cdot 10^5$	
ΔS (J/moleK)					19	390	
ΔG_{298} (J/mole)					$7.434 \cdot 10^4$	$7.378 \cdot 10^4$	

The two tables indicate that K increases with temperature, implying improved dissolution/reaction with increasing temperature. Furthermore, the values of K and equation (9) confirm that $[\text{SiO}^{2-}]$ is much smaller than $[\text{OH}^-]$ indeed, so that the assumption that the process is governed by the diffusion of the SiO_3^{2-} ion is correct (Brouwers and Van Eijk [1]).

With these K one can determine the standard free energy of reaction ΔG by

$$K = e^{\frac{-\Delta G}{RT}} \quad (14)$$

ΔG is the sum of free energies of formation of the products in their standard states minus the free energies of formation of the reactants in their standard states (Paul [13, 14], Babushkin et al. [18]). In Tables 2 and 3 the resulting ΔG are included using $R = 8.31439$ J/moleK.

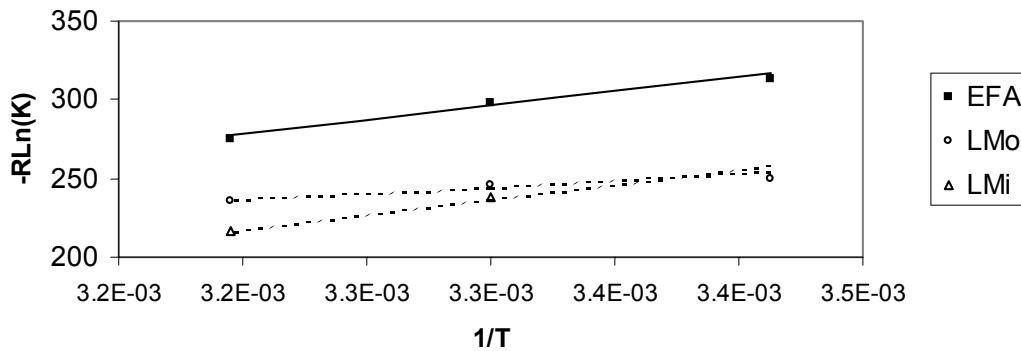


Figure 1. $R \ln K$ versus $1/T$ for LM (inner and outer region) and EFA (outer region only) solid fly ash.

The connection of ΔG with enthalpy and entropy of reaction is

$$\Delta G = \Delta H - T\Delta S \quad (15)$$

in which ΔH and ΔS are the sum of standard heats of formation and of the standard entropies, respectively, where each sum is constituted by the sum of the products minus the sum of the reactants. In order to specify ΔH and ΔS , $-R \ln(K)$ has been set out against $1/T$ for LM and EFA in Figure 1, taking the values of Tables 2 and 3. A straight line has been fitted through the experimental values, whereby

$$-R \ln(K) = \frac{\Delta H}{T} - \Delta S \quad (16)$$

see equations (14) and (15). The fitted values of ΔH and ΔS have been included in Tables 2 and 3.

Next, with the standard free energy of reaction ΔG , one is in a position to determine the free energy, enthalpy and entropy of formation of LM and EFA glass phase. In Table 4, the free energy, enthalpy and entropy of formation (ΔG^0 , ΔH^0 and S^0 , respectively) of some substances are listed ($T = 298 \text{ K}$), taken from Paul [13] and Babushkin et al. [18], employing $1 \text{ cal} = 4.184 \text{ J}$.

Table 4. Thermodynamic properties, taken from Babushkin et al. [18] (with exception of HTiO_3^- , which is taken from Paul [13]), and computed values.

	ΔH^0 (J/mole)	S^0 (J/moleK)	ΔG^0 (J/mole)
<i>literature</i>			
H^+	0	0	0
OH^-	- 229,999	- 10.753	- 157,277
AlO_2^-	- 918,806	- 20.92	- 823,411
SiO_3^{2-}	-	-	- 939,726
Ca^{2+}	542,665	- 55.23	- 552,706
Mg^{2+}	- 461,746	- 119.66	- 455,261
Na^+	- 240,454	- 58.99	- 262,211
K^+	- 252,295	- 102.17	- 282,671
Fe^{3+}	- 50,752	- 279.07	- 17,866
HTiO_3^-	-	-	- 467,353
H_2O	- 285,830	69.915	- 237,178
SiO_2 (gl)	- 901,568	46.861	- 848,641
SiO_2 (β -quartz)	- 911,066	41.840	- 856,674
$2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ (cr)	- 3,378,412	124.18	- 3,173,397
<i>computed</i>			
EFA outer region (gl)			- 1,547,777
LM outer region (gl)			- 1,419,672
LM inner region (gl)			- 1,419,112

Unfortunately, from SiO_3^{2-} and HTiO_3^- only ΔG^0 is available, so that it is only possible to determine ΔG^0 of the fly ash (and not ΔH^0 nor S^0).

Firstly, ΔG of the EFA and LM reaction is computed at 298K using equation (15) and the fitted values of ΔH and ΔS as listed in Tables 2 and 3. The resulting ΔG_{298} is being included in these tables as well. Considering reaction (7), ΔG^0 of EFA and LM glass now follow from:

$$\begin{aligned} \Delta G^0 = & -\Delta G_{298} - (2+2\alpha-2\beta-2\gamma-6\delta+\varepsilon)\Delta G_{OH^-}^0 + \Delta G_{SiO_3^{2-}}^0 + 2\alpha \Delta G_{AlO_2^-}^0 + \\ & \beta \left(\frac{x_C}{x_C + x_M} \Delta G_{Ca^{2+}}^0 + \frac{x_M}{x_C + x_M} \Delta G_{Mg^{2+}}^0 \right) + 2\gamma \left(\frac{x_N}{x_N + x_K} \Delta G_{Na^+}^0 + \frac{x_K}{x_N + x_K} \Delta G_{K^+}^0 \right) \quad (17) \\ & + 2\delta \Delta G_{Fe^{3+}}^0 + \varepsilon \Delta G_{HTiO_3^-}^0 + (1+\alpha-\beta-\gamma-3\delta) \Delta G_{H_2O}^0 \end{aligned}$$

Taking x_C , x_M , x_N , x_K , α , β , γ , δ , and ε from Table 1, the value of ΔG_{298} listed in Tables 2 and 3, and taking the free energies of formation from Table 4, ΔG^0 of EFA and LM is computed using equation (17) and included in this latter table as well.

Note that in reaction equation (7), β and γ represent the total molar content of earth alkalis and alkalis to molar content of silica, respectively. But to compute ΔG^0 , the actual contents of MgO, CaO, Na₂O and K₂O have to be accounted of. For that reason, the molar ratios $x_C/(x_M + x_C)$ etc. are appearing in equation (17).

From Table 4 one can conclude that with increasing α (i.e. A/S molar ratio) $-\Delta G^0$ increases. For EFA, α takes a value of about 0.29 and for LM about 0.25, and indeed, $-\Delta G^0$ of EFA is larger. Furthermore, one can see that for LM the values pertaining to inner and outer are very close. From this information it can be concluded that $-\Delta G^0$ is mainly governed by α .

In order relate the computed values of $-\Delta G^0$ with values reported in literature, values of $-\Delta G^0$ of silica (quartz and vitreous, $\alpha = 0$) and of 2SiO₂.Al₂O₃ ($\alpha = 0.5$) are also included in Table 4. One can see that $-\Delta G^0$ of LM and EFA are located between the values of silica and of 2SiO₂.Al₂O₃. Moreover, they are in line with the trend that for larger α , $-\Delta G^0$ also increases, confirming the reliability of the computed values of $-\Delta G^0$.

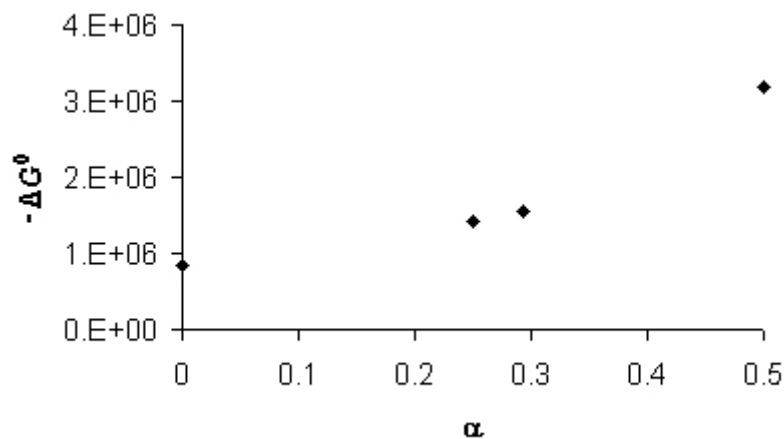


Figure 2. $-\Delta G^0$ versus α (A/S molar ratio).

In Figure 2, $-\Delta G^0$ is set out graphically against α , whereby the value of $-\Delta G^0$ is taken from vitreous silica ($\alpha = 0$) and from EFA and LM outer regions.

For most fly ashes, α lies in the range 0.25-0.29. For these fly ashes a tentative value of $-\Delta G^0$ can be obtained from the values of LM and EFA determined here, e.g. by interpolation. For values in the range 0-0.25 and 0.29 to 0.5, interpolation between silica and LM and between EFA and $2\text{SiO}_2.\text{Al}_2\text{O}_3$, respectively, is recommended. The latter range generally holds for slags. A direct measurement (e.g. by dissolution experiments, applying a shrinking core model, the chemical reaction mechanism and the thermodynamic analysis) of $-\Delta G^0$ would be more accurate, but also more elaborate. Interpolation as proposed here will readily provide a value that can be useful for tentative reactivity computations.

4. CONCLUSIONS

Pietersen [2, 3] has carefully executed and reported dissolution experiments of several types of pulverised powder coal (class F) fly ashes (Table 1). To this end, the silica release in time was measured for various pOH and temperatures. In order to understand the dissolution and reaction behaviour of these fly ashes, in particular the EFA and LM fly ash, Brouwers and Van Eijk [1] derived a shrinking core model. They have applied the model to said experiments, yielding values of the reactivity time τ (eq. (11)) for both inner and outer region (τ_i and τ_o), which are summarised in Tables 2 and 3. Furthermore, it was found that the dissolution rate is proportional to $[\text{OH}]^{0.9-1}$ for the outer region (EFA and LM), and to $[\text{OH}]^{1.4}$ in inner region (information available about LM only).

Here, a reaction mechanism for the glass phase of the fly ash glass is put forward that accounts for its oxide composition (silica, aluminium oxide, iron oxide, titanium oxide, alkali and earth alkali content) and which also could be useful for slags.). From the proposed reaction mechanism and equilibrium constant, it follows that the solubility of the fly ashes is as a function of $[\text{OH}]^a$. The parameter a solely depends on the oxide composition of the glass phase. Using the average composition of EFA and LM fly ash, the power a takes a value of 1.022 (EFA) and 1.208 (LM). This result suggests that the outer layer is poorer in silica and aluminiumoxide, i.e. that K_2O , Na_2O , CaO , MgO , and Fe_2O_3 are concentrated in the exterior hull, which is in line with findings in previous publications.

Combining the equilibrium constant and the experimental data at various temperatures, also the free energy, enthalpy and entropy of reaction are computed of EFA and LM glass phase. Finally, these data are used to compute the free energy of formation ΔG^0 of both glasses. It follows that the free energy of formation is mainly governed by the molar ratio (α) of the major constituents SiO_2 and Al_2O_3 . The values obtained are in line with those of known substances, silica ($\alpha = 0$) and $2\text{SiO}_2.\text{Al}_2\text{O}_3$ ($\alpha = 0.5$). With this information one can assess ΔG^0 of (fly ash and slag) glass phases with deviating A/S molar ratio, and subsequently, to assess their reactivity in a cement environment.

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