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1 Corrigendum to “The dissolution rates of simulated UK
2 Magnox - ThORP blend nuclear waste glass as a function of
3 pH, temperature and waste loading” [Miner. Mag. 79
4 (2015) 1529 – 1542]

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31 **Abstract**

32 We revise the data fitting in our original paper [The dissolution rates of simulated UK Magnox - ThORP
33 blend nuclear waste glass as a function of pH, temperature and waste loading, Miner. Mag. 79 (2015)
34 1529 – 1542]. The intrinsic rate constant data were calculated incorrectly, the corrected data are
35 presented herein. To support the corrected analysis we have also taken the opportunity to report some
36 additional 90°C data. The conclusions of the original paper remain sound.

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39 **Introduction**

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

45
$$r_i = \vec{k} v_i a_{H^+}^\eta \exp\left(\frac{-E_a}{RT}\right) \left[1 - \left(\frac{Q}{K_g}\right)^\sigma\right] \quad (1)$$

46 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
47 the stoichiometric coefficient for element i , E_a the activation energy, RT the product of the gas constant
48 and the absolute temperature, a_{H^+} the hydrogen ion activity, η the power-law coefficient, Q (unitless)
49 the activity product of the rate-limiting reaction, K_g the pseudo-equilibrium constant for the rate-
50 controlling phase and σ the overall reaction order. Under conditions of the single pass flow through
51 method considered in this paper, calculation of the dissolution rate using Equation (1) assumes that the
52 saturation state of the system, given by Q/K_g is equal to zero ($Q \approx 0$), so that Eqn (1) becomes:

53
$$r_i = \vec{k} v_i a_{H^+}^\eta \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

54 Taking logs gives:

55
$$\log R_i = \log \vec{k} + \eta \text{pH} - \frac{E_a}{2.303RT} \quad (3)$$

56

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

58 Following further analysis of the data in Cassingham et al. (2015), it became apparent that the forward
59 rate constant, activation energy, E_a and the pH power law coefficient, η , were, erroneously calculated
60 sequentially, rather than simultaneously. The fact that the solution conditions under which the data
61 were collected were far from equilibrium, implying congruent dissolution, should have led to pH and
62 temperature independent values for η . As can be seen in Tables 4 - 6 of our original article, these
63 parameters are not independent. It also became apparent that there were minor errors on the
64 tabulated dissolution rate data. Herein we present the corrected data and analysis, as performed by
65 simultaneous non-linear regression of the dissolution rate data, according to McGrail et al. (1997).

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67 **Kinetic data for Magnox – ThORP blend nuclear waste glass simulants**

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

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92 Table 1. Normalised dissolution rate (in $\text{g m}^{-2} \text{d}^{-1}$) of Si (R_{Si}), B (R_{B}) and Na (R_{Na}) and for MT25 and MT30 blend
 93 simulated waste glass as a function of pH (pH measured at temperature [pH(T)] and pH calculated at room
 94 temperature [pH(23°C)] are both stated) and temperature, including the magnitude of the difference in
 95 normalised dissolution rate (ΔR_i) between the two compositions.

pH (23 °C)	pH (T)	Temperature (°C)	MT25 $R_i / \text{g m}^{-2} \text{d}^{-1}$	MT30 $R_i / \text{g m}^{-2} \text{d}^{-1}$	$ \Delta R_i $ $/ \text{g m}^{-2} \text{d}^{-1}$
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

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

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

	η	$E_a/\text{kJ mol}^{-1}$	$\log(\vec{k}/\text{g m}^{-2} \text{d}^{-1})$	$\vec{k}/\text{g m}^{-2} \text{d}^{-1}$	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

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113 As the regression is conducted on $\log R_i$, values a value of $\log \vec{k}$ is obtained, hence this is reported along
 114 with the estimated errors in $\log \vec{k}$ in Table 2. For completeness, values of \vec{k} and $\Delta \vec{k}$ (the estimated
 115 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
 116 order of 10%, when standard propagation of error manipulation is undertaken, the value of $\Delta \vec{k}$ lies
 117 between two and three times the value of \vec{k} , implying that \vec{k} may become negative which is physically
 118 impossible; accordingly the maximum negative error has been taken as being equal to \vec{k} . Estimating
 119 the error in \vec{k} by evaluating $10^{\lceil \log \vec{k} + \Delta(\log \vec{k}) \rceil}$ and $10^{\lfloor \log \vec{k} - \Delta(\log \vec{k}) \rfloor}$ yields similar or slightly smaller negative

120 errors and notably larger positive errors to those reported in Table 2. Overall the size of the $\Delta \vec{k}$ values
121 indicate that the calculated \vec{k} values have limited meaning.

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