Corrigendum to "The dissolution rates of simulated UK Magnox – ThORP blend nuclear waste glass as a function of pH, temperature and waste loading" [*Miner. Mag.* **79**, (2015) 1529–1542]

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Abstract

We revise the data fitting in our original paper [The dissolution rates of simulated UK Magnox - ThORP blend nuclear waste glass as a function of pH, temperature and waste loading, *Miner. Mag.* **79** (2015) 1529–1542]. The intrinsic rate constant data were calculated incorrectly, the corrected data are presented herein. To support the corrected analysis we have also taken the opportunity to report some additional 90°C data. The conclusions of the original paper remain sound.

KEYWORDS: Nuclear waste, glass dissolution, high pH.

Introduction

IN our 2015 paper (Cassingham *et al.*, 2015) an analysis of UK Magnox – ThORP blend glass dissolution kinetics was presented as a function of composition, temperature, pH and solution chemistry according to the Transition State Theory (Eyring, 1935). The modified version of this kinetic rate equation for glass (Grambow, 1985), is given by:

$$r_i = \vec{k} v_i a_{H^+}^{\eta} \exp\left(\frac{-E_a}{RT}\right) \left[1 - \left(\frac{Q}{K_g}\right)^{\sigma}\right] \quad (1)$$

where r_i (in g m^{-2} d^{-1}), is the dissolution rate of element i, $\vec{k}$ (in g m^{-2} d^{-1}) the forward rate constant, v_i the stoichiometric coefficient for element i, E_a the activation energy, RT the product of the gas constant and the absolute temperature, a_{H^+} the hydrogen ion activity, η the power-law coefficient,

Q (unitless) the activity product of the rate-limiting reaction, K_g the pseudo-equilibrium constant for the rate-controlling phase and σ the overall reaction order. Under conditions of the single-pass flow-through method considered in this paper, calculation of the dissolution rate using equation 1 assumes that the saturation state of the system, given by Q/K_g is equal to zero ($Q \approx 0$), so that equation 1 becomes:

$$r_i = \vec{k} v_i a_{H^+}^{\eta} \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

Taking logs gives:

$$\log R_i = \log \vec{k} + \eta \text{pH} - \frac{E_a}{2.303RT} \quad (3)$$

where $R_i = r_i/v_i$ is the normalized release rate for element i.

Following further analysis of the data in Cassingham *et al.* (2015), it became apparent that the forward rate constant, activation energy, E_a and the pH power law coefficient, η, were erroneously calculated sequentially, rather than simultaneously. The fact that the solution conditions under which the data were collected were far from equilibrium,

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TABLE 1. Normalized dissolution rate (in g m^{-2} d^{-1}) of Si (R_{Si}), B (R_B) and Na (R_{Na}) and for MT25 and MT30 blend simulated waste glass as a function of pH (pH measured at temperature [pH(T)] and pH calculated at room temperature [pH(23°C)] are both stated) and temperature, including the magnitude of the difference in normalized dissolution rate (ΔR_i) between the two compositions.

pH (23°C)	pH (T)	Temperature (°C)	MT25 R_i/g m^{-2} d^{-1}	MT30 R_i/g m^{-2} d^{-1}	$\|\Delta R_i\|$ /g m^{-2} d^{-1}
R_{Si}					
8	8.00	23	0.011 ± 0.004	0.015 ± 0.006	0.004 ± 0.002
8	7.90	40	0.119 ± 0.036	0.105 ± 0.032	0.014 ± 0.006
8	7.60	70	0.945 ± 0.284	0.882 ± 0.218	0.063 ± 0.025
8	7.50	90	2.590 ± 0.318	1.716 ± 0.194	0.874 ± 0.146
10	10.00	23	0.027 ± 0.010	0.034 ± 0.009	0.007 ± 0.003
10	9.75	40	0.321 ± 0.096	0.436 ± 0.143	0.115 ± 0.051
10	9.30	70	4.148 ± 1.245	4.848 ± 1.454	0.700 ± 0.297
10	9.25	90	18.761 ± 2.934	9.166 ± 2.874	9.595 ± 3.362
12	12.00	23	0.642 ± 0.249	0.778 ± 0.217	0.136 ± 0.065
12	9.30	40	4.403 ± 1.323	6.038 ± 3.156	1.635 ± 0.985
12	10.70	70	45.786 ± 6.767	61.292 ± 7.829	15.506 ± 3.029
R_B					
8	8.00	23	0.006 ± 0.077	0.005 ± 0.004	0.001 ± 0.013
8	7.90	40	0.051 ± 0.015	0.032 ± 0.003	0.019 ± 0.006
8	7.60	70	0.395 ± 0.119	0.369 ± 0.091	0.026 ± 0.011
8	7.50	90	0.560 ± 0.074	0.816 ± 0.110	0.256 ± 0.048
10	10.00	23	0.030 ± 0.010	0.024 ± 0.009	0.006 ± 0.003
10	9.75	40	0.107 ± 0.032	0.189 ± 0.080	0.082 ± 0.043
10	9.30	70	2.548 ± 0.772	1.570 ± 0.471	0.978 ± 0.417
10	9.25	90	4.640 ± 1.344	28.724 ± 11.291	24.084 ± 11.830
12	12.00	23	0.489 ± 0.189	0.536 ± 0.208	0.047 ± 0.026
12	9.30	40	2.160 ± 0.651	2.641 ± 0.401	0.481 ± 0.162
12	10.70	70	12.059 ± 5.220	14.915 ± 4.480	2.856 ± 1.505
R_{Na}					
8	8.00	23	0.011 ± 0.011	0.016 ± 0.004	0.005 ± 0.005
8	7.90	40	0.101 ± 0.030	0.057 ± 0.022	0.044 ± 0.021
8	7.60	70	1.006 ± 0.305	0.899 ± 0.221	0.107 ± 0.042
8	7.50	90	1.583 ± 0.209	1.910 ± 0.253	0.327 ± 0.061
10	10.00	23	0.056 ± 0.022	0.050 ± 0.019	0.006 ± 0.003
10	9.75	40	0.225 ± 0.068	0.544 ± 0.167	0.319 ± 0.137
10	9.30	70	4.827 ± 2.064	3.146 ± 1.335	1.681 ± 1.013
10	9.25	90	15.138 ± 3.797	70.455 ± 24.434	55.316 ± 23.674
12	12.00	23	1.963 ± 0.760	1.803 ± 0.497	0.160 ± 0.076
12	9.30	40	4.715 ± 1.421	5.684 ± 0.859	0.969 ± 0.327
12	10.70	70	33.049 ± 5.749	18.763 ± 5.647	14.286 ± 4.966

implying congruent dissolution, should have led to pH and temperature independent values for η. As can be seen in Tables 4–6 of our original article, these parameters are not independent. It also became apparent that there were minor errors on the tabulated dissolution rate data. Herein we present the corrected data and analysis, as performed by simultaneous non-linear regression of the dissolution rate data, according to McGrail *et al.* (1997).

TABLE 2. Calculated η values, activation energies and forward rate terms together with the correlation coefficient of the fit, and estimated error terms for MT25 and MT30 waste simulant glasses.

	η	E_a /kJ mol^{-1}	log ($\vec{k}$/g m^{-2} d^{-1})	$\vec{k}$/g m^{-2} d^{-1}	r^2
MT25					
B	0.49 ± 0.05	76.6 ± 6.3	7.4 ± 0.9	$(2.5^{+5.2}_{-2.5}) \times 10^7$	0.96
Na	0.52 ± 0.05	80.9 ± 6.4	8.1 ± 1.0	$(1.3^{+2.9}_{-1.3}) \times 10^8$	0.96
Si	0.47 ± 0.06	88.9 ± 6.9	9.8 ± 1.0	$(0.6^{+1.5}_{-0.6}) \times 10^{10}$	0.96
MT30					
B	0.55 ± 0.05	89.9 ± 5.6	9.0 ± 0.9	$(1.0^{+1.8}_{-1.0}) \times 10^9$	0.97
Na	0.53 ± 0.06	85.1 ± 6.9	8.8 ± 1.0	$(0.6^{+1.5}_{-0.6}) \times 10^9$	0.96
Si	0.50 ± 0.06	82.1 ± 8.3	8.5 ± 1.3	$(0.3^{+9.5}_{-0.3}) \times 10^8$	0.94

Kinetic data for Magnox – ThORP blend nuclear waste glass simulants

Table 1 presents the normalized dissolution rates of MT25 (Magnox-ThORP glass with a 25 wt.% waste loading) and MT30 (Magnox-ThORP glass with a 30 wt.% waste loading) as a function of pH and temperature. The differences between each composition (ΔR_i) are also highlighted. Table 1 is a corrected version of table 3 in Cassingham *et al.* (2015). We have also taken the opportunity to report some additional 90°C data, which were used to improve the multivariate data fitting.

In Cassingham *et al.* (2015) the values of the activation energies and the η values were obtained by separate linear regressions, while holding either pH or temperature constant. In fact, it has been shown that a multivariate analysis should be used to avoid erroneously indicating that E_a depends on pH or η on temperature (McGrail *et al.*, 1997). In addition, the intrinsic rate constant, $\vec{k}$, was reported as the intercept of the pH power law coefficient regression. Table 2 gives the corrected values for all three terms as calculated by simultaneous linear regression over pH and $1/(2.303RT)$ using equation 3 for MT25 and MT30. By performing this analysis, the values obtained for η and E_a for each species considered (B, Na and Si) are not significantly different, within the margins of error (Table 2), demonstrating that the MT25 and MT30 glass compositions undergo congruent dissolution.

As the regression is conducted on log R_i a value of log $\vec{k}$, is obtained, hence this is reported along with the estimated errors in log $\vec{k}$ in Table 2. For completeness, values of $\vec{k}$ and $\Delta\vec{k}$ (the estimated error in $\vec{k}$) are also reported in Table 2. As the estimated error, $\Delta(\log \vec{k})$, in log $\vec{k}$ is typically of the order of 10%, when standard propagation of error manipulation is undertaken, the value of $\Delta\vec{k}$ lies between two and three times the value of $\vec{k}$, implying that $\vec{k}$ may become negative which is physically impossible; accordingly the maximum negative error has been taken as being equal to $\vec{k}$. Estimating the error in $\vec{k}$ by evaluating $10^{[\log\vec{k}+\Delta(\log\vec{k})]}$ and $10^{[\log\vec{k}-\Delta(\log\vec{k})]}$ yields similar or slightly smaller negative errors and notably larger positive errors to those reported in Table 2. Overall the size of the $\Delta\vec{k}$ values indicate that the calculated $\vec{k}$ values have limited meaning.

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