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subject: MgO hydration rates for the CRA-2026 under AP-208

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1. Executive Summary

Loss on Ignition (LOI) data was from inundated hydration experiments on Martin Marietta magnesium oxide (MgO) was analyzed. The experimental work was conducted under Test Plan (TP) TP 06-03 [1]; experiments began in 2006 and continued through 2024 under various PIs [1, 2]. This analysis was conducted under Analysis Plan (AP) AP-208 [3]. This report provides rough estimates of inundated MgO hydration rates in Waste Isolation Pilot Plant (WIPP)-relevant brines for use in the upcoming Compliance Recertification Application (CRA) 2026 Performance Assessment (PA), CRA-2026 PA. The humid-hydration rate will not be updated for the CRA-2026 PA, nor do we expect this parameter to have an appreciable impact on PA.

The rates provided herein are only from the experiments on Martin Marietta MgO and do not include the that of Premier MgO. The rates provided herein are consistent with the current MgO hydration model in PA, which assumes a zeroth order kinetic model. We make no claims on the adequacy of this model, other than that it is consistent with previous PA(s).

[1] SNL WIPP: Sandia National Laboratories at the Waste Isolation Pilot Plant (WIPP). WIPP is located ~26 miles southeast of Carlsbad, New Mexico, U.S.A., built 2,150 feet underground in the Salado Formation, a Permian evaporite deposit in the northern Delaware Basin.

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2. Introduction

Experiments on the hydration of Martin Marietta MagChem 10 WTS MgO (MM MgO) began in 2006 and continued through 2024 under various PIs [1, 2]; WTS-60 is a grade of MagChem 10. Hydration occurs when MgO is placed in an aqueous solution,

$$MgO(s) + H_2O(aq,g) \leftrightarrow Mg(OH)_2(s) \quad (1)$$

where the solid-phase product on the right-hand side of reaction (1) has the mineral name brucite, and the solid-phase reactant on the left hand side has the mineral name periclase. Hydration can occur in both inundated or humid conditions, owing to the strongly thermodynamically favored forward direction of reaction (1). Reaction (1) is important in Performance Assessment (PA) because of the water-sequestering ability of MgO, which could affect releases related to aqueous-solubilized actinides [4]. MgO is the Waste Isolation Pilot Plant's (WIPP) engineered barrier; more information on its purpose and function is given in [5].

3. Background and Previous Work

Of interest to this report is the previous work given in [6-8]. In [6], a summary of MM MgO experimental hydration Loss on Ignition (LOI) data from Test Plan (TP) TP 06-03 is given in a series of tables, along with potential fits of the chemical kinetics. In [8], an explanation of MgO-hydration kinetics models is given, along with a section on how to convert such models into results that can be used in the Brine and Gas modeling code (BRAGFLO [9]) for PA. Finally in [7], a justification for the parameter values and distribution type used in previous PA(s) is given. A detailed background on previous MgO hydration studies will not be given here. Rather, that will be accomplished in the full report under Analysis Plan (AP) AP-208.

4. Fitting Method

A Bayesian regression was utilized to determine the rate constants for MgO hydration. The model used is consistent with the current zeroth order kinetic MgO hydration model in PA,

$$W = K\,t + I\,, \quad (2)$$

where W is the ratio of the mole fraction of brucite at time t to the initial mole fraction of periclase at t_0,

$$W = \frac{X_{Mg(OH)_2,t}}{X_{MgO,t_0}}\,, \quad (3)$$

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where t is time (in years), I is an intercept (dimensionless), and K is a rate constant with units of years^{-1}. The intercept here, while not entirely physical (i.e. there's no hydration in the experiments at $t = 0$), allows for an additional degree of freedom in the model, which will be shown in Section 5 to be beneficial for long-duration prediction. That benefit, of course, comes at the expense of poorer predictions at short times. Given that PA is a 10,000-year simulation, it appears reasonable to fit the data using Equation (2) and then use only the K value in PA, neglecting the initial behavior on the order of years. It is our opinion that this is a reasonable compromise as opposed to changing the BRAGFLO code and performing a full Quality Assurance (QA) documentation of this change.

A Bayesian regression [10, 11] uses Bayes theorem to calculate the posterior probability density $p(\xi, \sigma \mid y_o, M)$ on the model parameters,

$$p(\xi, \sigma \mid y_o, M)\, p(y_o \mid M) = p(y_o \mid \xi, \sigma, M)\, p(\xi, \sigma \mid M) \tag{4}$$

where $\xi = (K, I)$ is the vector of model parameters, $y_o = (W_{t_0}, W_{t_1}, \ldots, W_{t_n})$ is the vector of experimental observations, and M is the model that we subjectively chose (Equation (2)). In Equation (4), $p(y_o \mid \xi, \sigma, M)$ is the likelihood, which represents the probability density of obtaining the experimental data for a given model M and model parameters ξ. Here, we chose a normal distribution for $p(y_o \mid \xi, \sigma, M)$, which maximizes information entropy for a continuous variable on an unbounded domain [12],

$$p(y_{io} \mid \xi, \sigma, M) = \left(2\pi\sigma^2\right)^{-\frac{n}{2}} \exp\left[-\frac{S(\xi)}{2\sigma^2}\right], \tag{5}$$

where $S(\xi)$ is just the sum of square error between the data and the model,

$$S(\xi) = \sum_{i=1}^{n} R_i^2 , \tag{6}$$

where the residuals are given by

$$R_i = W_{t_i} - K t_i - I . \tag{7}$$

The adequacy, or lack thereof, of the likelihood model given by Equations (5)-(6), will be shown in Section 5.5 by comparing the resulting residuals R_i to a normal distribution.

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4.1. Computational details

In Equation (4), the term $p(\xi,\sigma|M)$ represents the prior probability density distribution, which encodes any prior information. For this analysis, we assumed independent normal distributions for the prior on K and I with scale = 20 and mean = 0. For σ, a half Cauchy distribution was used as the prior with $\beta = 10$. The previous work on Premier MgO could be used as the basis for a prior as well; however, it is our opinion that this should be performed in a full X-ray Diffraction (XRD)/LOI analysis rather than in the present rough estimate. Alternatively, one could argue that the data from previous work on Premier MgO at least influenced the prior distribution by setting the prior means = 0, with scale factors that extend well beyond the K values obtained from the Premier experiments [8].

Given the likelihood of Equation (5), and the priors described in the previous paragraph, the remaining task is the calculation of a posterior distribution on the model parameters ξ and likelihood scale parameter σ. This was accomplished through a Markov-Chain Monte Carlo (MCMC) algorithm (Gibbs sampling) within the pyMC code package [13]. The code for this step can be seen within the Python file Bayesian_Regression.py; the posterior samples on the pair (ξ,σ) from this step are given in the Excel file posterior_samp.xlsx. The code to obtain the posterior predictive distribution, plotted in Sections 5.3-5.4 is also calculated in the Python file Bayesian_Regression.py. The samples are stored in the Excel file posterior_ppc.xlsx. An explanation of how these steps are performed is given in [10, 14].

4.2. Data Source and storage

The values of W fit in the analysis presented herein were taken straight from [6], without further processing. No additional data are used. The Python code pulls the data from the file: All-MgO-hydration.xlsx. All python code, results files, and the above data file are stored in /data/cvs/CVSLIB/WIPP_EXTERNAL/MgOhydration/CRA-2026/.

5. Results

5.1. Figure Explanation

In what follows, we present the experimental data plotted against the Bayesian regression of the model given by Equation (2). In the prediction figures (Figure 1, Figure 2, Figure 5, Figure 6), the experimental data is plotted as black dots. The mean model is shown with a red straight line. The 90th percent credible region (between the 5th and 95th quantiles on model predictions) on the model is plotted as the blue shaded region around the red line; this is analogous to a standard error on the model prediction in frequentist

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nomenclature. The 90th percent prediction region (called the posterior predictive credible region in Bayesian terminology) is plotted as the green shaded region; this is analogous to a prediction interval in frequentist nomenclature. The percentiles here should be taken with a dose of salt (pun intended), given that the deviations seen between the model and the data (see Sections 5.3 - 5.5) contain significant deterministic error (bias) due to the model being a simplification. Statistics (Bayesian and frequentist) assumes that the data is unbiased and randomly distributed about the model via some known or estimable and measurable distribution. As will be seen, there is bias, especially at short times in the residuals. Bias correction isn't feasible at this time (in the context of model estimation for PA), as it would require changing the BRAGFLO code.

5.2. Brine Types and Ratios

In what follows, experiments using both GWB and ERDA-6 brine are modeled. Generic Weep Brine (GWB) represents intergranular Salado brine [15]. Synthetic Castile brine is called ERDA-6; the composition of which was originally obtained from Energy Research and Development Administration (ERDA) Well # 6 [16].

Brine ratios used in the experiments are explained and justified in TP 06-03 [1]. For the GW3M and ER3M experimental series, the initial brine ratio was 3 grams of MgO to 11 ml of brine. For the GW20M and ER20M series, the initial brine ratio was 3 grams of MgO to 77 mL of brine. The *M* in the name of the experimental series (e.g. GW3*M*) indicates that these experiments were performed on MM MgO without sieving of the material (original mixture of particles); GW stands for GWB brine and ER stands for ERDA-6 brine.

As will be seen in Sections 5.3 - 5.4, some of the values of W are close to 1 for the experimental series in GWB brine. This occurred because hydrate phases other than brucite were formed in this brine. Hence, for GWB we expect the rough estimate of rates given herein will be high compared to the results that could be obtained in a full XRD/LOI analysis, because the molecular weights of those hydrates are greater than that of brucite. In ERDA-6, only small amounts of non-brucite hydrates are formed, hence those rates should be similar to what could be obtained from a full XRD/LOI analysis.

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5.3. Generic Weep Brine (GWB) Mixed Particle Results

The figures Figure 1 - Figure 2 show the results of the Bayesian regression for the GW3M and GW20M series. The plots given here and in Section 5.4 indicate why the intercept I is beneficial in this simplified modeling. Had we forced $I = 0$, many of the experimental data points (in black) would lie outside the prediction interval (green shaded region). It's clear from the graphs that a zeroth order model does a poor job of prediction at short times but appears adequate at longer times.

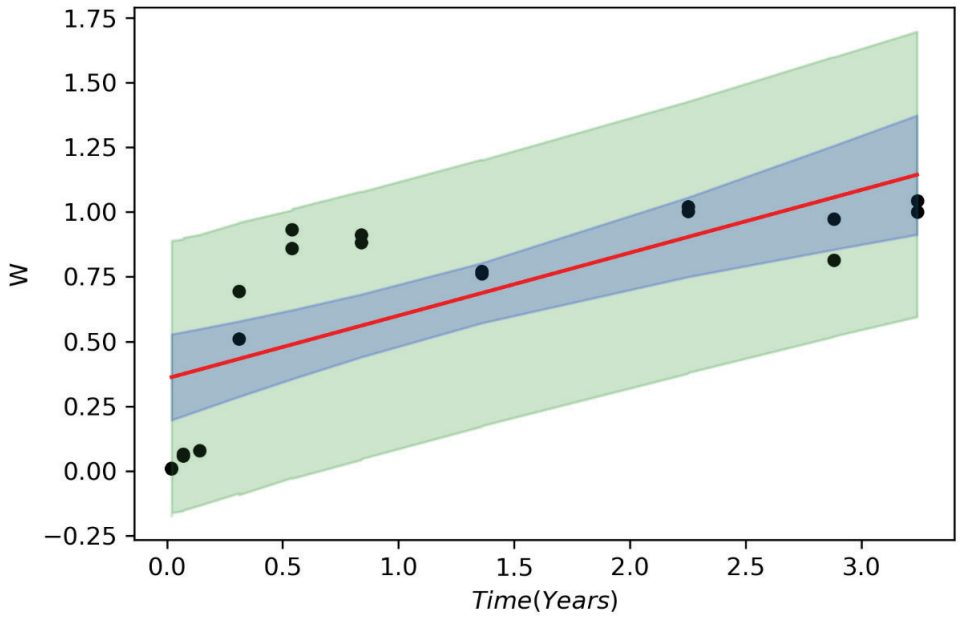

Figure 1. Bayesian regression prediction results for the GW3M series. See Section 5.1 for an explanation of the figure.

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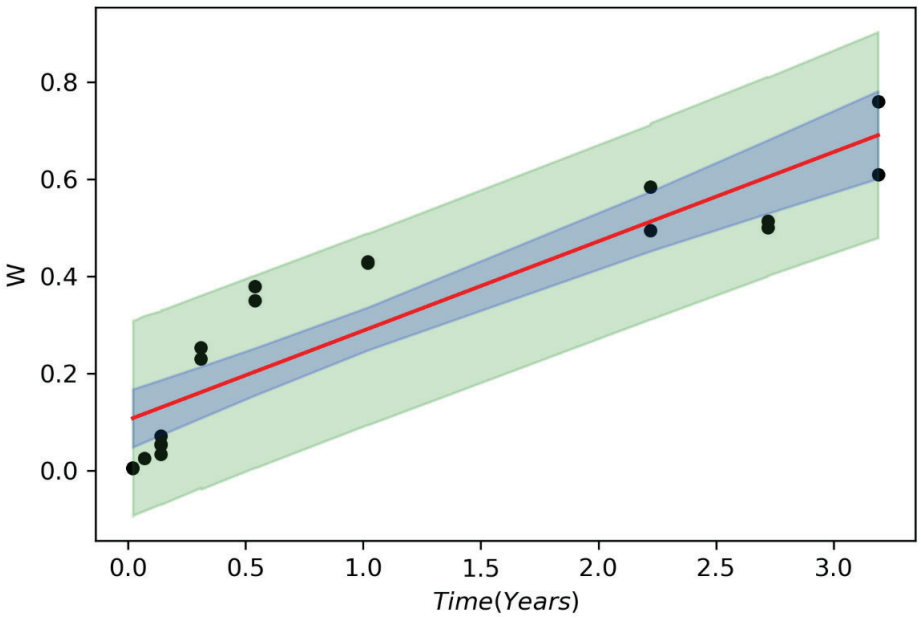

Figure 2. Bayesian regression prediction results from the GW20M series.

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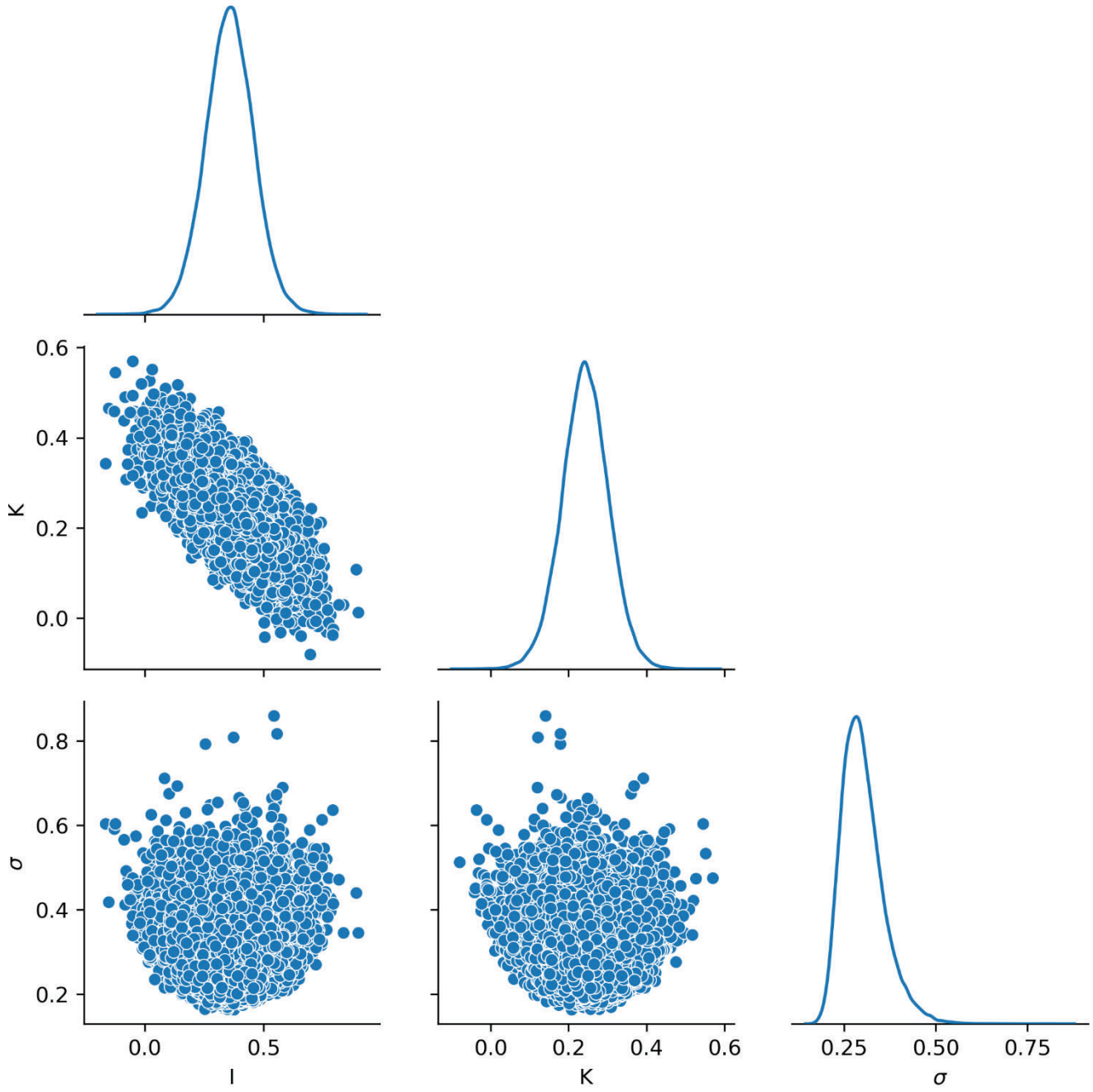

Figure 3. Marginalized distributions on ξ and σ, along with pair distributions for each pair for GW3M.

Figure 3 shows the marginalized posterior probability distribution on the model parameters and the likelihood scale factor σ for the fit of GW3M series. Marginalized here means that each plot on the diagonal of Figure 3 has integrated out the effect of the other parameters from the resulting joint parameter distribution samples given in posterior_samp.xlsx. To see this firsthand, one can open the Excel file and plot samples as a histogram for a particular variable (K, I, σ), while ignoring the specific value of the other parameters. The model parameters K and I are correlated, as can be seen by the

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(K, I) pair distribution plot in Figure 3. This has little to do with the adequacy of the model and would still occur (to some degree) even if the model was physically correct.

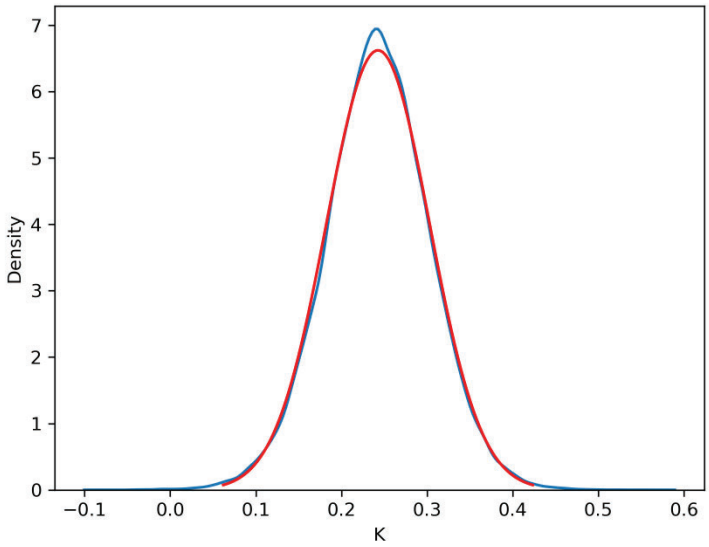

Figure 4. Marginalized posterior distribution on K for the GW3M series (blue) and a fitted normal distribution (red) using estimated parameters described in the text.

Performance Assessment (PA) requires a known distribution type and parameters for the model parameters used. To demonstrate that the posterior distribution on K is roughly normal, a normal distribution is plotted along with the marginalized posterior distribution on K in Figure 4. The mean of the normal distribution was taken as the mean of the marginalized posterior distribution of the samples of K. To determine the scale parameter σ_K for this distribution, we note that for a normal distribution of mean equal to zero and standard deviation equal to 1, the difference between the 5th and 95th quantile is 3.28151,

$$InvCDF(N(0,1), p = 0.95) - InvCDF(N(0,1), p = 0.05) \approx 3.28151, \tag{8}$$

Where $InvCDF(N(0,1), p)$ is the inverse cumulative distribution function for a normal distribution with mean equal to zero and standard deviation equal to one, at a cumulative probability value of p. Hence, the scale parameter can be found from

$$\sigma_K = \frac{K_{95th} - K_{5th}}{3.28151} \ . \tag{9}$$

Alternatively, one could simply calculate the standard deviation of the posterior samples. The estimated normal distribution does a reasonable job of modeling the posterior distribution on K, hence we

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recommend PA use a normal distribution, but with the distribution truncated such that $K > 0$; negative hydration rates would cause brucite to dehydrate, which we don't believe is physically likely under WIPP-relevant conditions. The code used to generate the plots in Figure 3 - Figure 4 is given in Bayesian_Regression_Other_Plots.py.

5.4. ERDA-6 Mixed Particle Results

Figure 5 - Figure 6 show the results of the Bayesian regression for the ER3M and the ER20M series.

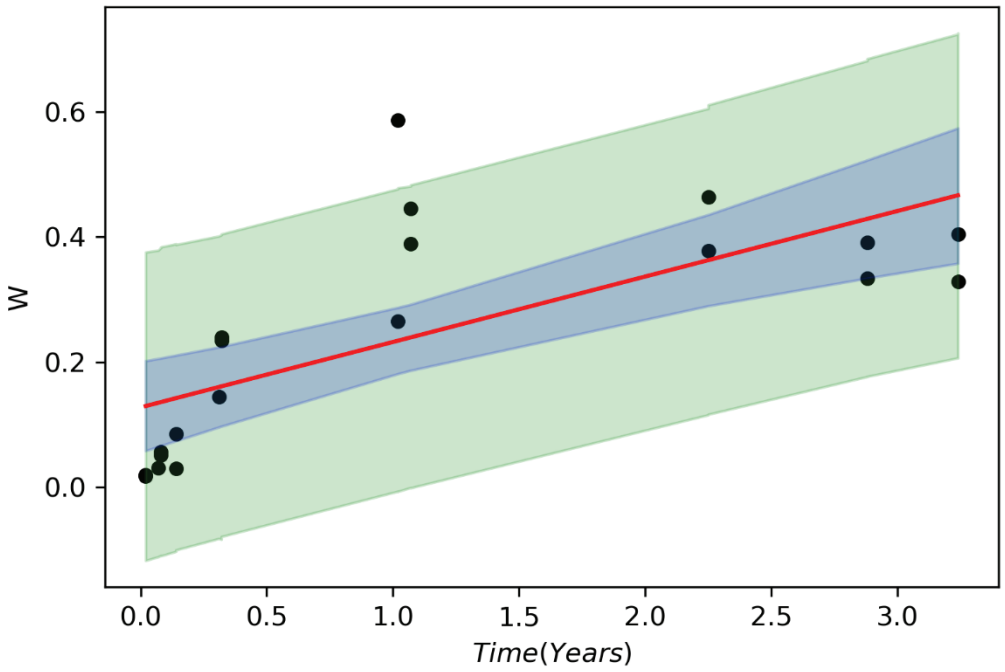

Figure 5. Bayesian regression prediction results from the ER3M series.

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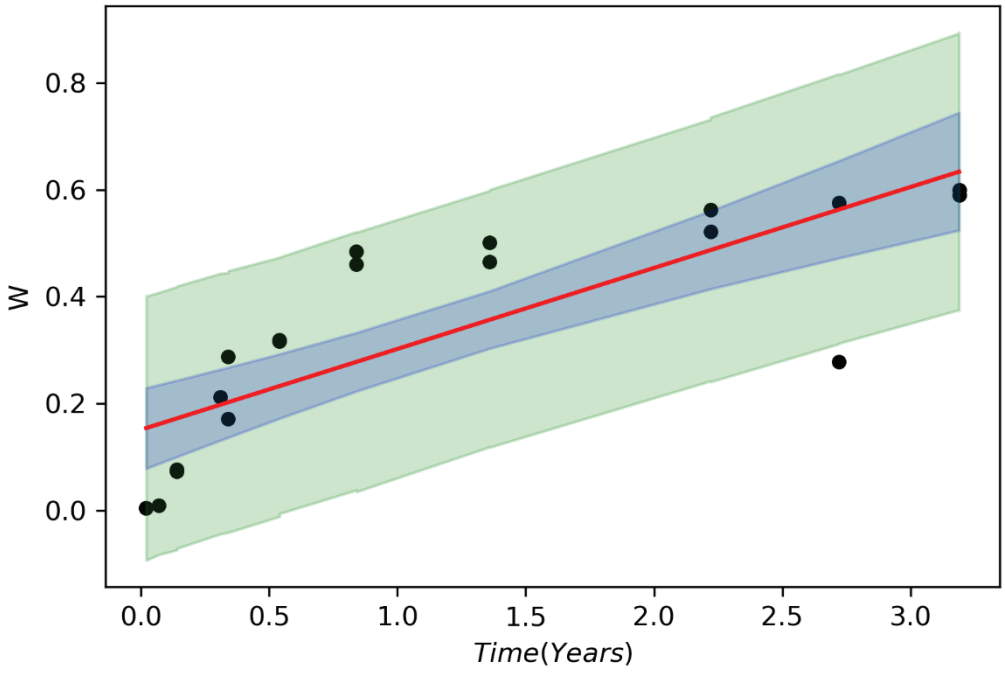

Figure 6. Bayesian regression prediction results from the ER20M series.

5.5. Summary of all Results

The fitted model parameters are given below in Table 1. These rates can be compared to that used for the CRA-2014, based on rates obtained from experiments on Premier MgO, shown in Table 2 of [8]; the rates for Martin Marietta MgO are roughly twice that of Premier MgO.

Table 1. Summary statistics from Bayesian regression.

Experiment	K_{95th}	$\bar{K}$	K_{5th}	I_{95th}	$\bar{I}$	I_{5th}	σ_{95th}	$\bar{\sigma}$	σ_{5th}
GW3M	0.34	0.24	0.14	0.52	0.36	0.19	0.41	0.29	0.22
GW20M	0.22	0.18	0.15	0.16	0.10	0.04	0.16	0.11	0.09
ER3M	0.15	0.10	0.06	0.20	0.13	0.06	0.19	0.14	0.11
ER20M	0.20	0.15	0.10	0.23	0.15	0.07	0.19	0.14	0.11

Using the mean model parameters, we can take the experimental data and subtract the mean model and plot the *Z*-scaled residuals on a probability plot to compare with the assumption that the deviations are normally distributed. *Z*-scaling means calculating normalized residuals from

$$Z_i = \frac{R_i - \bar{R}}{\sqrt{V(R)}}, \tag{10}$$

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where R_i is given by (7), $\bar{R}$ is the mean of R, and $V(R)$ is its variance. This is accomplished in Figure 7; the code used to produce this plot is given in Bayesian_Regression_Other_Plots.py. Looking at Figure 7, GW3M and ER20M show reasonable agreement with a normal distribution, whereas GW20M and ER3M less so.

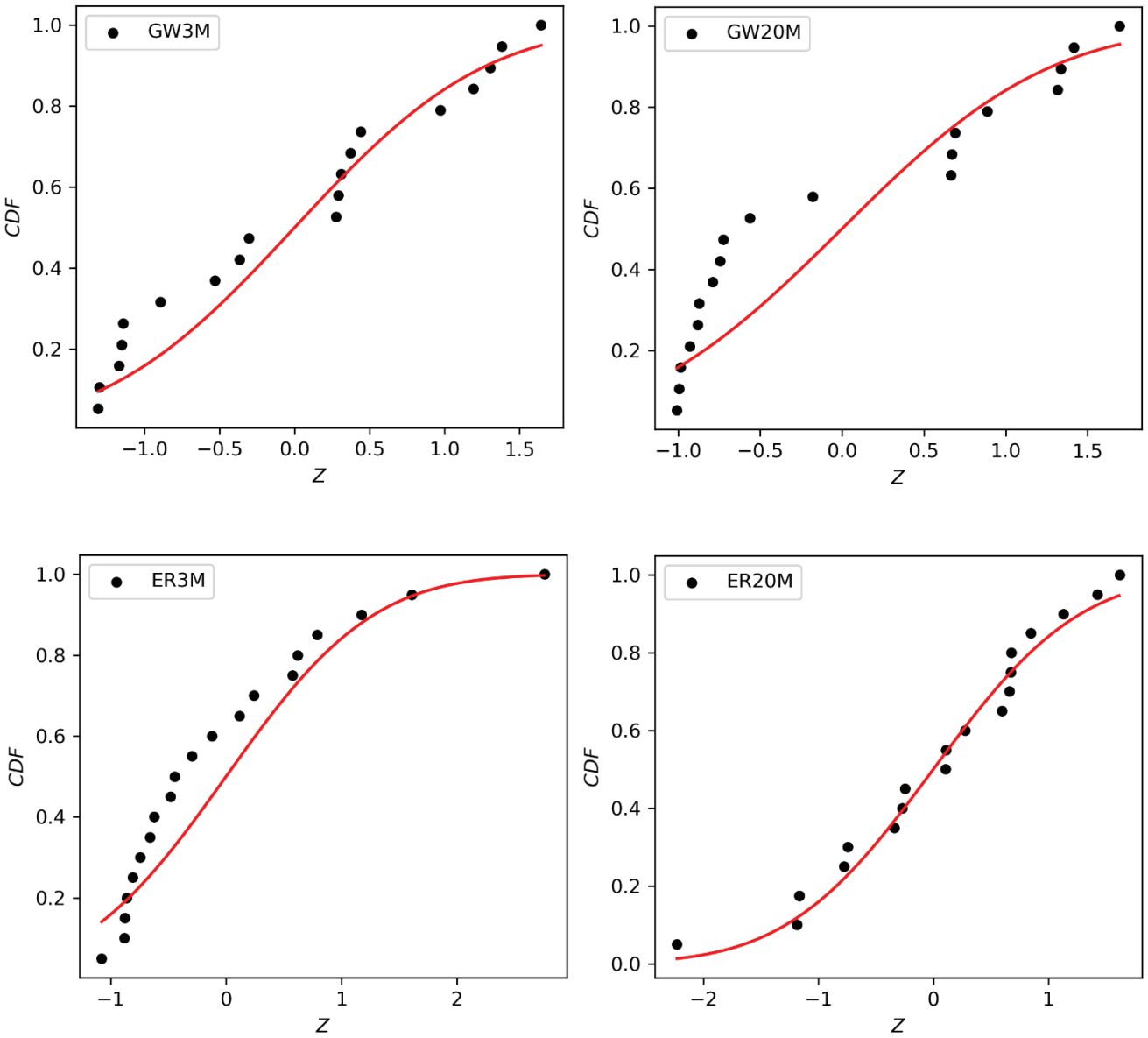

Figure 7. Probability plots for the residuals (R_i) from the four brine experiments (black dots), compared to a normal distribution (red curve). Each graph legend indicates the hydration series of the experimental data. Only the residuals from GW3M and ER20M appear to be a reasonable fit to a normal distribution.

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5.6. Conversion to BRAGFLO Units

In this section, we convert the results from Table 1 into units that can be used by BRAGFLO. To do so, we follow Equation (4) of [8], dividing the K values of Table 1 by 3.1557 x 10^7 sec/year, and by the molecular weight of MgO = 0.040304 kg/mol. The results are given in Table 2. As explained in Section 5.3, we recommend a normal distribution truncated so rates can't be negative, with the mean given by $\bar{K}$. As described in Section 5.3, the scale parameter for that normal distribution can be found from Equation (9) or by calculating the standard deviation of the posterior samples on K. To minimize the amount of information in this report, we chose to use Equation (9).

The scale parameter is shown in Table 2 along with the results from previous studies on Premier MgO taken from [8]. The rates differ by about a factor of two.

Table 2. MgO Hydration rates in BRAGFLO units and scale

Experiment	K_{95th} (mol/kg/s)	$\bar{K}$ (mol/kg/s)	K_{5th} (mol/kg/s)	σ_K (mol/kg/s)	*Premier Rate* (mol/kg/s)	*Premier Standard Error* (mol/kg/s)
GW3M	2.7 x 10^{-7}	1.9 x 10^{-7}	1.1 x 10^{-7}	5 x 10^{-8}	5.2 x 10^{-8}	3 x 10^{-9}
GW20M	1.7 x 10^{-7}	1.4 x 10^{-7}	1.2 x 10^{-7}	2 x 10^{-8}		
ER3M	1.2 x 10^{-7}	8.2 x 10^{-8}	4.7 x 10^{-8}	2 x 10^{-8}	5.2 x 10^{-8}	2 x 10^{-9}
ER20M	1.6 x 10^{-7}	1.2 x 10^{-7}	8.2 x 10^{-8}	2 x 10^{-8}		

The mean rates $\bar{K}$ between the 3M and 20M series for each brine are similar, as are the scale factors σ_K. For conservatism, we recommend using the lower of the rates for each brine and the larger σ_K; the differences aren't significant in our opinion. Hence, we arrive at parameter values for the CRA-2026 in Table 3, using a normal distribution, truncated at $\pm 3\,\sigma_K$ or zero, whichever is smaller but greater than zero.

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Table 3. MgO Hydration Parameters for the CRA-2026

Parameter	Units	Description	Distribution Parameters	Distribution Type
WAS_AREA:BRUCITES	mol/kg/s	MgO inundated hydration rate in GWB brine	Mean = 1.4×10^{-7} S.E.= 5×10^{-8} Max = 2.9×10^{-7} Min = 0	Truncated Normal
WAS_AREA:BRUCITEC	mol/kg/s	MgO inundated hydration rate in ERDA-6 brine	Mean = 8.2×10^{-8} S.E. = 0.2×10^{-8} Max = 8.8×10^{-8} Min = 7.6×10^{-8}	Truncated Normal

6. Funding Statement

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7. References

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