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Sandia National Laboratories
Waste Isolation Pilot Plant

Analysis of MgO Hydration Laboratory Results and Calculation of Extent of Hydration and Resulting Water Uptake versus Time under Postulated WIPP Conditions

Work carried out under Analysis of MgO Hydration and Carbonation Test Results, Analysis Plan AP-108, Rev. 0

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1 INTRODUCTION

Brine, in the waste-containment area of the Waste Isolation Pilot Plant (WIPP), participates in processes that can affect WIPP performance, such as dissolution of radionuclides into an aqueous phase. Commercial granular Premier magnesium oxide (MgO) material, emplaced in the WIPP waste-containment areas primarily to control the partial pressure of carbon dioxide gas (p_{CO_2}), can also capture water (H_2O). MgO reacts with H_2O to form hydrated MgO solids (a hydration reaction), such as $Mg(OH)_2$. Formation of hydrated solids incorporates liquid and gaseous H_2O into a solid phase. The quantity of H_2O present at any time may be determined by a material balance between the quantity of H_2O that has entered the repository and the quantity of H_2O that has been captured by reacting with MgO and by other processes. A means to estimate H_2O capture is needed to do the material balance, and this analysis fills that need.

This report documents an analysis of results from studies of hydration of granular Premier MgO to form $Mg(OH)_2$. The studies were carried out at Sandia National Laboratories in the Carlsbad Program Group (SNLCPG, Bryan and Snider, 2001a and 2001b; Johnsen, S. 2006a and 2006b; Snider, 2001a, 2001b, 2002a and 2002b). The objective of this analysis is to determine an integrated (over time) rate equation for hydration of Premier MgO in WIPP-relevant brines and quantified rate constants. The equation gives the mole fraction conversion (W) of MgO to $Mg(OH)_2$ as a function of time (t). It can be used to calculate H_2O capture, since the quantity of H_2O captured is a function of W. It is assumed that hydration will continue in the presence of H_2O until all of the emplaced Premier MgO has been hydrated, that is, to $W = 1$.

In general, a rate equation relates the overall rate of reaction to pertinent system parameters. An empirical rate equation is usually formulated by trial and error, sometimes guided by previous experience. It is not based on a chemical and/or physical model of the reaction. A mechanistic rate equation is based on a known or postulated model of the chemical and/or physical processes that limit the rate of reaction. For example, the reaction rate may be limited by one or more of the slowest among first or second order chemical reactions on a solid surface – a heterogeneous chemical reaction mechanistic rate model. Alternatively, the rate may be limited by slow diffusion of reactants and products through one or more phases to and from the reaction zone – a mass transport mechanistic rate model.

In some cases, more than one kind of process significantly limits the overall rate of reaction. For example, a solid homogeneous particle with negligible porosity reacts with a component of a surrounding fluid phase at the particle's outer surface to form fluid phase products. Reactants diffuse through the fluid to the solid, and products diffuse away. Furthermore, the chemical reaction rate and the diffusion rate both significantly affect the overall rate. As the particle is consumed by reaction at its outer surface, it shrinks, and the surface area of solid/fluid contact decreases. The chemical reaction rate is proportional to the surface area. In that case, the mechanistic rate model will include rates of surface area change, chemical reaction, and mass transport (Levenspiel, 1962a).

The rate equation selected in this analysis must be adequate to extrapolate, when necessary, from the value of *W* achieved in the SNLCPG laboratory studies to $W = 1$. A mechanistic, rather than empirical, rate equation is preferable for extrapolation beyond the experimental range of *W*, because knowledge of the mechanism provides confidence in the range of applicability of the equation.

This analysis report begins with background information (Section 2), including MgO hydration results from the SNLCPG hydration studies with commercial granular Premier MgO. Plots of experimental results from the laboratory studies are also given. Then, relevant findings from published literature used for this analysis are described (Section 3). An analysis of the experimental results follows (Section 4). An integrated rate equation with quantified parameters and associated uncertainties was selected, meeting the objective of the analysis. Finally, application of the rate equation and parameters to the calculation of *W* as a function of *t* is illustrated with example calculations (Section 5).

This work was carried out under Analysis of MgO Hydration and Carbonation Test Results, Analysis Plan AP-108, Rev. 0 (Nowak, 2003).

2 BACKGROUND

The SNLCPG inundated hydration studies (Bryan and Snider 2001a and 2001b, Snider 2002a) were carried out with commercial granular Premier MgO slurries in DI water, 4 molar NaCl, ERDA-6 brine, and GWB brine at laboratory temperature (approximately 25°C) and atmospheric pressure. ERDA-6 is characteristic of brine that may enter the disposal area upon human intrusion. GWB is characteristic of the Salado formation brine that may enter the repository by seepage. The molar ratio of H_2O to MgO was ~30:1.

Two sets of inundated hydration measurements were performed. The first set, designated "HY" in this report, was for samples taken between March 13, 2001 and March 5, 2002. The second set, designated "HY2", was for samples taken from another group of reaction vessels between May 9, 2002 and October 26, 2004. Set HY includes inundated hydration measurements for all four aqueous solutions, while set HY2 includes measurements with ERDA-6 and GWB brines only.

The inundated MgO hydration results (Johnsen 2006a and 2000b) selected for this analysis from the SNLCPG hydration studies are shown in Figures 1 through 4 as plots of *W* versus *t*. The plots were generated by Microsoft Excel with the "Insert, Chart" function (filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls"). Some results for GWB brine shown in Figure 4 were rejected in the analysis as discussed in Section 4.1.

The SNLCPG humid hydration (HH) studies (Snider 2001a, 2001b and 2002b) were carried out with commercial granular Premier MgO while varying relative humidity and laboratory temperature at atmospheric pressure. The humid MgO hydration results for the 25°C and 75% relative humidity experiments were selected for this analysis, since these conditions are similar to the conditions in the WIPP and are shown in Figure 5 as plots of *W* versus *t*. The plots were generated by Microsoft Excel with the "Insert, Chart" function (filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls").

For all but one set of results, W is < 1 at the end of the experiment. However, it is possible that more than enough brine can enter the repository to fully hydrate the MgO, or in other words $W = 1$. The quantity of H_2O captured by hydration is directly related to the value of W, given the stoichiometry of the hydration reaction. A rate equation that can be used to extrapolate from the laboratory results to $W = 1$ is needed. Complete hydration of MgO both in inundated and humid conditions is shown in several published studies (Birchal et al. 2001; Bratton and Brindley, 1964; Feitknecht and Braun, 1967; Filippou et al. 1999; Fruhwirth et al. 1985; Layden and Brindley, 1963; Razouk and Mikhail, 1958).

3 MgO HYDRATION FINDINGS IN THE PUBLISHED LITERATURE AND APPLICATIONS TO RESULTS OF THE SNL LABORATORY STUDIES

In a published study (Smithson and Bakhshi, 1969), an empirical integrated rate equation for irreversible reaction was fit to MgO hydration results. The authors found that plots of $-\ln(1-W)$ versus t are nearly linear for all of their observed rate curves for MgO hydration in water. Equation (1) expresses that relationship. They stated that it is only coincidental that empirical equation (1) is the same as the mechanistic rate equation for first order, homogeneous reactions, and no inference should be made about the reaction mechanism. The successful fit of an empirical rate equation to measured results does not preclude the possibility that a mechanistic equation would also fit the results.

$$-\ln(1-W) = K_{Emp}t \qquad (1)$$

where

K_{Emp} = a rate constant, $(\text{year})^{-1}$, and

t = time (year).

Integrated mechanistic rate equation (2) for rate control by an irreversible chemical reaction on the surface of a shrinking core of unreacted solid (Levenspiel, 1962b) was applied successfully to hydration rates of MgO (Bratton and Brindley, 1964; Filippou et al. 1999; Fruhwirth et al. 1985; Layden and Brindley, 1963). In this mechanism, the rate is independent of the presence of any product layer surrounding an unreacted core. The term "shrinking core" is often used to generalize a mechanistic concept to include the possibility that mass transport through a product layer surrounding a "core" of unreacted solid influences the reaction rate. To avoid confusion, this analysis will use the term "particle" for the unreacted solid when referring to the mechanistic model behind equation (2)

$$1-(1-W)^{1/3} = K_R t \qquad (2)$$

where

K_R = a rate constant, $(\text{year})^{-1}$.

Applied to hydration, equation (2) is for rate control by the reaction of a constant concentration of water molecules with the surface of a shrinking particle of unreacted MgO, a reasonable mechanism to consider. Since a mechanistic rate equation, rather than an empirical one is preferred for extrapolation from experimental results, this analysis includes evaluation of fits of mechanistic equation (2) to SNLCPG hydration results, even though Smithson and Bakhshi (1969) did not fit their own MgO hydration results to that equation.

Also included in this analysis is mechanistic integrated rate equation (3) for rate control by diffusion through a layer of reaction products around a shrinking core (particle) (Levenspiel, 1962a). Similar rate equations were used by Birchal et al. (2001), Bratton and Brindley (1964), Filippou et al. (1999), Fruhwirth et al. (1985) and Rocha et al. (2004) to analyze MgO hydration results. Bratton and Brindley (1964), Filippou et al. (1999) and Fruhwirth et al. (1985) found that equation (2) was a better fit to the hydration data, while Birchal et al. (2001) and Rocha et al. (2004) found that equation (3) was a better fit to the hydration data. This is most likely due to the higher temperature ranges examined by Birchal et al. (2001) and Rocha et al. (2004) compared with Bratton and Brindley (1964), Filippou et al. (1999) and Fruhwirth et al. (1985). Applied to hydration, this equation is for rate control by diffusion of H_2O molecules from an outer zone of constant H_2O concentration through gaseous H_2O or brine in pores, cracks, or larger gaps in surrounding solid (possibly granular) $Mg(OH)_2$ reaction product to the surface of the MgO particle. An H_2O concentration gradient would be caused by depletion of H_2O near the particle, a reasonable situation to consider.

$$1-3(1-W)^{2/3}+2(1-W)=K_D t \qquad (3)$$

where
K_D = a rate constant, $(\text{year})^{-1}$.

An analysis of MgO hydration results from SNLCPG studies using equations (1), (2), and (3) is presented in Section 4.

4 ANALYSIS OF RESULTS FROM SNLCPG MgO HYDRATION STUDIES

This analysis began with selection of an integrated rate equation for the SNL hydration results. All available results for DI water, 4 molar NaCl, and ERDA-6 brine were used. Some of the results for GWB brine were rejected with justification (Section 4.1). Only the humid hydration results at 25°C and 75% relative humidity were used. The selection was made from the rate equations (1), (2), and (3) found in the literature as described in Section 3. An approximation (not necessary for DI water or humid hydration) used with equations (1) and (2) is that there are negligible temporal changes in the water concentration due to consumption of liquid water by the hydration reaction. The equivalent approximation for equation (3) is that there are negligible changes in the water concentration outside the concentration gradient (ideally, at infinite distance). Those approximations yield a potential error in concentration of H_2O no greater than 3%, since the starting molar ratio of H_2O to MgO was ~30:1. A potential 3% error in H_2O concentration is acceptable for this analysis.

The linear regression results show that equations (1) and (2) fit the hydration results equally well. Since a mechanistic rate relationship, rather than an empirical one, is preferred for extrapolation from experimental results, mechanistic rate equations (2) and (3) were chosen for further analysis. Linear regressions for equation (3) do not fit hydration results as well as regressions for equation (2), particularly at early times. Therefore, integrated rate equation (2) was selected. Values of the rate constant K_R in equation (2) were determined for all four aqueous media and humid hydration using regression analysis. Equation (2), with values of rate constant, K_R, fulfills the objective of this analysis.

Plots of results and linear regressions were used for both selection of an integrated rate equation (Section 4.2) and determination of values of the rate constant K_R in the selected rate equation (Section 4.3). The plots were generated by Microsoft Excel with the "Insert, Chart" function (filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls"). The linear regression tools that were used are described in Sections 4.2 and 4.3.

4.1 Rejection of Some Results for GWB Brine

Seven points in the GWB HY2 hydration results were not used in the selection of the integrated rate equation nor were used for the determination of the rate constant value. Two of the HY2 measurements had values of $W > 1$ which were rejected, because the rate equations are invalid for $W > 1$, and $W > 1$ is not physically possible. The rejected values are so described in Figure 4. Also shown in Figure 4 are five HY2 measurements that were judged to have occurred after the reaction was complete and the hydration rate was zero. The HY2 measurements were judged to have occurred after the reaction was complete as the measurements were <5% of complete conversion (W=1) and were later than measurements which showed conversions greater than one. Those results are therefore not meaningful for determining reaction kinetics and were not used. The remainder of the GWB HY2 hydration results were not used in the final determination of the rate as explained below in section 4.3.

4.2 Selection of an Integrated Rate Equation for Hydration of Commercial Granular Premier MgO

Equation (1) predicts that a plot of $-\ln(1-W)$ versus t should be linear with slope K_{Emp}. Similarly, equations (2) and (3) predict linear relationships between $1-(1-W)^{1/3}$ and t with slope K_R, and between $1-3(1-W)^{2/3}+2(1-W)$ and t with slope K_D, respectively. Linear regression analysis was used to determine the quality of fit to results and the slopes for these linear relationships.

The linear regression trendline tool of the chart generator in Microsoft Excel ("Chart" in the "Insert" dropdown menu) was used to generate regression lines. The equation for the linear regression line and the corresponding coefficient of determination (R^2, the proportion of variation in values on the vertical axis explained by the regression line) are shown in the upper right hand corner of each chart. The R^2 value was used to compare the linear regression lines for equations (1-3). Charts and results of the linear regressions are documented in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls" and are illustrated in figures described below. Initially, results from sets HY and HY2 were analyzed separately. Discussion of the analysis of results from the set HY follows.

Linear regressions lines for equations (1) and (2) fit the HY results nearly equally well as shown by comparisons among the plots in Figures 6 through 15. Since a mechanistic rate relationship, rather than an empirical one, is preferred for extrapolation from experimental results, mechanistic equations (2) and (3) were chosen for further analysis.

Comparisons of Figures 16 through 20 with Figures 7, 9, 11, 13 and 15 show that linear regression lines for equation (3) do not fit the HY results as well as lines for equation (2), when comparing the R^2 value. The linear regression lines for equation (3) do not fit particularly well at early times or for GWB brine. Therefore, equation (2) was chosen for further analysis of HY results, based on the R^2 value and visual inspection of the fit.

There is more scatter in the HY2 results than in the HY results, making the choice of the equation with the best fit to the HY2 results more difficult. Therefore, the integrated rate equation (2), used to analyze the HY results, was chosen for further analysis of the HY2 results as well. The linear regression fits for equation (2) to HY2 results are shown in Figures 21 and 23.

4.3 Determination of Values of the Rate Constant K_R In the Selected Integrated Rate Equation

Equation (2) was chosen, as described in Section 4.2, for further analysis of the hydration results. Accordingly, values of the rate constant K_R were equated to the slopes of linear regressions for equation (2) to results in the HH, HY and HY2 sets. Values of K_R were obtained from HY results for DI water, 4 molar NaCl, from HY and HY2 results for ERDA-6 and GWB brines and from the HH humid hydration results. Further analysis was done to determine a single value of K_R for ERDA-6 and GWB, from the HY and HY2 data sets and is discussed below.

Slopes of the regression lines and associated standard errors were calculated with the "Regression" data analysis tool in Microsoft Excel. The values of the slopes, K_R are the values designated "Coefficient of X Variable 1" in the SUMMARY OUTPUT table in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls." The standard error, s, for each K_R is also given in the SUMMARY OUTPUT table. These results are shown in Table 1.

Further analysis was done to determine single values K_R and s for both ERDA-6 and GWB brines. The HY2 results for ERDA-6 show a trend that is consistent with the trend in the HY results, as seen in Figures 11, 21, and 22. A technical judgment was made to derive a single value of K_R and of s for ERDA-6 brine by combining the HY and HY2 results for ERDA-6 into a single set. The resulting final values of K_R and s, calculated as described above with the "Regression" data analysis tool in Microsoft Excel, are shown in the third row of Table 2. The corresponding plot with the linear regression line appears in Figure 22.

The HY2 results for GWB brine (Figure 23) show a sudden increase in W after 1.5 years that doesn't appear to be consistent with the trend in W at shorter times. No explanation for that behavior was found in what is known about the experimental conditions or the procedure used for the HY2 study. Therefore, the HY2 results for GWB brine were judged to be anomalous and excluded from the analysis (see Appendix A). The HY results for GWB brine are slower than the HY2 results and so the exclusion of the HY2 results will cause the predicted hydration to be slower than the data shown in Figure 4. Furthermore, values of K_R and s from HY results for GWB brine are much closer with those from the combined HY and HY2 ERDA-6 results, from the DI water results, and from the 4 molar NaCl results. The solution composition had some influence on hydration rate as the DI water rate is ~15% higher than for ERDA-6 and GWB brines and the 4 molar NaCl rate is ~27% lower than the rate in the brines. The final values (Table 2), $K_R = 0.0660$ year^{-1} and $s = 0.0043$ year^{-1}, derived from the HY results, were chosen for GWB brine, since the rate derived from the HY2 results was ~350% higher than the ERDA-6 results, which is much higher than the solution composition influence seen with other solutions (Table 1).

Supporting evidence for the above technical judgments about HY and HY2 results was obtained from statistical tests for the equality of population variances (σ^2) (in this case, estimated by the sample variances s^2) and population mean values (μ) (in this case, estimated by the sample means K_R) for normal populations represented by two independent samples. This evidence is supporting rather than definitive, because the tests are strictly valid only for normal populations. A test for normality, such as the often used Lilliefors test (See, for example, Iman and Conover 1983, pp. 153-155), is not possible, since only one value of K_R with corresponding standard error is available for each set of results. The Wilcoxon-Mann-Whitney rank sum test (See, for example, Iman and Conover 1983, pp. 280-281) for inferences about the differences between two means is appropriate for non-normal populations, but it is not applicable for the same reason. Normal distributions were assumed in order to apply the statistical test procedures. Details of the statistical test calculations are given in Appendix A.

For ERDA-6 brine, a test based on the F-distribution showed that the HY and HY2 results sets are likely to be samples from populations having the same variance. A test based on the Student's t-distribution and the above conclusion showed that sets HY and HY2 for ERDA-6 brine are likely to be samples from populations with the same mean. Practically speaking, the values of K_R and s from HY and HY2 for ERDA-6 are likely to characterize samples from the same population, a conclusion that supports combining HY and HY2 results for ERDA-6 brine.

For GWB brine, similar tests showed that HY and HY2 results sets are not likely to be samples from populations having the same standard deviation and mean. Practically speaking, the values of the parameters K_R and s from results sets HY and HY2 for GWB are not likely to characterize the same population. Therefore, combining the HY and HY2 results into a single set, as was done for ERDA-6 brine, is not supported. That is, both HY and HY2 results are unlikely to characterize hydration of Premier MgO equally well.

The rate parameters for DI water, 4 molar NaCl and humid hydration in Table 1 were retained as final values. They are given in the Table 2. It should be noted that the values of K_R and s in Table 2 are not necessarily applicable to MgO with chemical and physical properties other than those of the commercial Premier MgO used in the SNL studies.

The values given in Table 2 for ERDA-6, GWB and humid hydration were then converted into rates for use in BRAGFLO. BRAGFLO is a computer code used to calculate the brine and gas flow around the WIPP repository. As described in the BRAGFLO design document (Nemer, 2006), BRAGFLO uses zero order kinetics for MgO hydration and all other chemistry reactions. A conservative zero order kinetic rate constant can be determined by simply using the values in Table 2. The zero order chemical reaction would proceed at a constant rate and complete at the same time as the first order surface reaction model. The mole fraction conversion for the zero order reaction would always be less than or equal to the first order reaction. Furthermore, the BRAGFLO MgO hydration rates, shown in Table 3, need to have the units of mol MgO/kg MgO/sec. The conversion of the rate parameters (K_R, s) in Table 2 to the units for the BRAGFLO rates (K_B, s_B) is shown in equations (4) and (5).

$$K_B = \frac{K_R}{MW_{MgO}} \cdot \frac{year}{3.1557 \cdot 10^7 \text{ sec}} \tag{4}$$

$$s_B = \frac{s}{MW_{MgO}} \cdot \frac{year}{3.1557 \cdot 10^7 \text{ sec}} \tag{5}$$

where
MW_{MgO} = molecular weight of MgO, (0.040304 kg/mol).

5 ILLUSTRATION OF THE CALCULATION OF FRACTION OF MgO HYDRATED IN ERDA-6 AND GWB BRINES VERSUS TIME WITH THE MODEL FROM SECTION 4

Illustrative calculations of W versus t for ERDA-6 and GWB brines and humid hydration were completed using integrated rate equation (2) and values of K_R from Table 2. The calculations were performed by choosing values for W from 0 to 1 and calculating the corresponding values for t using functions provided in Microsoft Excel. This was used to illustrate the uncertainty in hydration time that results from the uncertainty in the calculated rates. Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls" gives the calculations and plots of W versus t created using the "chart" dropdown menu. Those plots are shown in Figures 24 through 26 for ERDA-6 and GWB brines and humid hydration, respectively.

Values of K_R at the lower 95% confidence level and the upper 95% confidence level are given in Table 4 for ERDA-6 and GWB brines and humid hydration. They are taken from "Upper 95%" and "Lower 95%" in the SUMMARY OUTPUT tables in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls." Results of calculations using those values of K_R are shown in Figures 24 through 26. Differences between values of W at the upper and lower 95% confidence levels are less than 15% of the central value. The results show that the hydration of granular commercial Premier MgO in ERDA-6 and GWB brines may be ~95% complete in ~10 years on average, while for humid conditions the hydration may be ~95% complete in ~25 years on average.

6 CONCLUSIONS

Mechanistic integrated rate equation (2) was chosen to analyze results of laboratory studies of MgO hydration carried out at SNLCPG. It describes the rate of reaction of a constant concentration of water molecules with the surface of a shrinking particle of unreacted MgO. The choice was based on quality of fit of linear regressions to the laboratory results, determined by both the R^2 value and distribution of errors. A mechanistic rate equation, rather than an empirical one, was preferred for extrapolation from experimental results, which may be necessary for WIPP-related applications. Such a rate equation can be used to calculate W, the extent of hydration of MgO, and therefore the amount of H_2O removed by incorporation into hydrated solids at any time, t.

$$1-(1-W)^{1/3} = K_R t \tag{2}$$

Values of the rate constant K_R were found to be in the range of 0.0254 year^{-1} to 0.0762 year^{-1} for the hydration of granular commercial Premier MgO in DI water, 4 molar NaCl, ERDA-6 and GWB brines and humid hydration. The values of the rate constant are not strongly dependent on the aqueous solution composition, but they may not apply to other samples of MgO with different particle size distributions, morphology, or impurity content. Illustrative calculations show that MgO hydration in the brines may be ~95% complete in less than ~10 years versus less than ~25 years in humid conditions. Differences between calculated values of W at the upper and lower 95% confidence levels of K_R are less than 15% of the central value.

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8 FIGURES

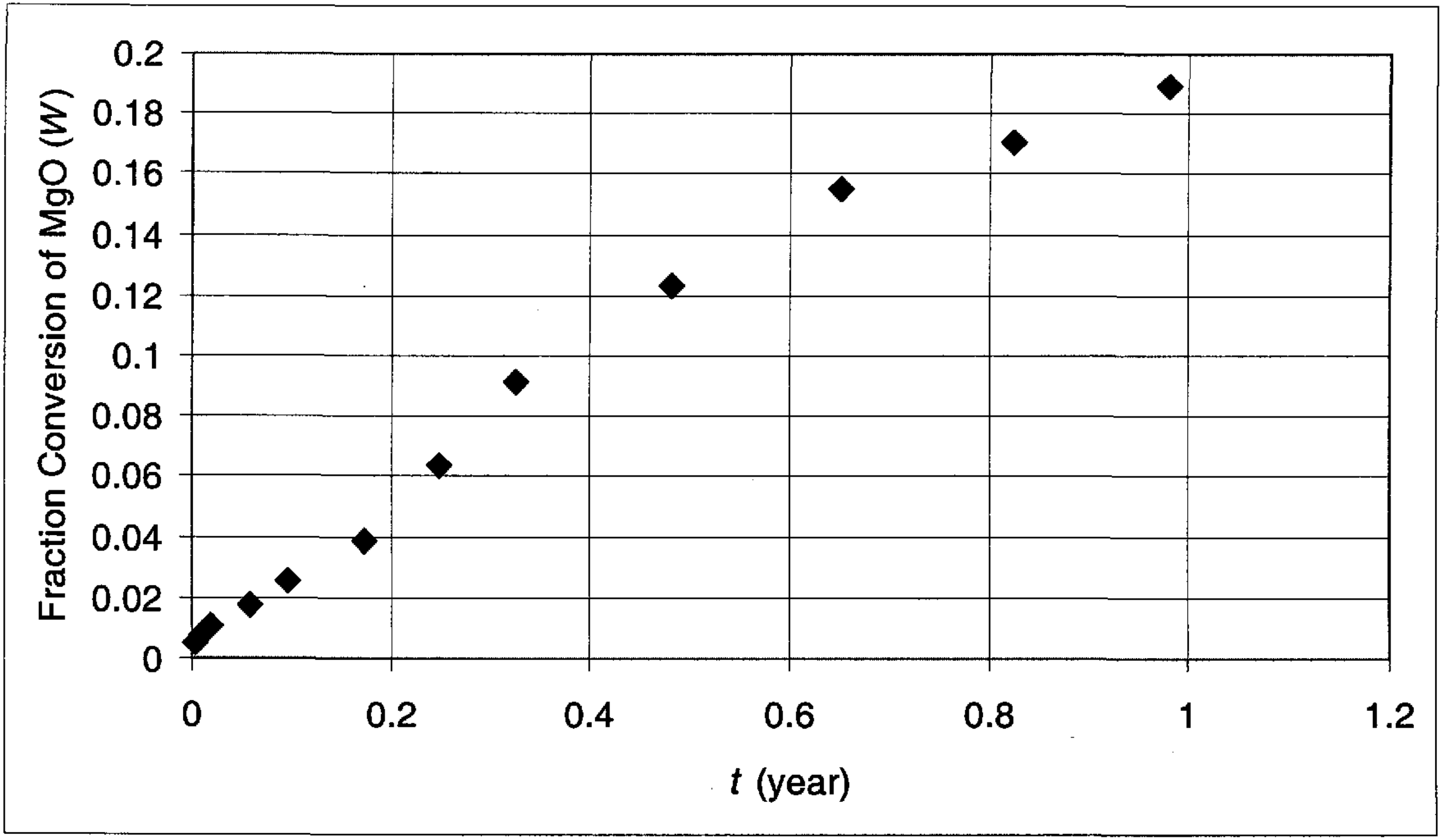

Figure 1. SNLCPG results for hydration in DI water plotted as mole fraction conversion of MgO, *W*, versus time, *t* (year).

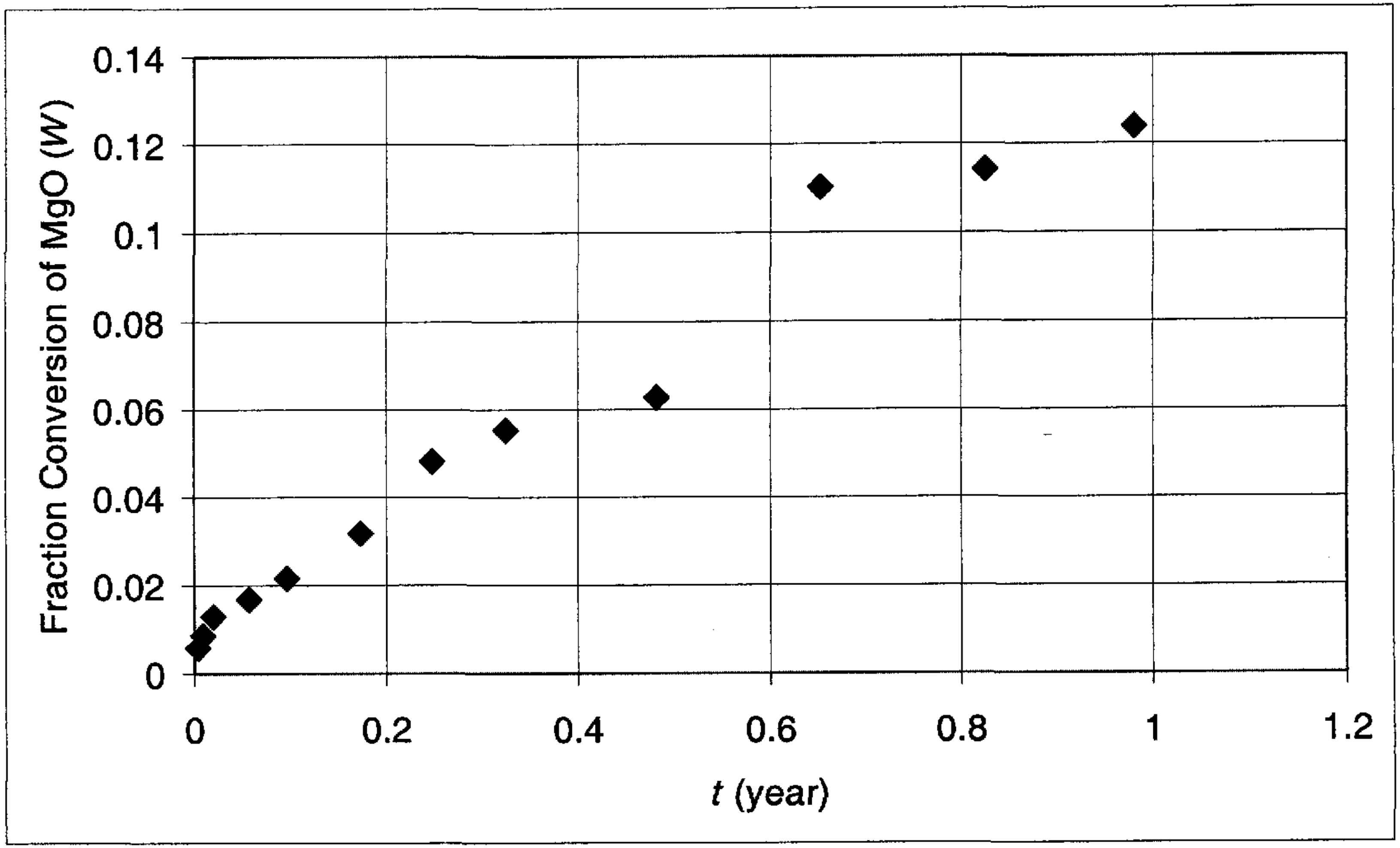

Figure 2. SNLCPG results for hydration in 4M(molar) NaCl plotted as fraction conversion of MgO, *W*, versus time, *t* (year).

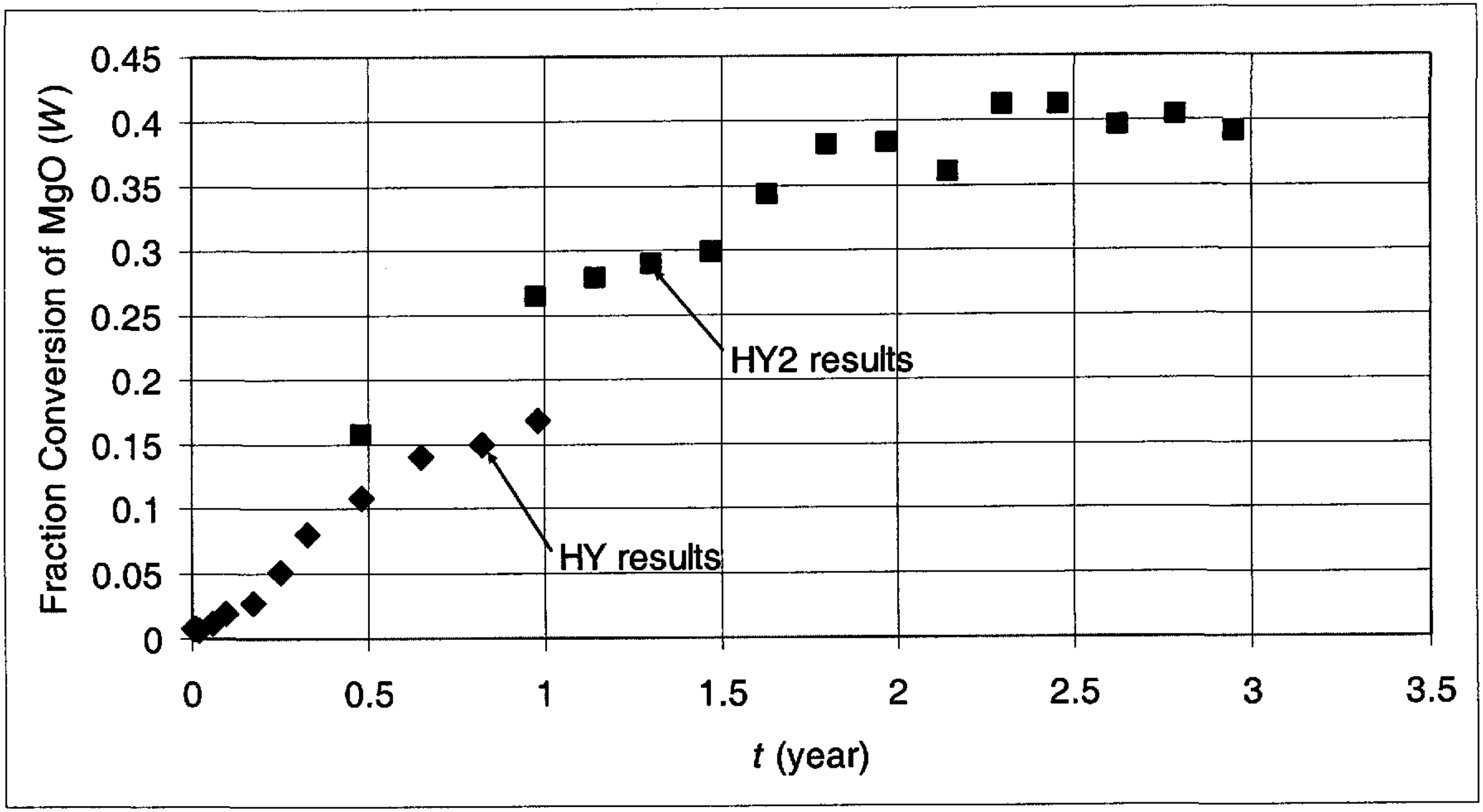

Figure 3. SNLCPG results for hydration in ERDA-6 brine plotted as fraction conversion of MgO, *W*, versus time, *t* (year).

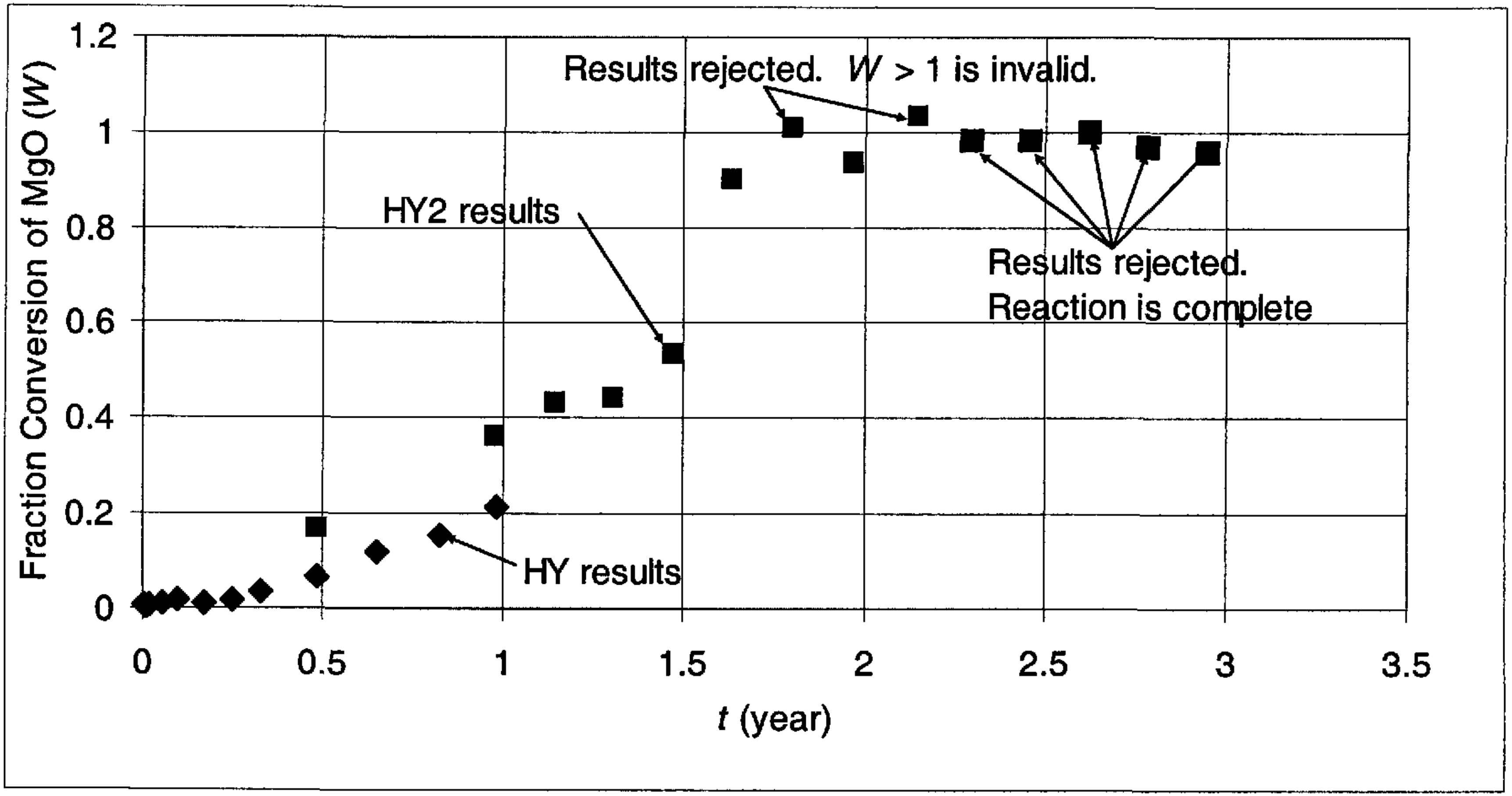

Figure 4. SNLCPG results for hydration in GWB brine plotted as fraction conversion of MgO, *W*, versus time, *t* (year). Some results were rejected at the beginning of the analysis for the stated reasons.

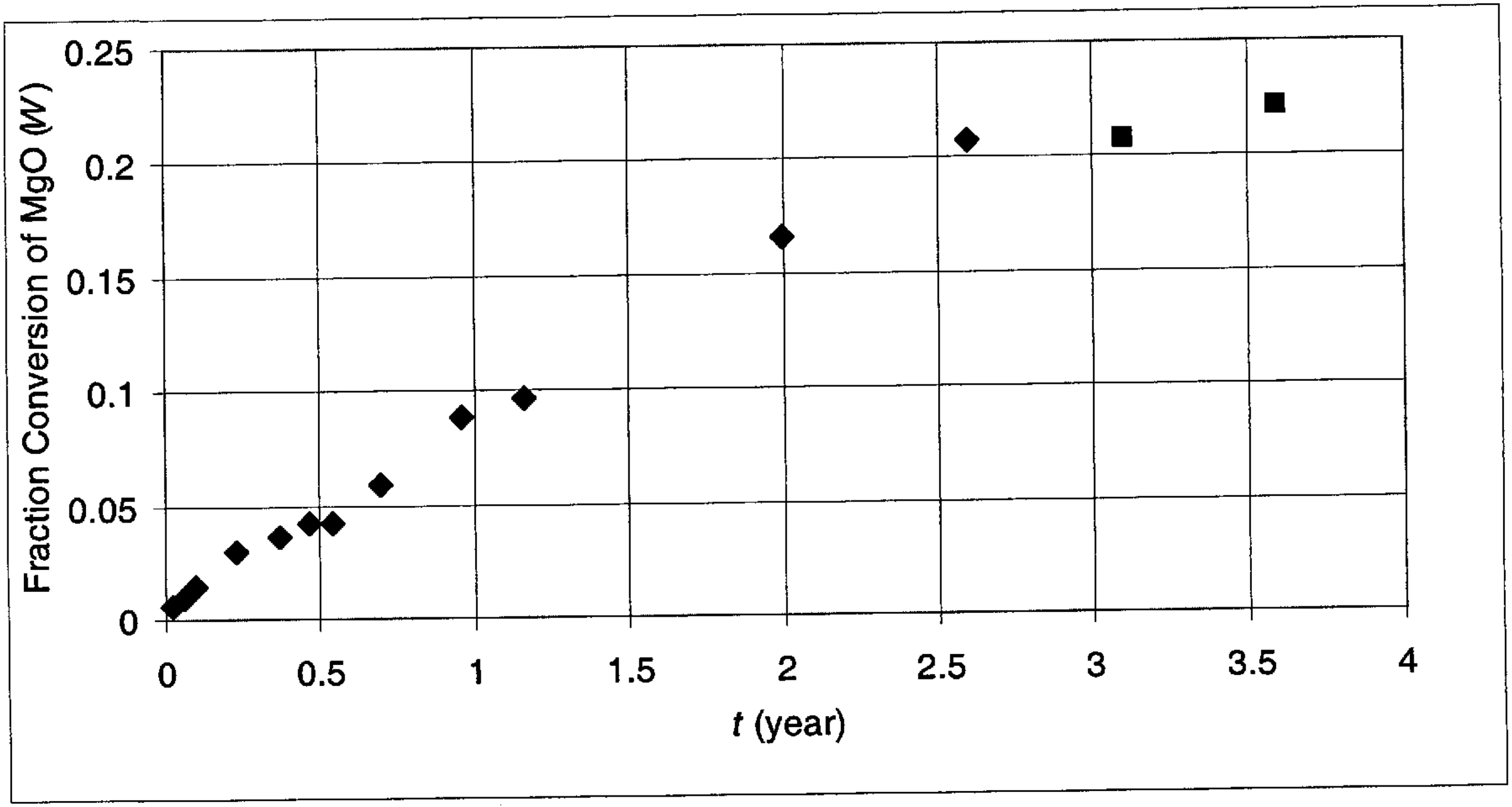

Figure 5. SNLCPG results for humid hydration @ 25°C and 75% relative humidity plotted as fraction conversion of MgO, *W*, versus time, *t* (year).

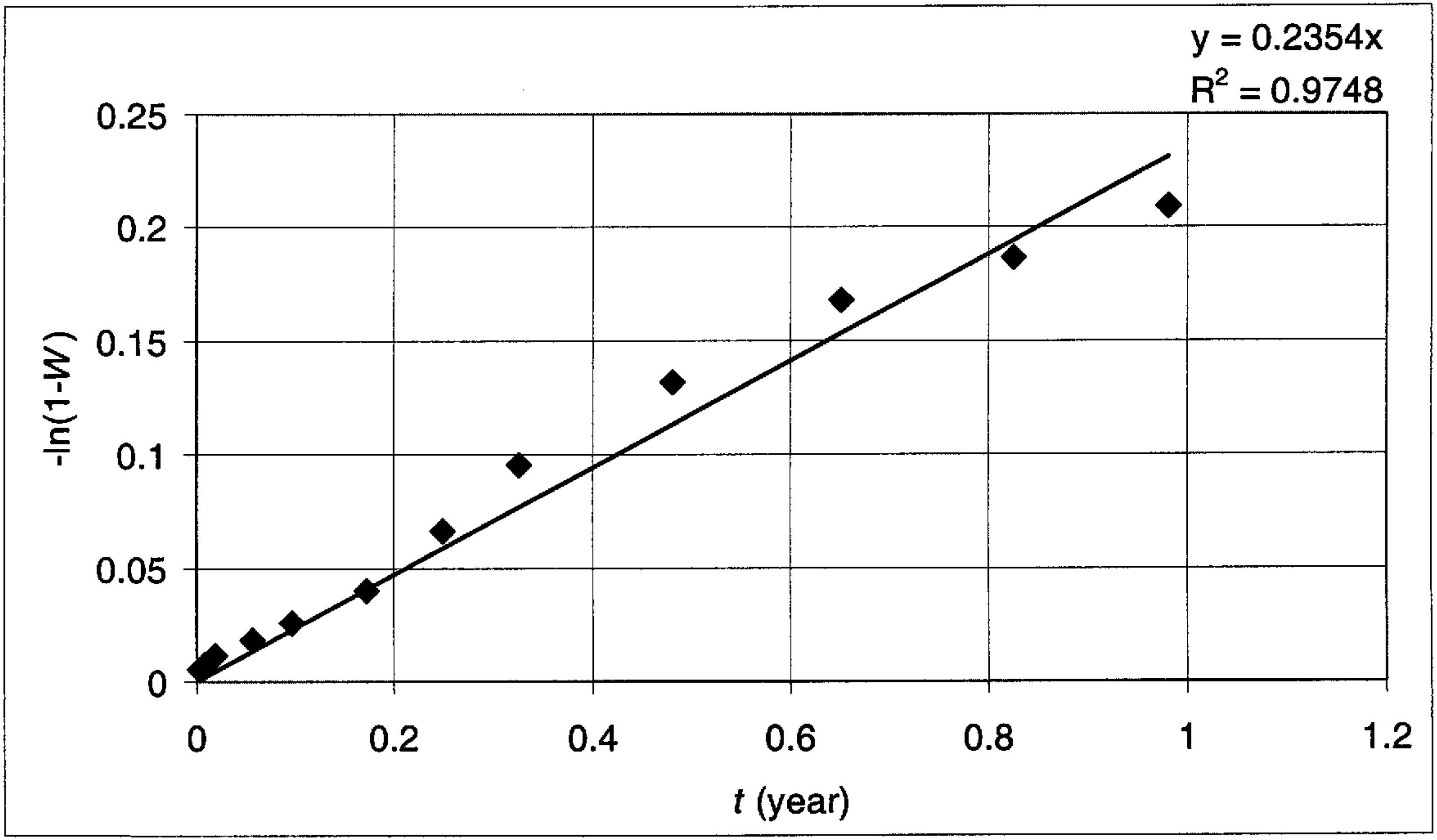

Figure 6. SNLCPG hydration results for DI water plotted as -ln(1-*W*) versus time, *t* (year), according equation (1). The straight line is a linear regression line with slope = K_{Emp}.

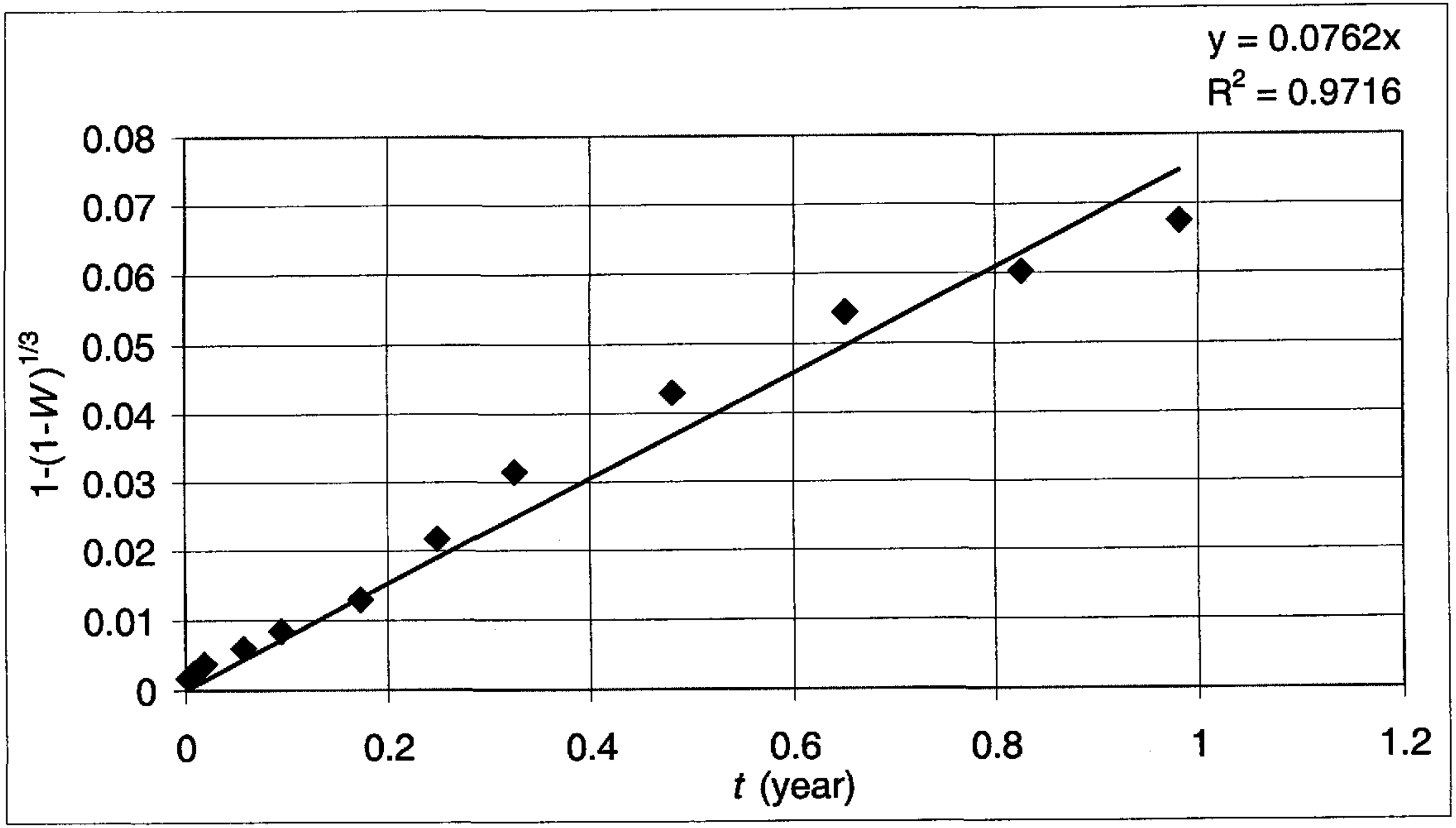

Figure 7. SNLCPG hydration results for DI water plotted as $1\text{-}(1\text{-}W)^{1/3}$ versus time, t (year), according equation (2). The straight line is a linear regression line with slope = K_R.

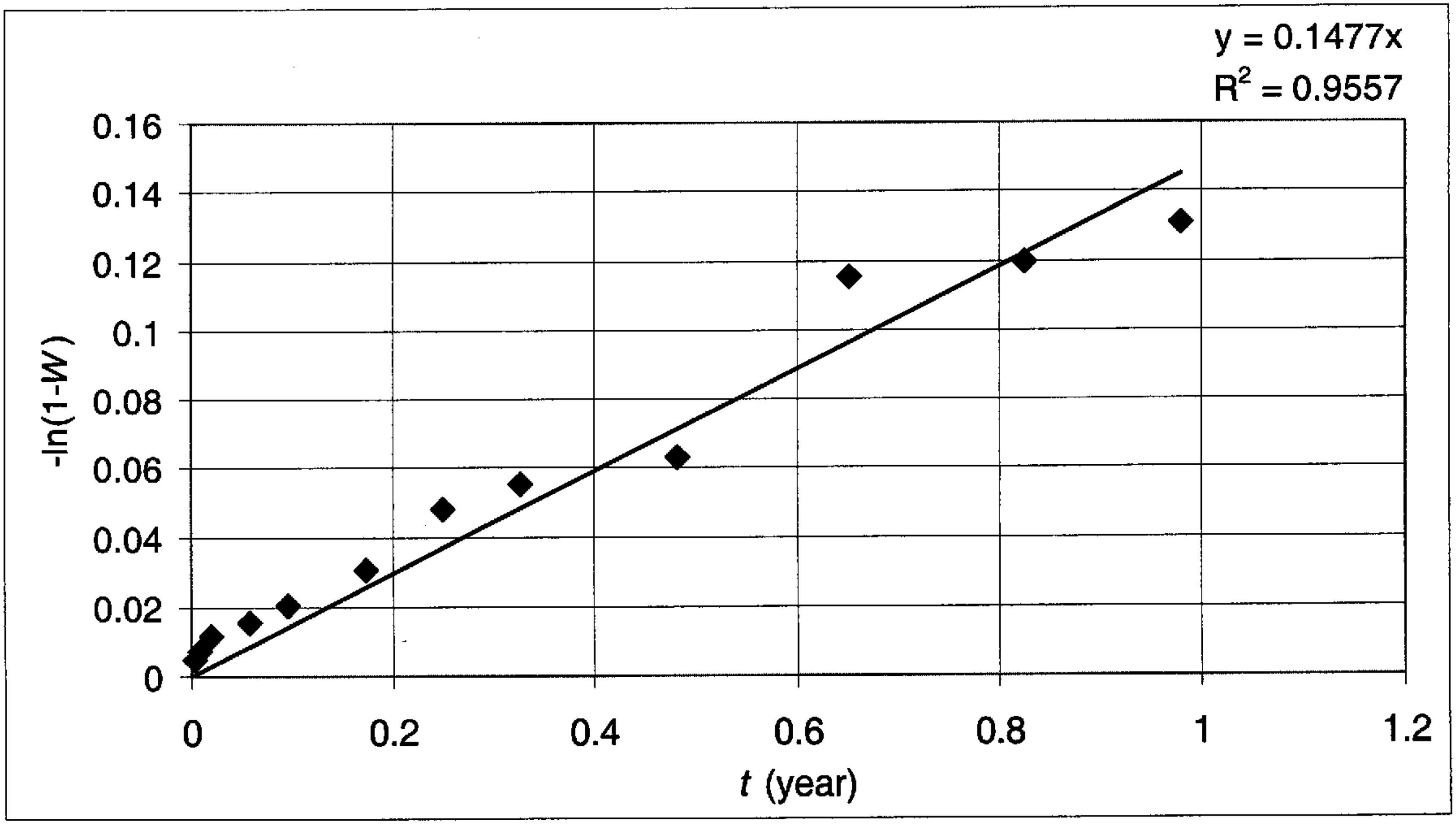

Figure 8. SNLCPG hydration results for 4 molar NaCl plotted as -ln(1-*W*) versus time, *t* (year), according equation (1). The straight line is a linear regression line with slope = K_{Emp}.

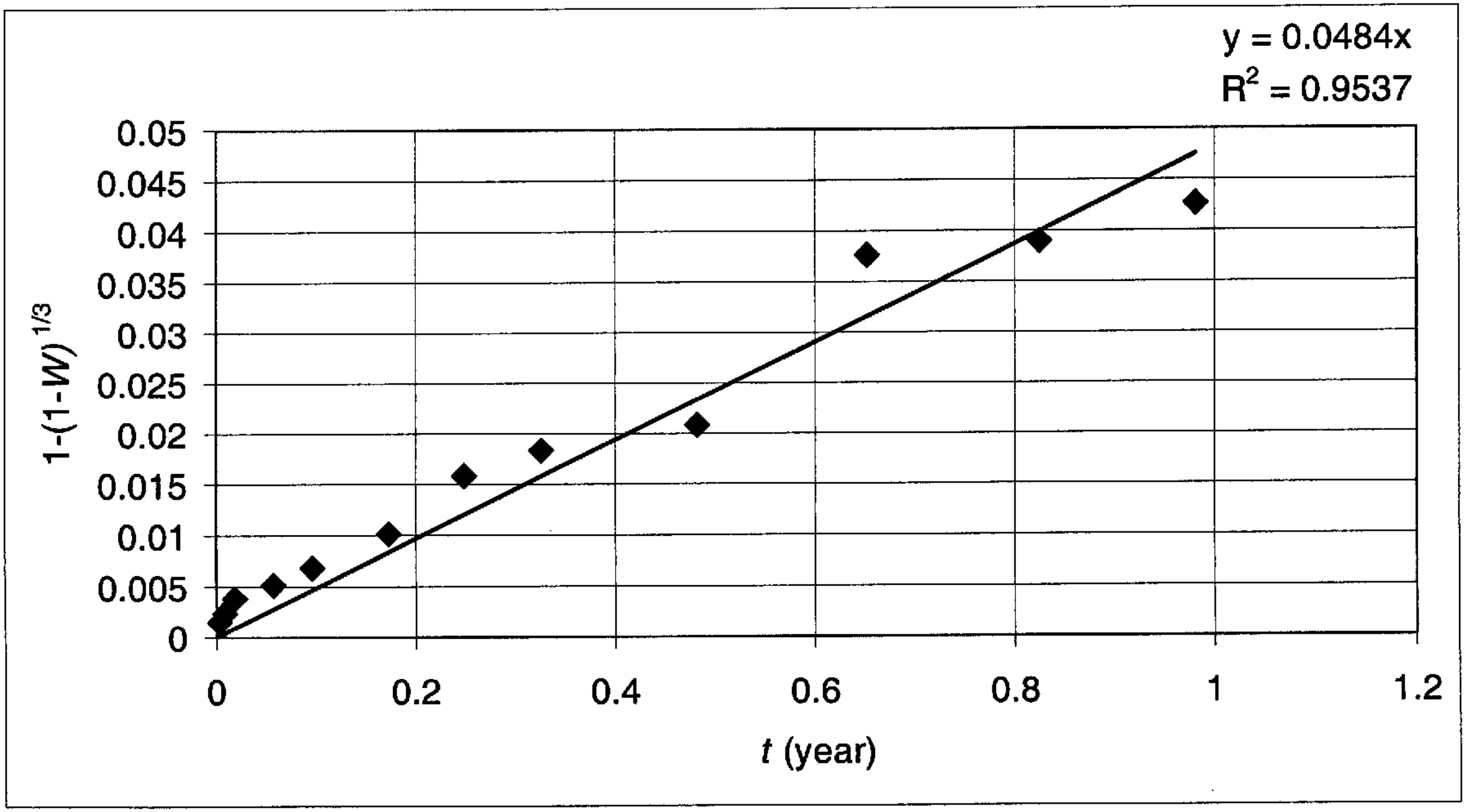

Figure 9. SNLCPG hydration results for 4 molar NaCl plotted as $1-(1-W)^{1/3}$ versus time, t (year), according equation (2). The straight line is a linear regression to the results, and the slope = K_R .

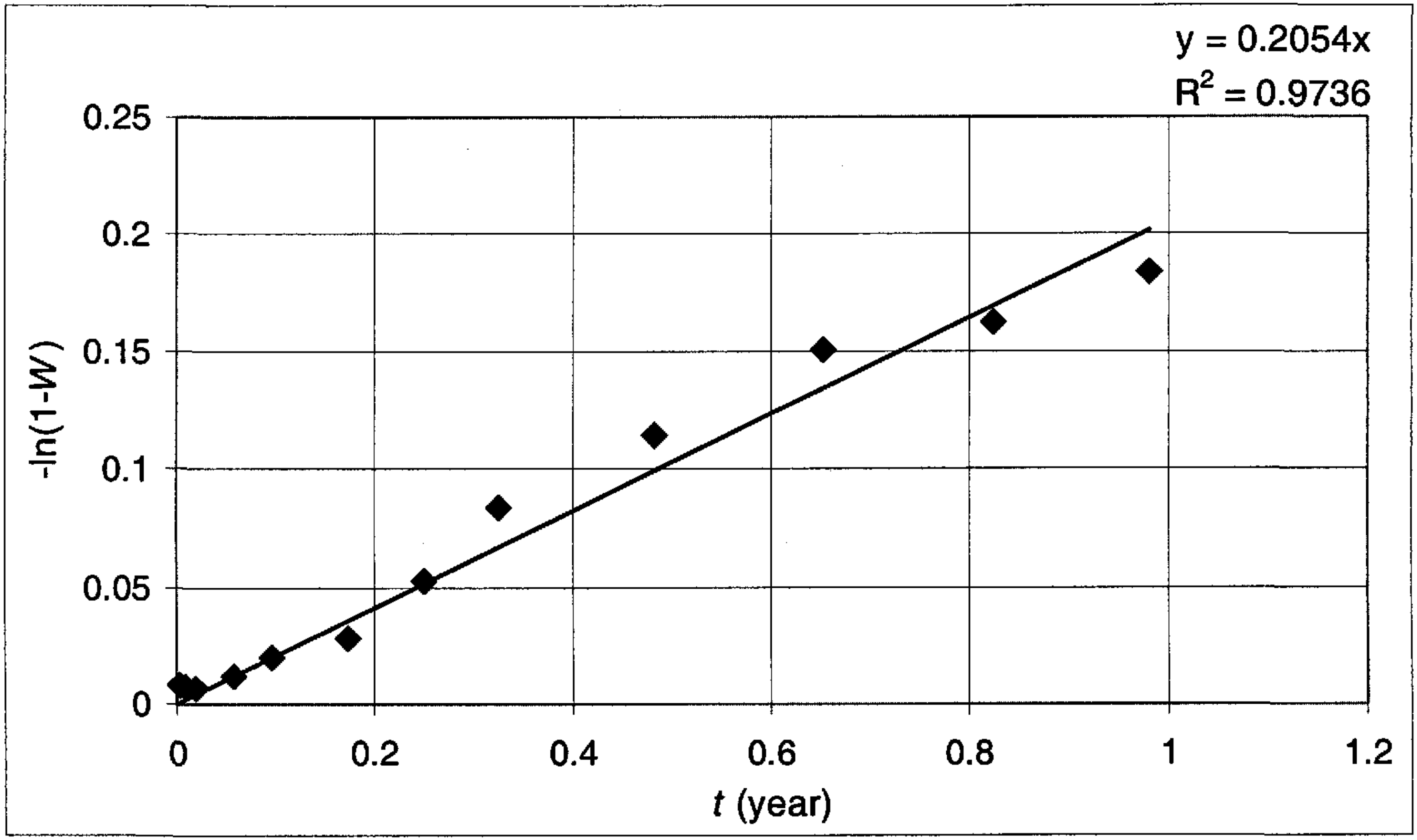

Figure 10. SNLCPG HY hydration results for ERDA-6 brine plotted as -ln(1-*W*) versus time, *t* (year), according equation (1). The straight line is a linear regression to the results, and the slope = K_{Emp}.

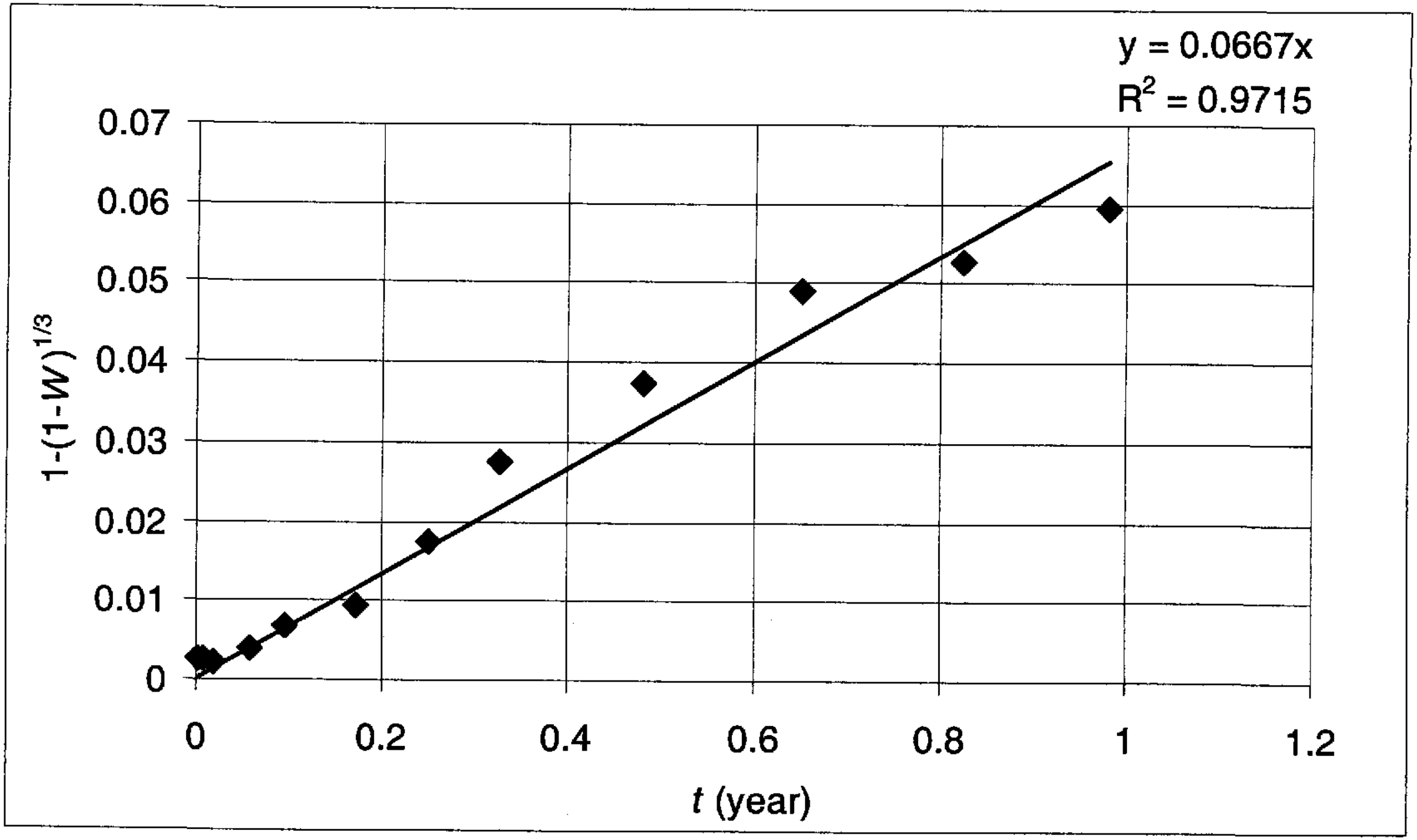

Figure 11. SNLCPG HY hydration results for ERDA-6 brine plotted as $1-(1-W)^{1/3}$ versus time, t (year), according equation (2). The straight line is a linear regression to the results, and the slope = K_R.

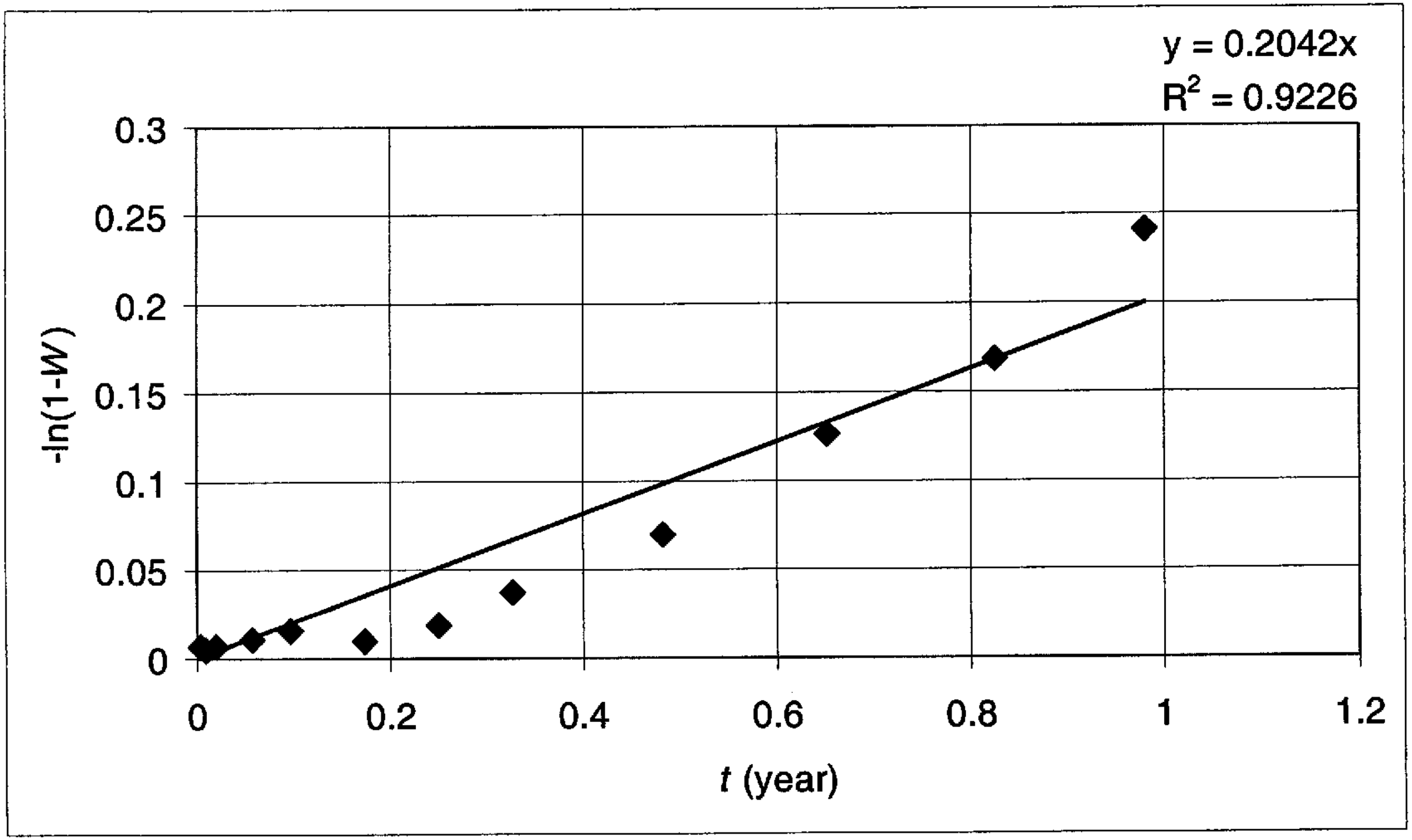

Figure 12. SNLCPG HY hydration results for GWB brine plotted as -ln(1-*W*) versus time, *t* (year), according equation (1). The straight line is a linear regression to the results, and the slope = K_{Emp}.

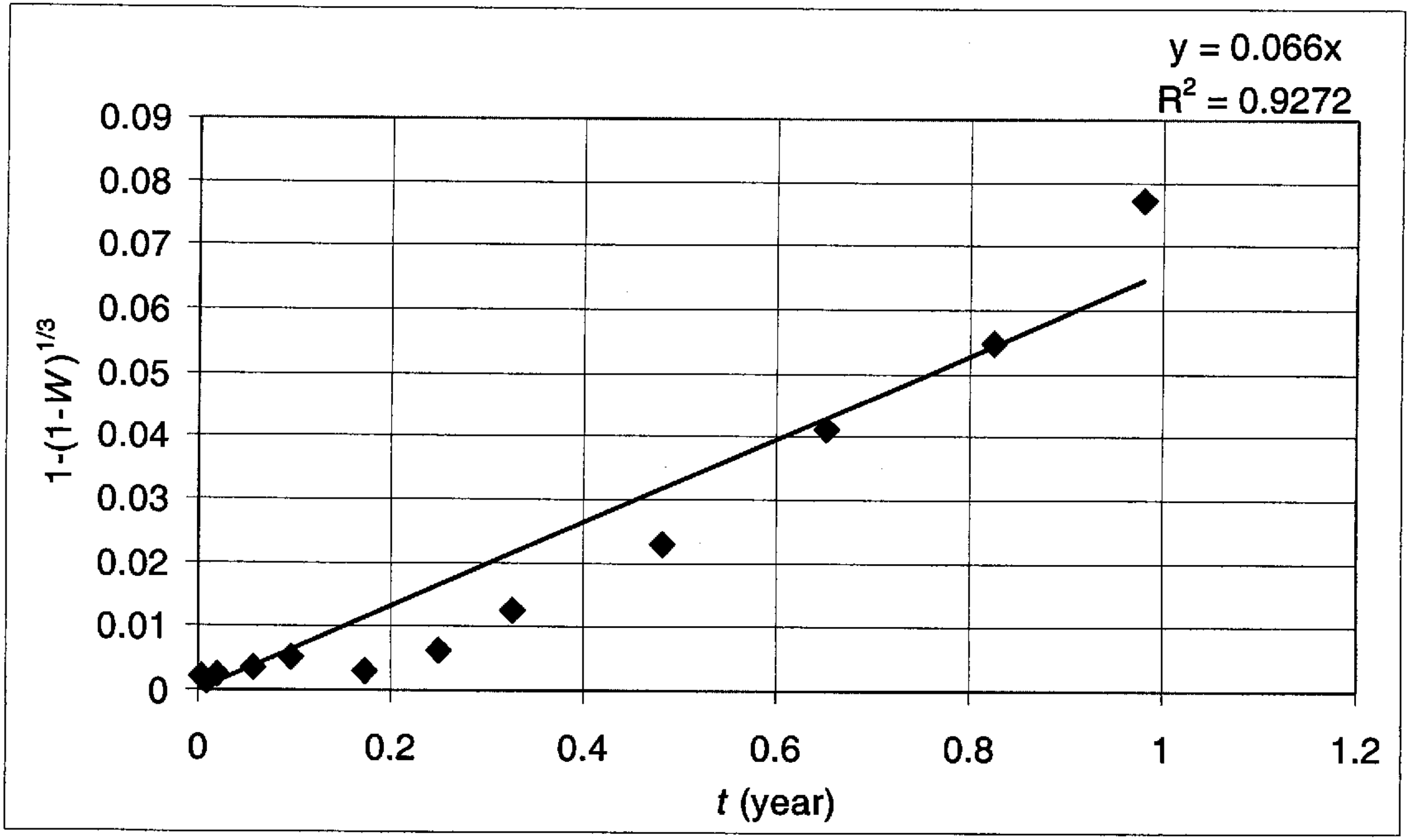

Figure 13. SNLCPG HY hydration results for GWB brine plotted as $1-(1-W)^{1/3}$ versus time, t (year), according equation (2). The straight line is a linear regression to the results, and the slope = K_R.

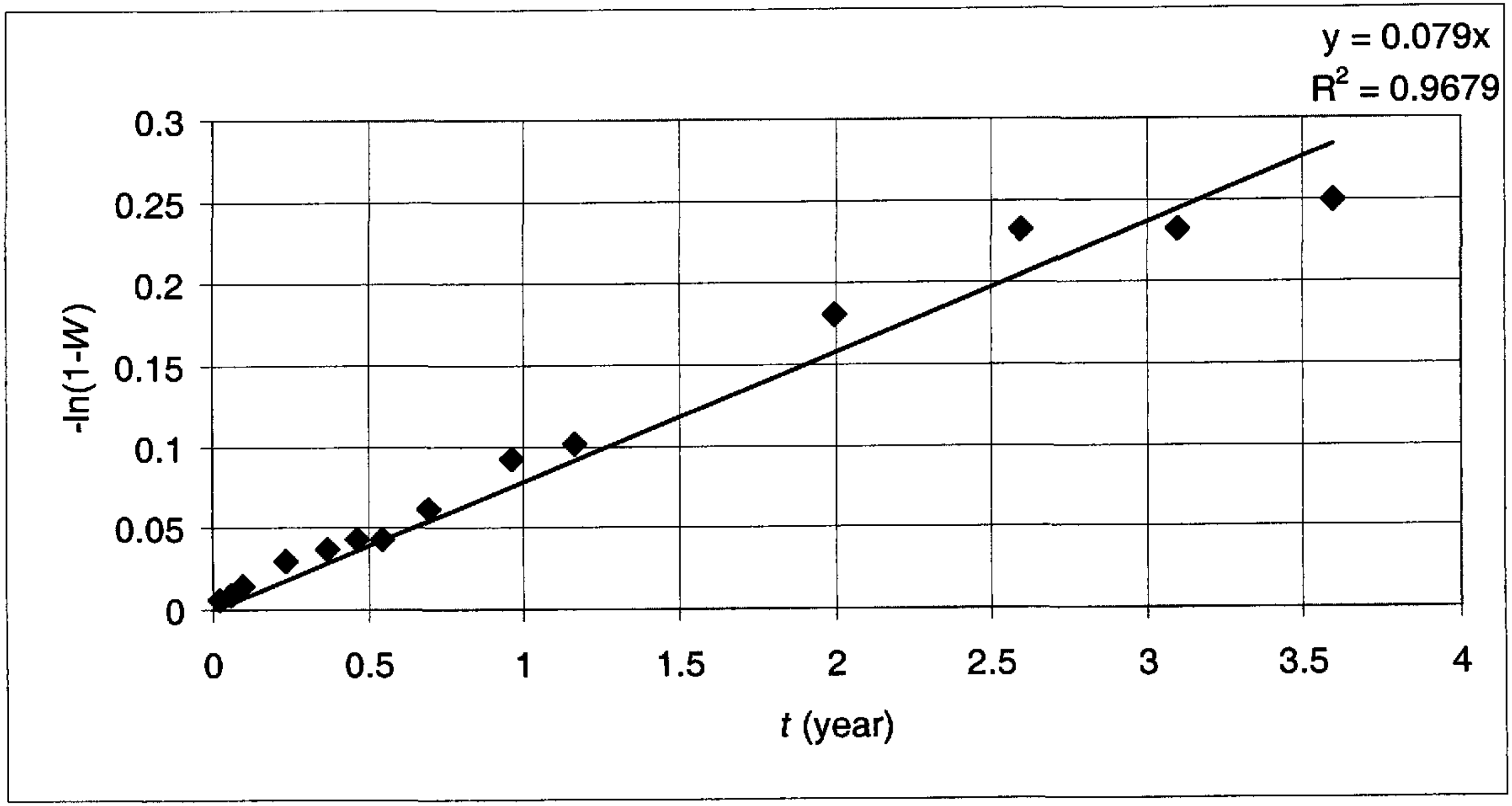

Figure 14. SNLCPG HH humid hydration results plotted as $-\ln(1-W)$ versus time, t (year), according equation (1). The straight line is a linear regression to the results, and the slope = K_{Emp}.

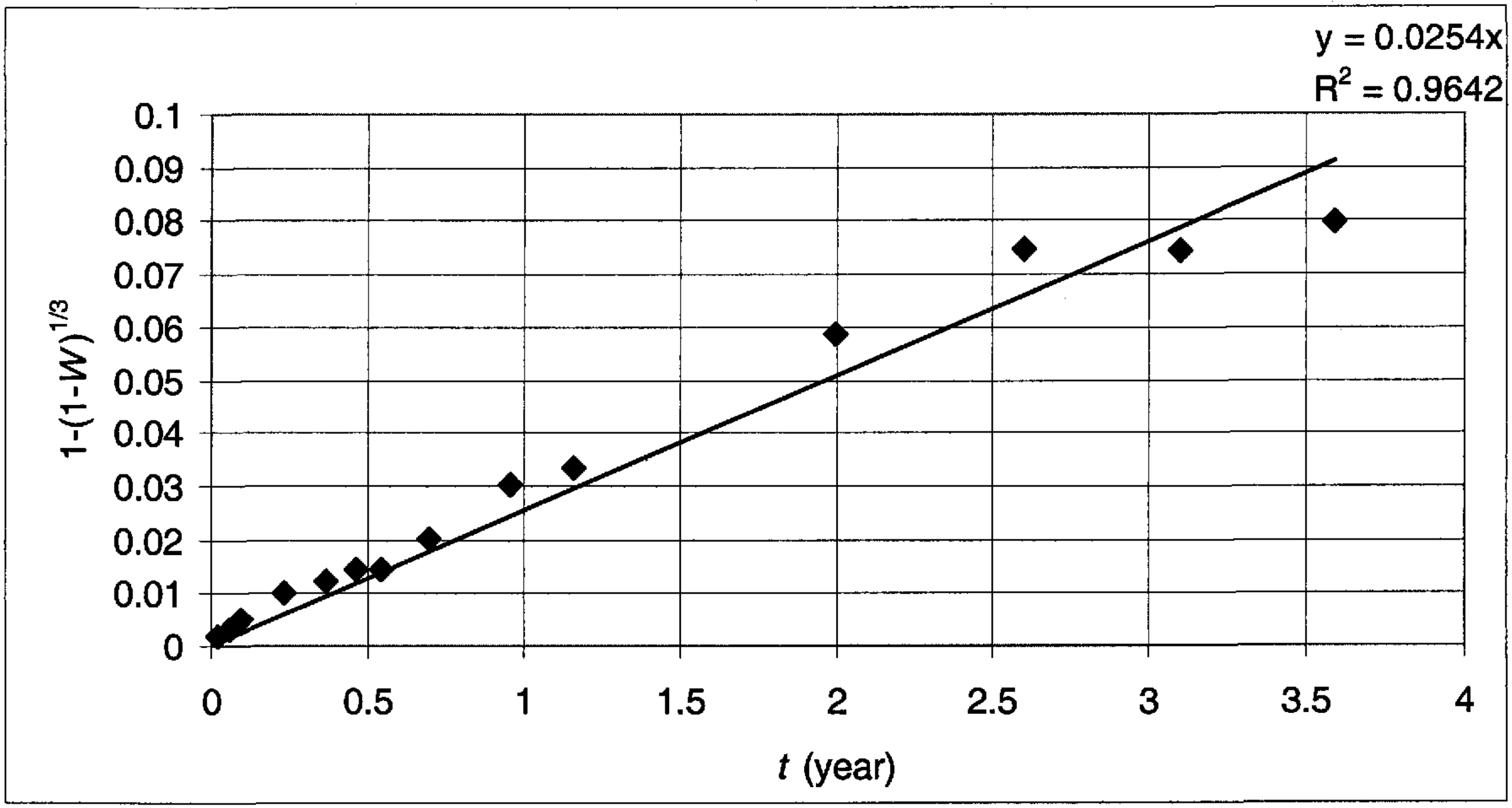

Figure 15. SNLCPG HH humid hydration results plotted as $1-(1-W)^{1/3}$ versus time, t (year), according equation (2). The straight line is a linear regression to the results, and the slope = K_R.

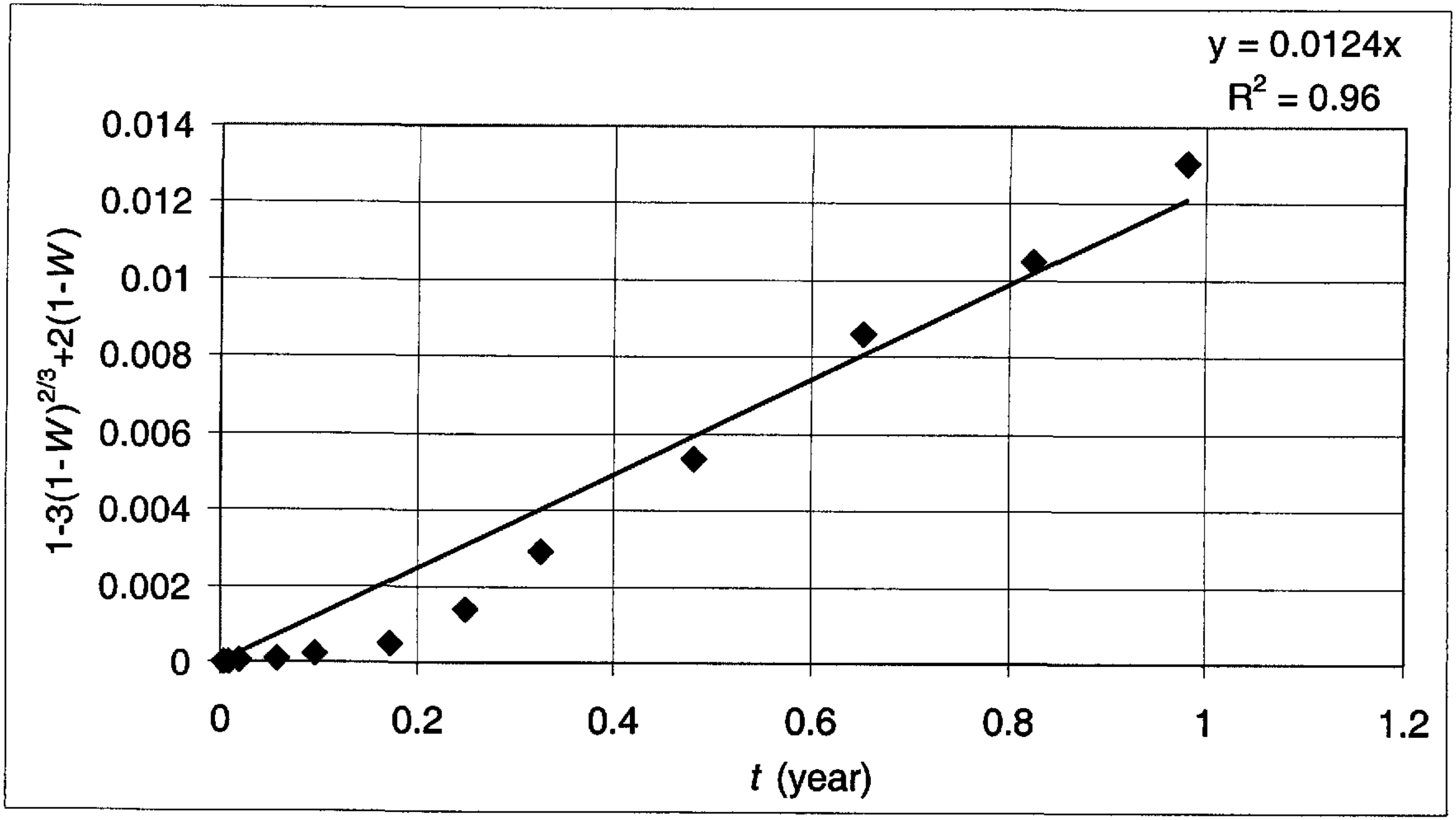

Figure 16. SNLCPG HY hydration results for DI water plotted as $1-3(1-W)^{2/3}+2(1-W)$ versus time, t (year), according to equation (3). The straight line is a linear regression to the results, and the slope = K_D.

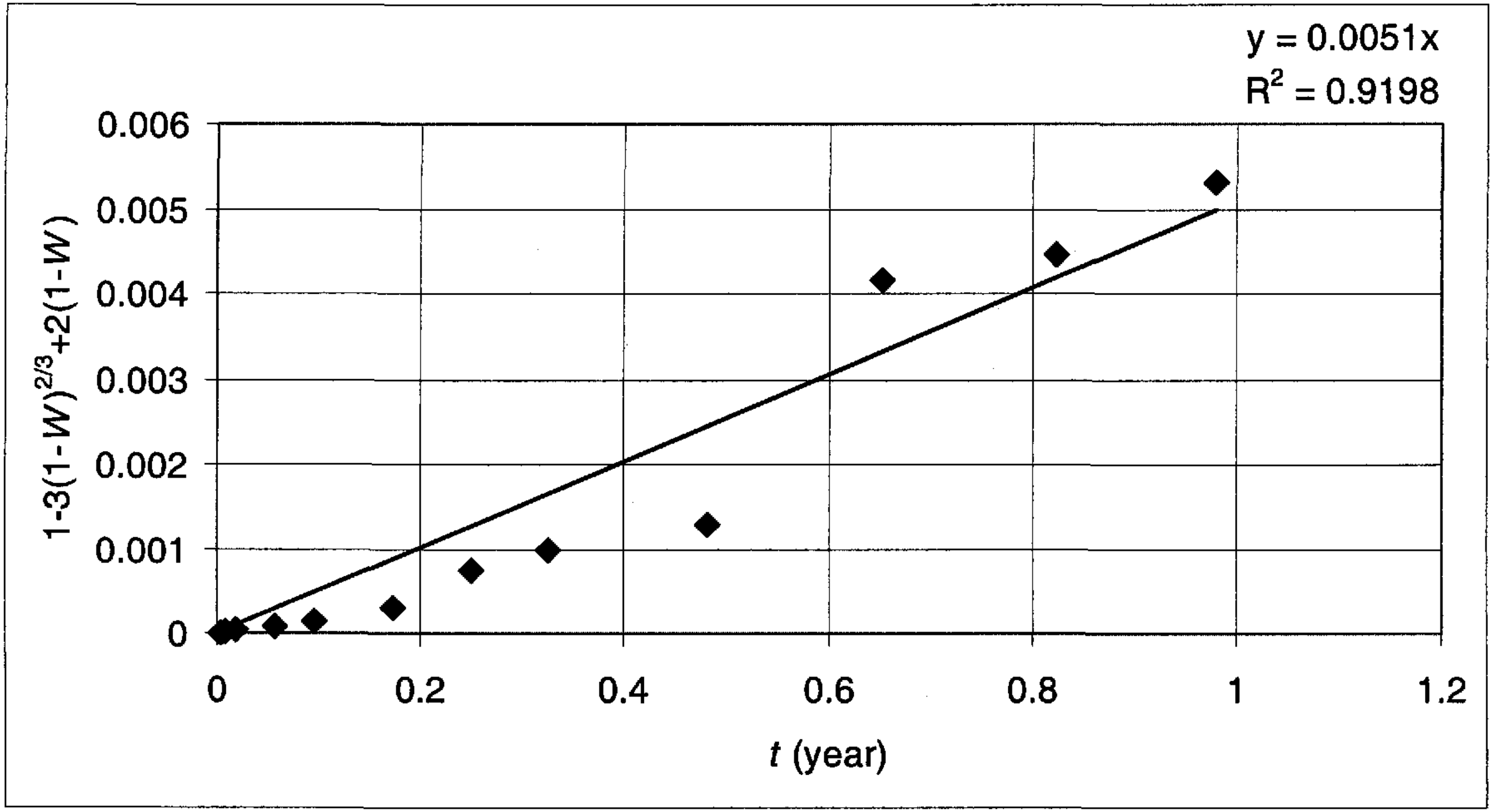

Figure 17. SNLCPG HY hydration results for 4 molar NaCl plotted as $1\text{-}3(1\text{-}W)^{2/3}+2(1\text{-}W)$ versus time, t (year), according to equation (3). The straight line is a linear regression to the results, and the slope = K_D.

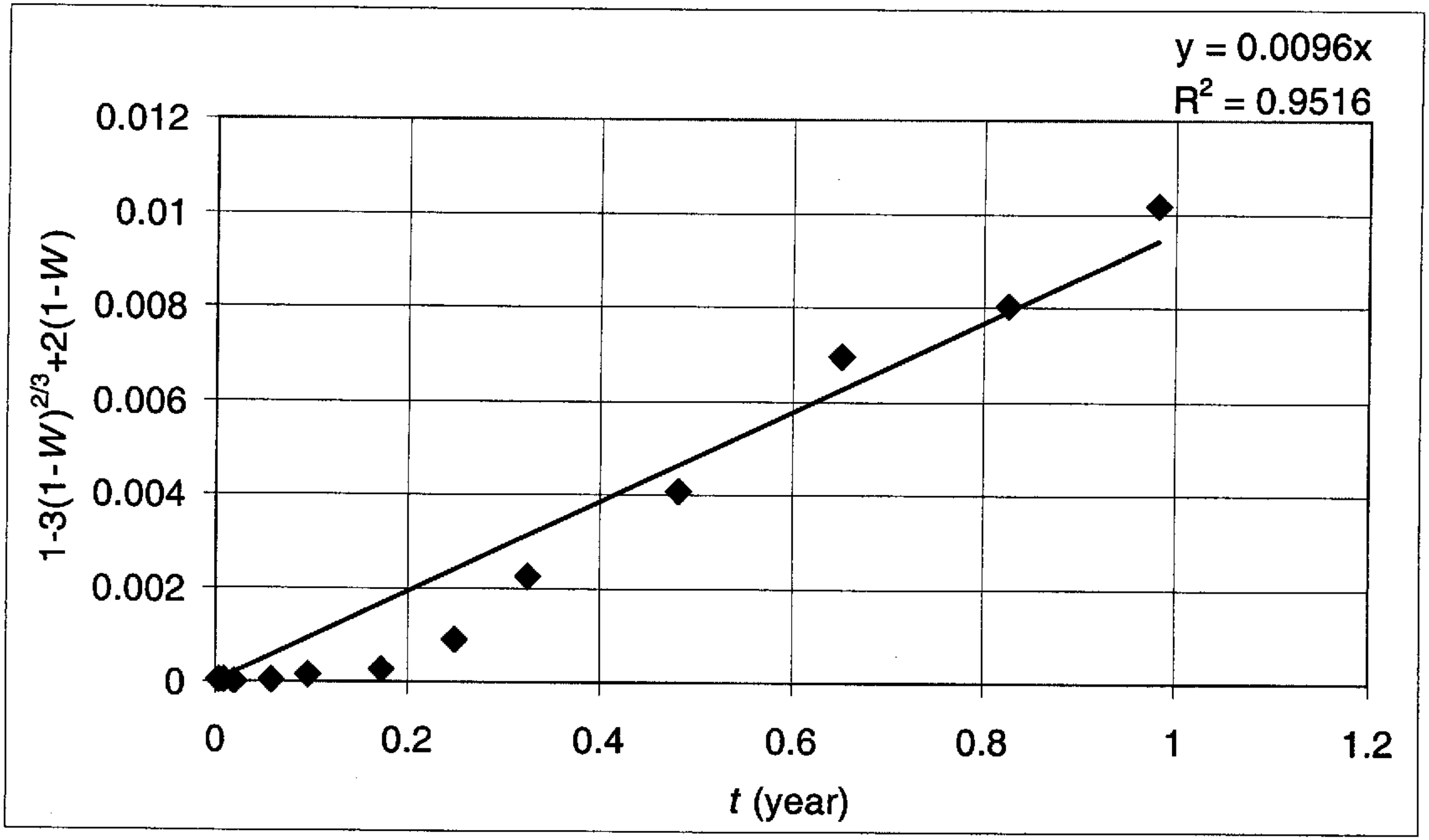

Figure 18. SNLCPG HY hydration results for ERDA-6 brine plotted as $1\text{-}3(1\text{-}W)^{2/3}+2(1\text{-}W)$ versus time, t (year), according to equation (3). The straight line is a linear regression to the results, and the slope = K_D.

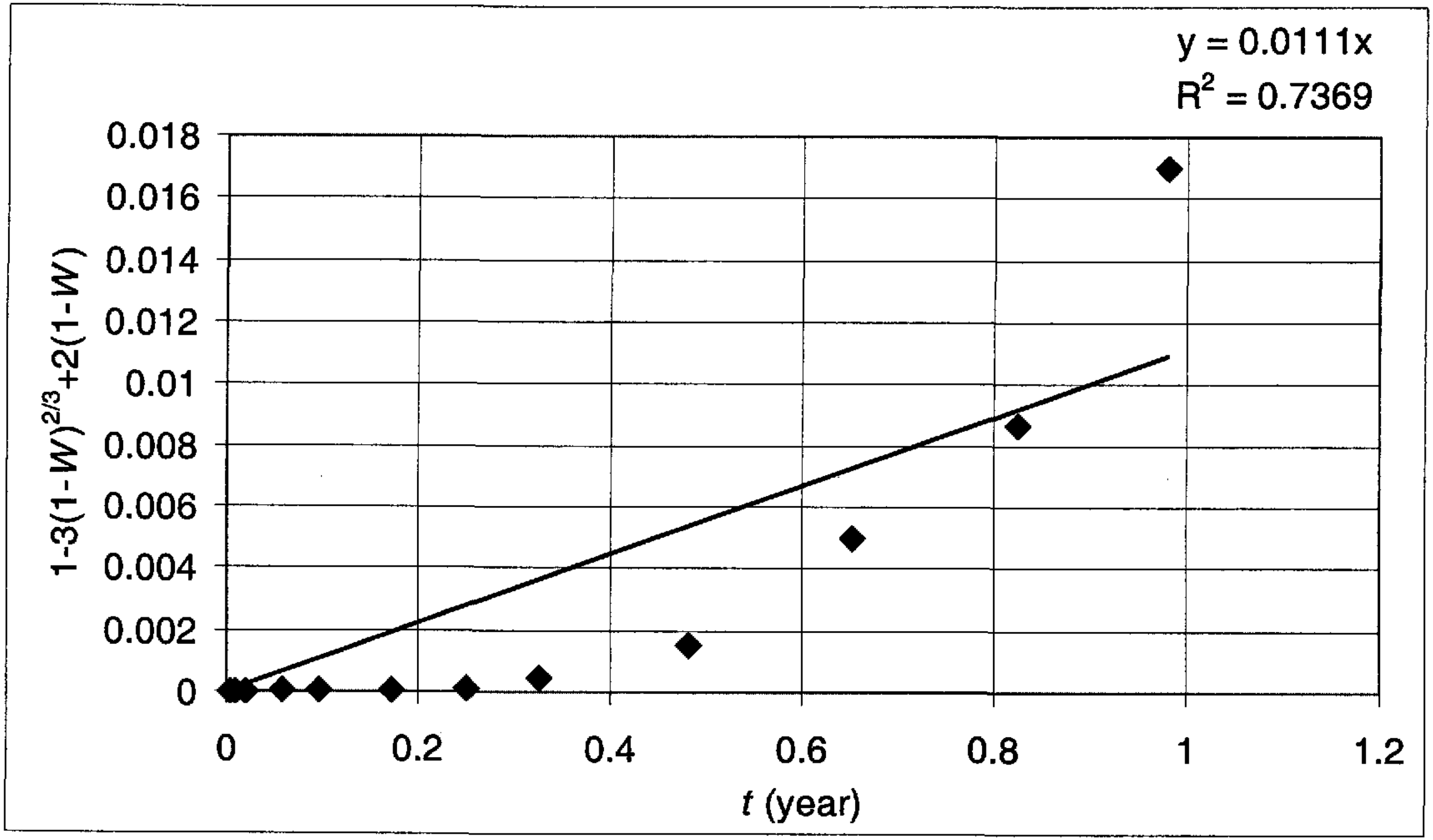

Figure 19. SNLCPG HY hydration results for GWB brine plotted as $1\text{-}3(1\text{-}W)^{2/3}+2(1\text{-}W)$ versus time, *t* (year), according to equation (3). The straight line is a linear regression to the results, and the slope = K_D.

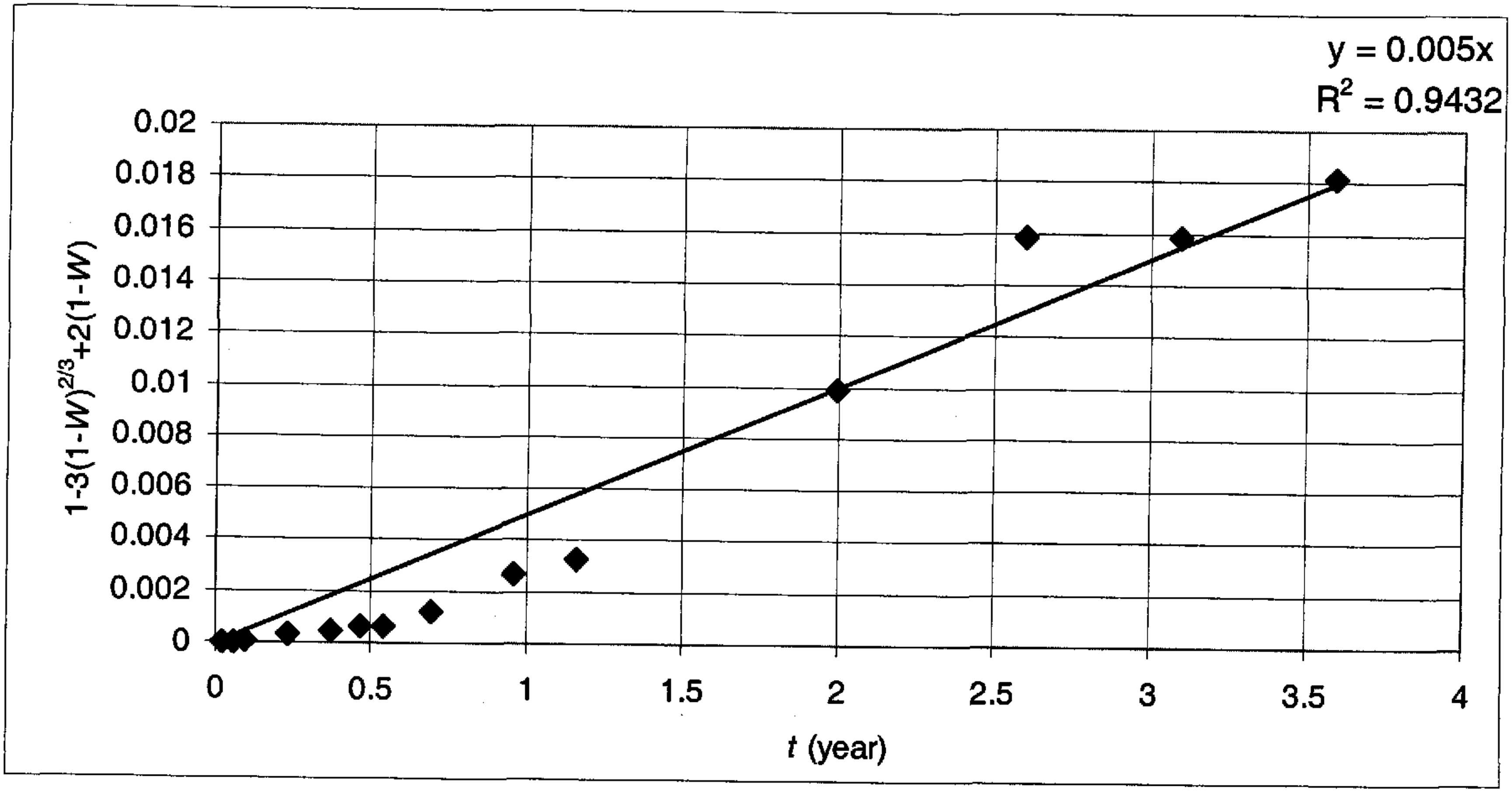

Figure 20. SNLCPG HH humid hydration results plotted as $1-3(1-W)^{2/3}+2(1-W)$ versus time, t (year), according to equation (3). The straight line is a linear regression to the results, and the slope = K_D.

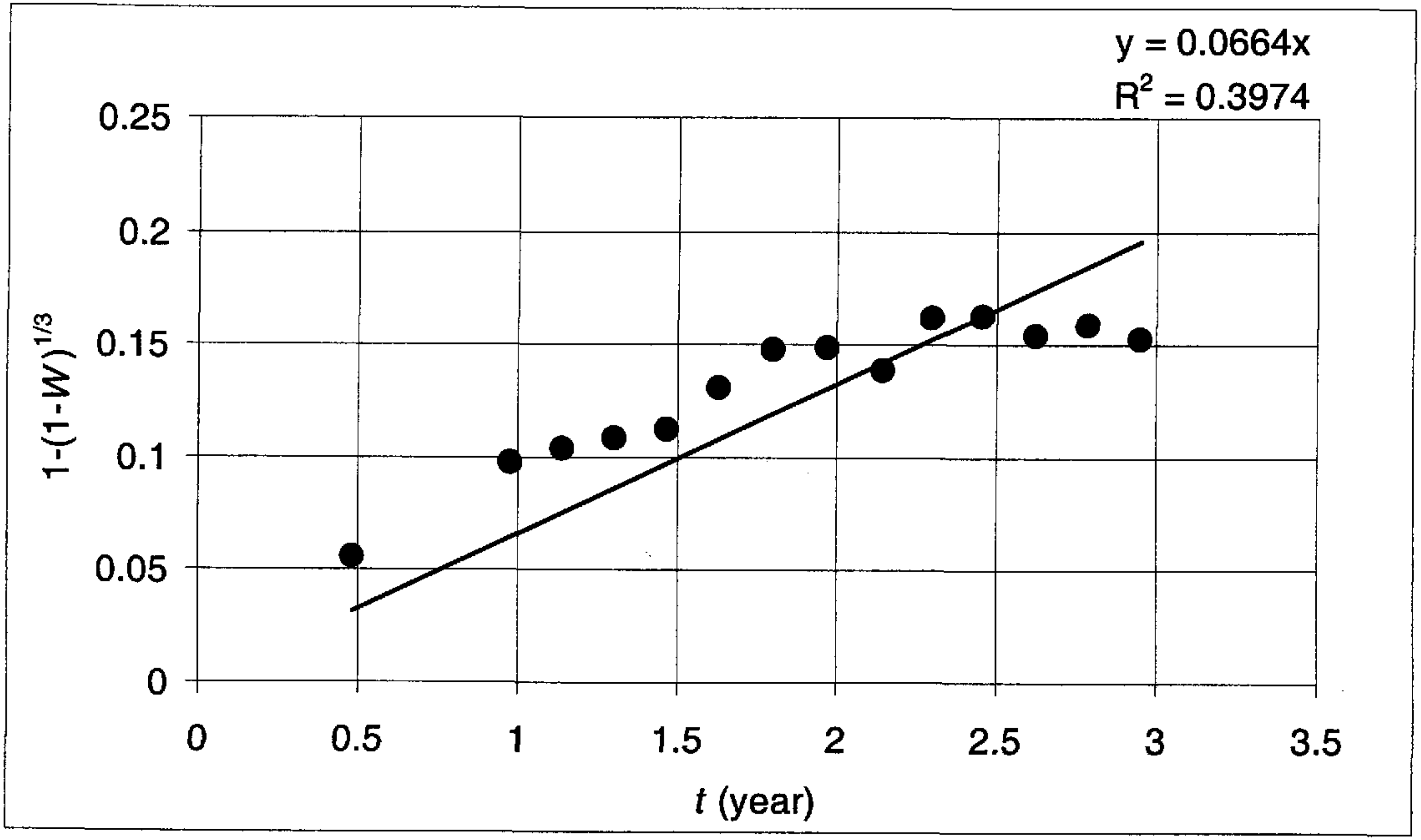

Figure 21. SNLCPG HY2 hydration results for ERDA-6 brine plotted as $1-(1-W)^{1/3}$ versus time, t (year), according equation (2). The straight line is a linear regression to the results, and the slope = K_R .

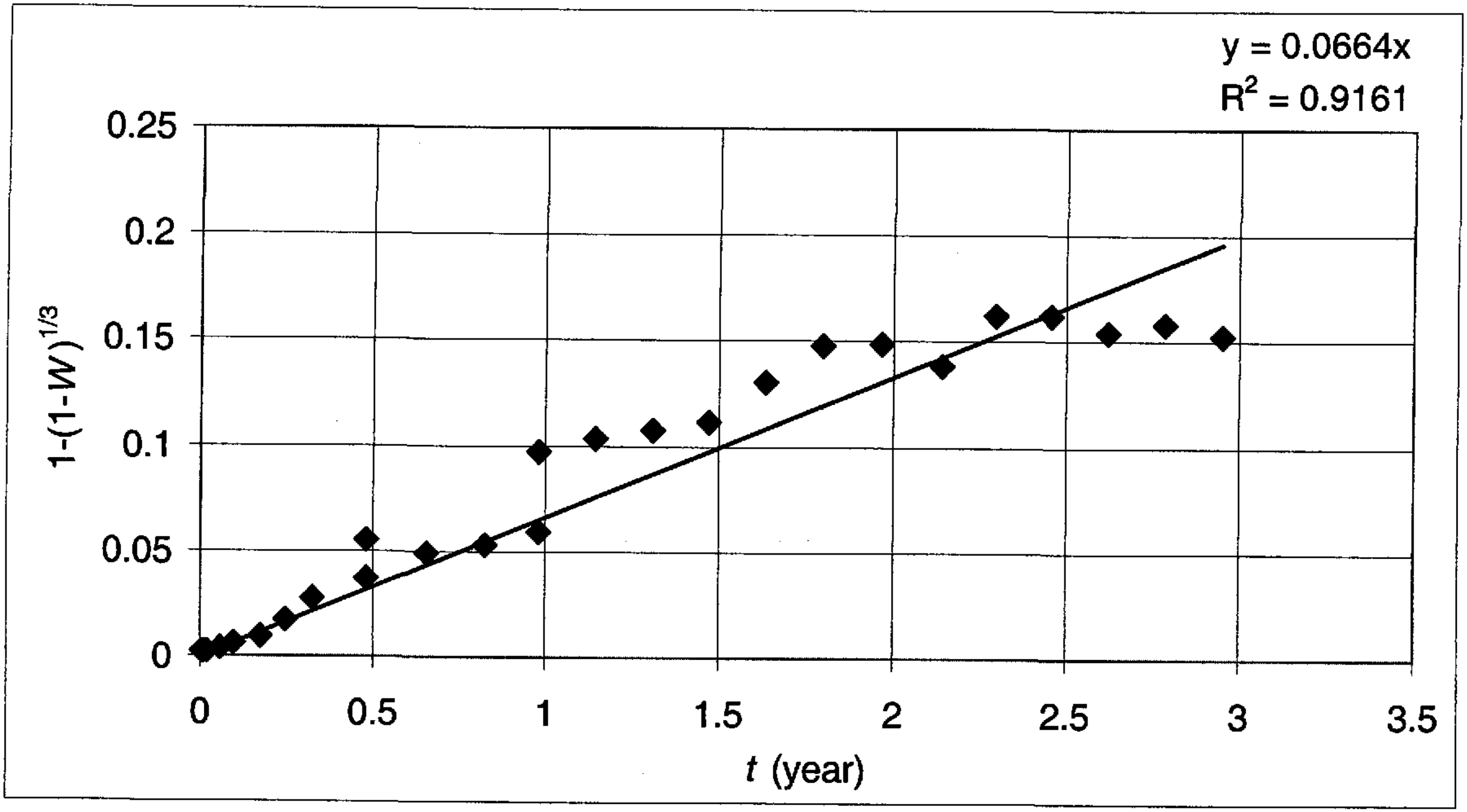

Figure 22. Combined SNLCPG HY and HY2 hydration results for ERDA-6 brine plotted as $1-(1-W)^{1/3}$ versus time, *t* (year), according equation (2). The straight line is a linear regression to the results, and the slope = K_R.

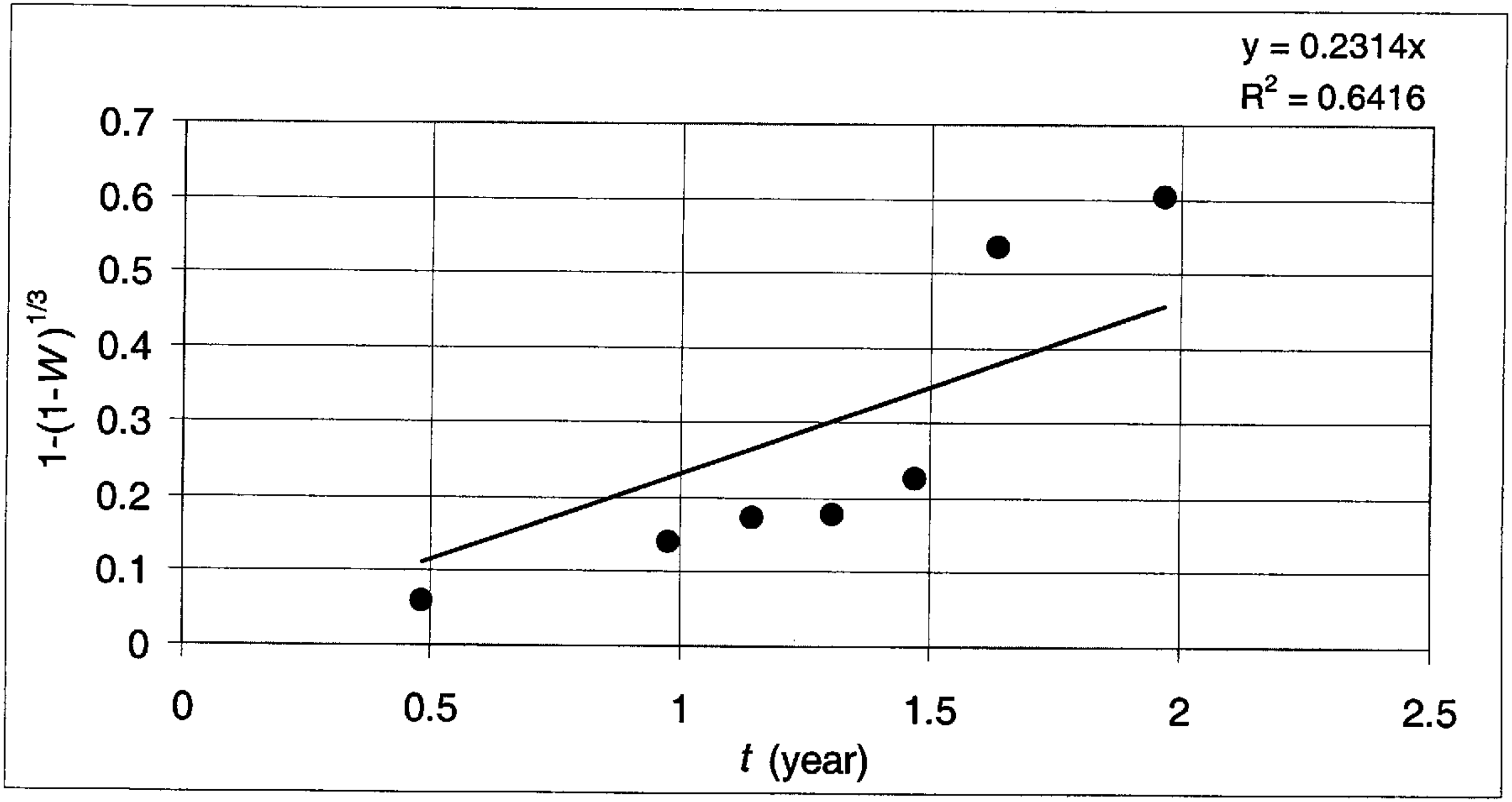

Figure 23. SNLCPG HY2 hydration results for GWB brine plotted as $1-(1-W)^{1/3}$ versus time, t (year), according to equation (2). The straight line is a linear regression to the results, and the slope = K_R.

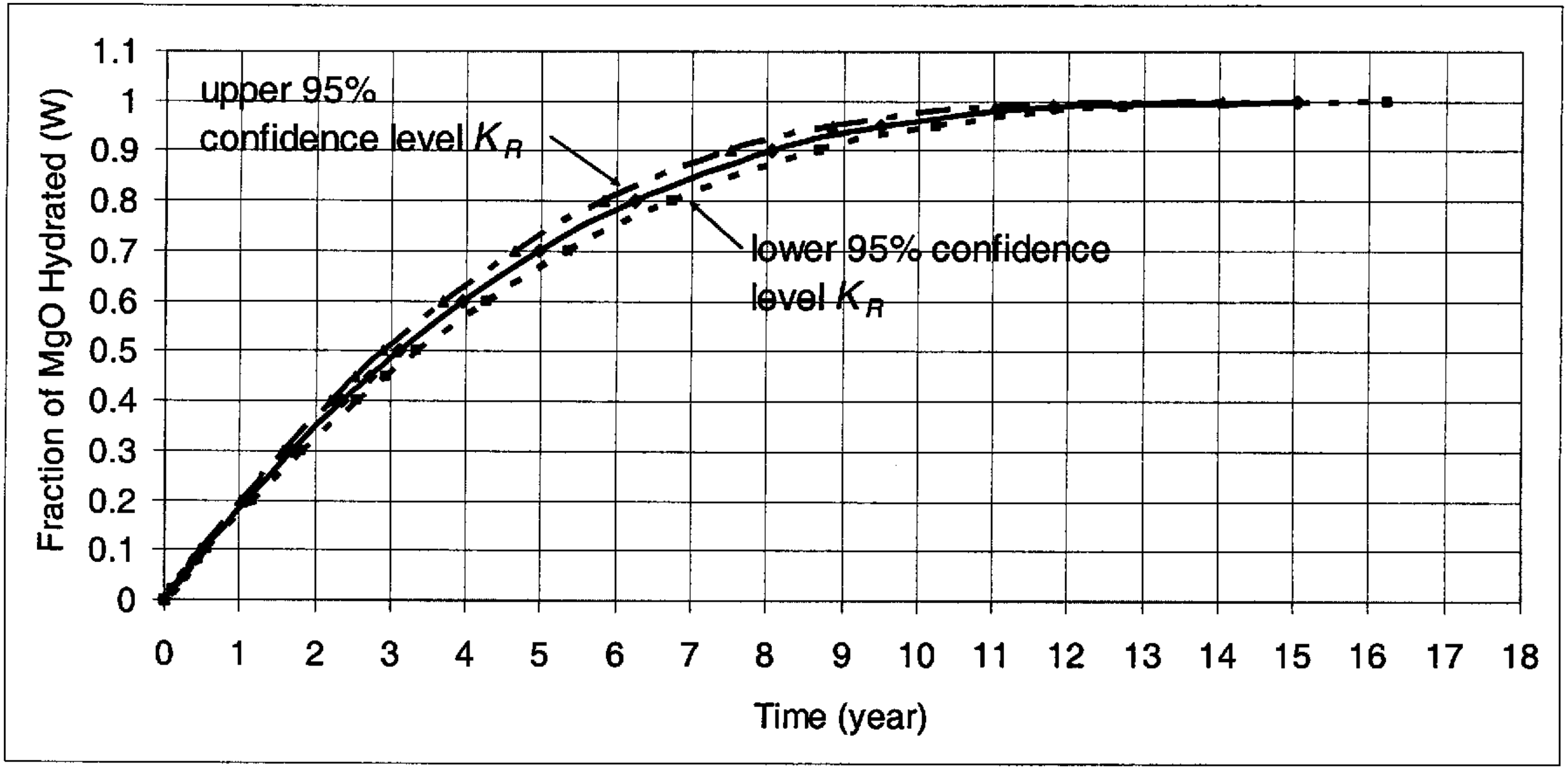

Figure 24. Calculated fraction of MgO hydrated, W, in ERDA-6 brine plotted versus time, t (year), using rate equation (2) and values of K_R from Tables 2 and 3.

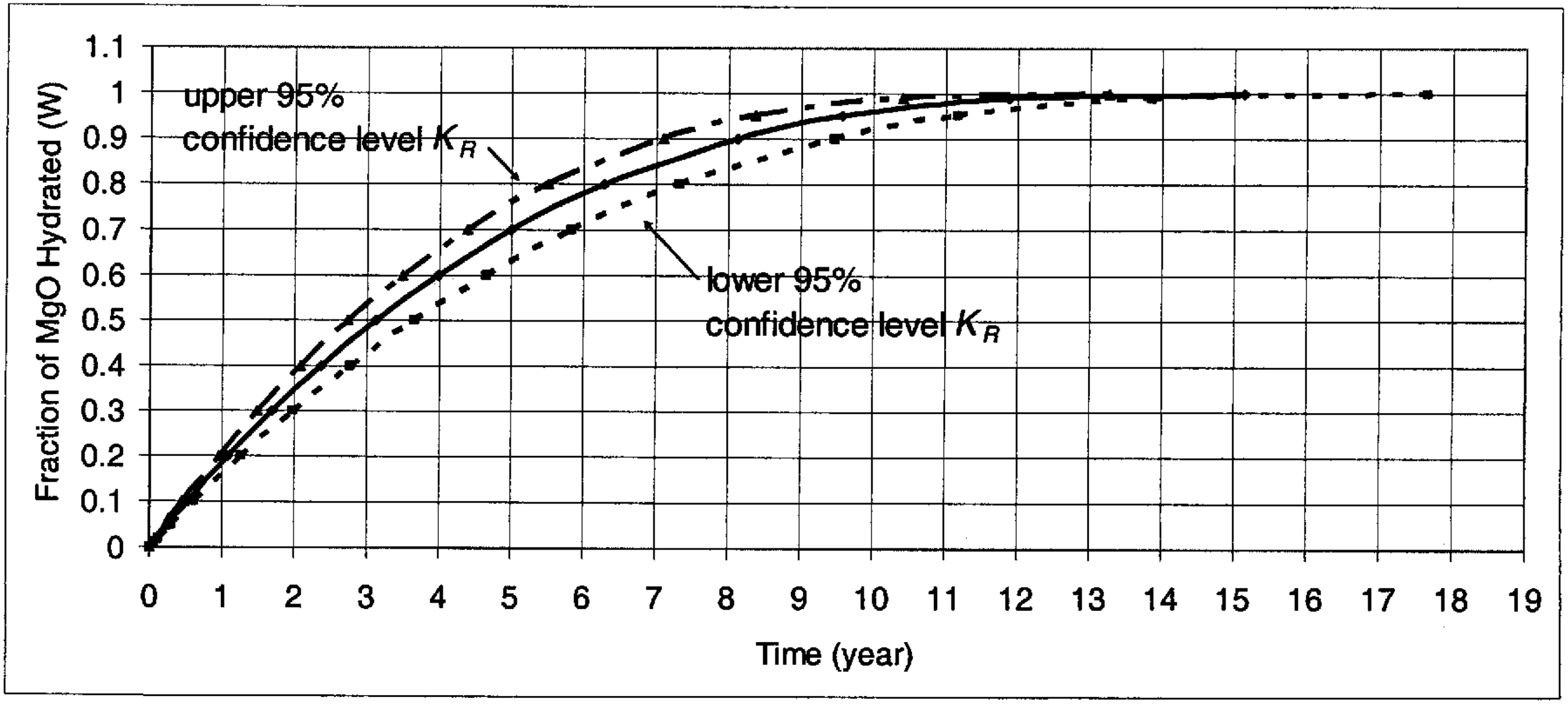

Figure 25. Calculated fraction of MgO hydrated, *W*, in GWB brine plotted versus time, *t* (year), using rate equation (2) and values of K_R from Tables 2 and 3.

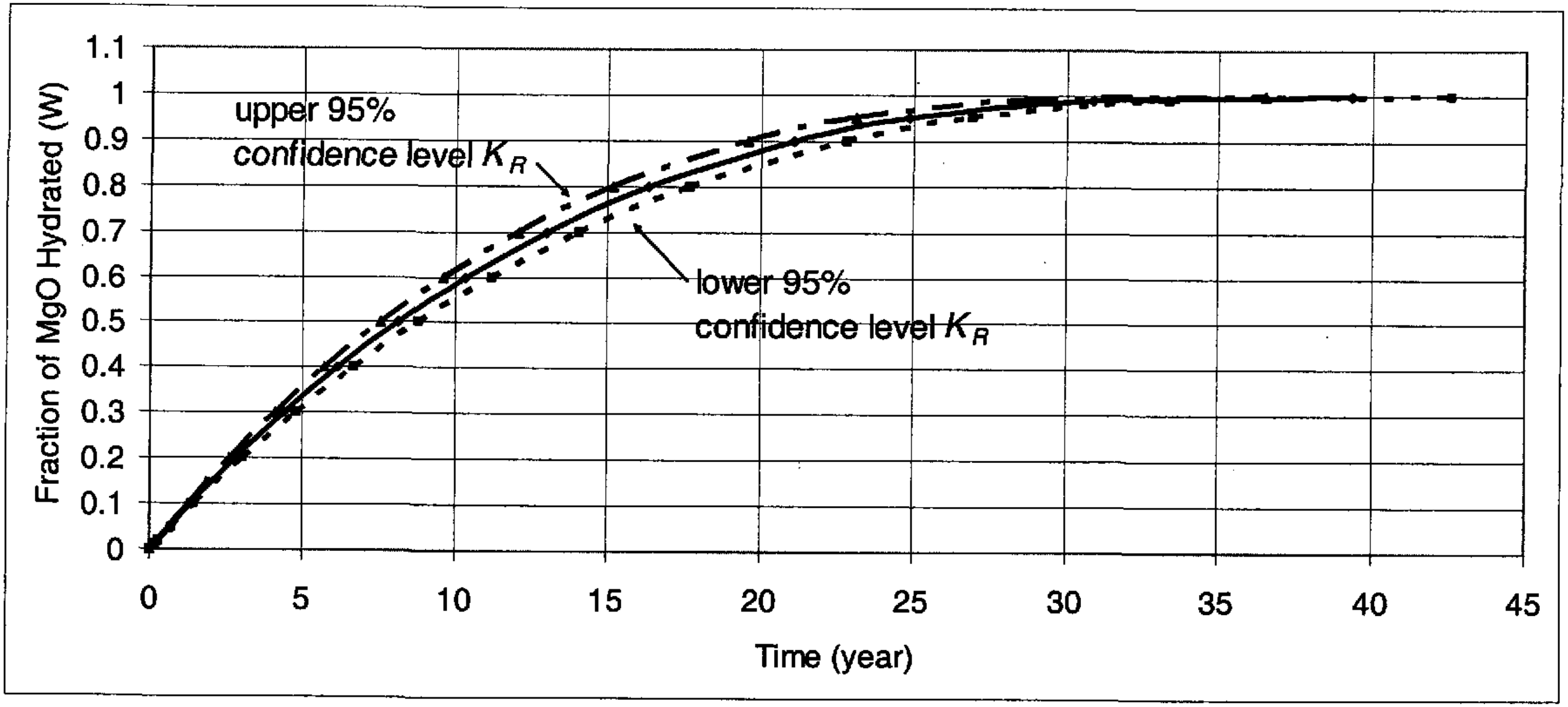

Figure 26. Calculated fraction of MgO hydrated, W, by humid hydration plotted versus time, t (year), using rate equation (2) and values of K_R from Tables 2 and 3.

9 TABLES

Table 1. Values of K_R with corresponding standard error, s, for equation (2), for each data set. Values of K_R are equal to the slopes of regression lines that were calculated with the "Regression" data analysis tool in Microsoft Excel. The value of each slope is the value designated "Coefficient of X Variable 1" in the pertinent SUMMARY OUTPUT table in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls." The Standard Error of the slope is also given in the pertinent SUMMARY OUTPUT table.

Data Set	**Aqueous Solution**	**Rate Constant, K_R, equation (2) year^{-1}**	**Standard Error, s, for K_R, Year^{-1}**
HY	DI water	0.0762	0.0026
HY	4 molar NaCl	0.0484	0.0021
HY	ERDA-6	0.0667	0.0023
HY2	ERDA-6	0.0664	0.0033
HY	GWB	0.0660	0.0043
HY2	GWB	0.2314	0.0348
HH	Humid	0.0254	0.0009

Table 2. Final values of K_R with corresponding standard deviation, s, for equation (2), for each solution. Values of K_R are equal to the slopes of regression lines that were calculated with the "Regression" data analysis tool in Microsoft Excel. The value of each slope is the value designated "Coefficient of X Variable 1" in the pertinent SUMMARY OUTPUT table in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls." The Standard Error of the slope is also given in the pertinent SUMMARY OUTPUT table.

Data Set	**Aqueous Solution**	**Rate Constant, K_R, Equation (2) Year^{-1}**	**Standard Error, s, for K_R, Year^{-1}**
HY	DI water	0.0762	0.0026
HY	4 molar NaCl	0.0484	0.0021
HY & HY2	ERDA-6	0.0664	0.0023
HY	GWB	0.0660	0.0043
HH	Humid	0.0254	0.0009

Table 3. Values of K_B and s_B for ERDA-6, GWB and humid hydration calculated from Table 2 and equations (4) and (5) in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls."

Aqueous Solution	**BRAGFLO hydration rate K_B, mol MgO/kg MgO/sec**	**BRAGFLO hydration Standard Error s_B, mol MgO/kg MgO/sec**
ERDA-6	5.2E-08	1.8E-09
GWB	5.2E-08	3.4E-09
Humid	2.0E-08	7.1E-10

Table 4. Values of K_R at the lower 95% confidence level and the upper 95% confidence level from "Upper 95% " and "Lower 95%" in the SUMMARY OUTPUT tables in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls."

Aqueous Solution	**Lower 95% Confidence Level K_R, Year^{-1}**	**Upper 95% Confidence Level K_R, Year^{-1}**
ERDA-6	0.0617	0.0712
GWB	0.0566	0.0754
Humid	0.0234	0.0274

APPENDIX A. TESTS FOR THE EQUALITY OF VARIANCES, s^2, AND MEAN VALUES, K_R, OF THE RATE CONSTANTS FOR ERDA-6 AND GWB BRINES

Procedures were applied for testing the equality of population variances (σ^2) (in this case, estimated by sample variances s^2) and population mean values (μ) (in this case, estimated by sample means K_R) for two independent samples from normal populations. A test to detect non-normal populations (such as the Lilliefors test) could not be applied, because just one value of K_R (not a set of values) was derived from each set of results. Therefore, normal distributions were assumed for the purpose of the calculations.

For ERDA-6 brine, a test based on the F-distribution showed that the sets HY and HY2 for ERDA-6 brine are likely to be samples from populations with the same σ^2. (See, for example, Iman and Conover 1983, pp. 274-275.) Calculations for the test were done as follows:

Let $s_X = s_{HY} = 0.0023$, from Table 1.

$(s_X)^2 = 5.290 \times 10^{-6}$

Let $s_Y = s_{HY2} = 0.0033$, from Table 1.

$(s_Y)^2 = 1.089 \times 10^{-5}$

n = number of observations, taken to be equal to the number of input results used for the regression calculation (See SUMMARY OUTPUT tables in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls."

Let $n_X = n_{HY} = 12$

Let $n_Y = n_{HY2} = 14$

Use the approximation that the population variances σ_X^2 and σ_Y^2 are estimated by the sample variances s_X^2 and s_Y^2.

The null hypothesis H_0 is $\sigma_X^2 = \sigma_Y^2$. That is to say, if H_0 is rejected, then results HY and HY2 are samples from populations with different variances, that is, $\sigma_X^2 \neq \sigma_Y^2$.

Choose the level of significance, $\alpha = 0.05$. That is, the maximum probability of erroneously rejecting the null hypothesis when it is true is 0.05.

The test statistic, F = the larger of the two sample variances divided by the smaller of the two sample variances.

Since $(s_Y)^2 > (s_X)^2$, then

$F = 1.089 \times 10^{-5} / 5.29 \times 10^{-6}$

$F = 2.059$

k = degrees of freedom = $n - 1$, and

since $(s_Y)^2 > (s_X)^2$, then

let $k_1 = n_Y - 1 = 13$, and

let $k_2 = n_X - 1 = 11$.

Reject H_0 at level of significance α if $F \geq F_{\alpha/2,k_1,k_2}$.

$F_{\alpha/2,k_1,k_2}$ = is the value of F in a tabulated distribution for values $\alpha/2$, k_1, and k_2.

Then, $F_{\alpha/2,k_1,k_2} = F_{0.025,13,11}$.

Values of F in Iman and Conover 1983, Table A5, pp. 445-450 are tabulated for $F_{1-(\alpha/2),k_1,k_2}$, and tabulated k_1 values are 12 and 15. Use $k_1 = 15$, the next larger value.

Therefore, choose $F_{0.975,15,11} = 3.330$ from Iman and Conover 1983, Table A5.

Reject the null hypothesis H_0 at $\alpha = 0.05$ if $F \geq F_{0.975,15,11}$.

Recall that $F = 2.059$

Since $F < F_{0.975,15,11}$ (2.059 < 3.330), the null hypothesis is not rejected at $\alpha = 0.05$.

That is, $\sigma_X^2 = \sigma_Y^2$ at $\alpha = 0.05$,

With that conclusion about variances, the two-sample t-test for populations with equal variances can be used next, given that the populations are assumed to be normal.

Next, a test based on the Student's t-distribution and equality of variances showed that HY and HY2 results sets for ERDA-6 brine are likely to be samples from populations having the same K_R. (See, for example, Iman and Conover 1983, pp. 272-274.) Calculations for the test were done as follows:

Values of s_X, $(s_X)^2$, s_Y, s_Y^2, n_X, and n_Y for ERDA-6 are the same as used above for the test for equality of variances .

Let $\bar{X}$ = the sample mean value of K_R derived from HY results = 0.0667 year^{-1} from Table 1.

Let $\bar{Y}$ = the sample mean value of K_R derived from HY2 results = 0.0664 year^{-1} from Table 1.

Use the assumption that the population variances σ_X^2 and σ_Y^2 are equal, as demonstrated above.

Let μ = the population mean.

μ_X = population mean value of K_R sampled by HY results.

μ_Y = population mean value of K_R sampled by HY2 results.

The null hypothesis H_0 is $\mu_X = \mu_Y$. That is to say, if H_0 is rejected, then results HY and HY2 are samples from populations with different means. That is, $\mu_X \neq \mu_Y$.

Choose the level of significance, $\alpha = 0.05$. That is, the maximum probability of rejecting the null hypothesis when it is true is 0.05.

The test statistic is T.

$$T = \frac{\bar{X} - \bar{Y}}{s_p \sqrt{1/n_X + 1/n_Y}}$$

where

$$s_p = \left[\frac{(n_X - 1)s_X^2 + (n_Y - 1)s_Y^2}{n_X + n_Y - 2} \right]^{1/2}$$

Calculate the pooled standard deviation, s_p as follows:

$$s_p = \left[\frac{(12-1)(5.29\times10^{-6})+(14-1)(1.089\times10^{-5})}{12+14-2}\right]^{1/2}$$

$$s_p = 2.885\times10^{-3}$$

Calculate the test statistic T as follows:

$$T = \frac{\bar{X}-\bar{Y}}{s_p\sqrt{1/n_X + 1/n_Y}}$$

$$T = \frac{0.0667-0.0664}{2.885\times10^{-3}\sqrt{1/12+1/14}}$$

$$T = 0.2643$$

Reject the null hypothesis H_0 at $\alpha = 0.05$ if $T > t_{(\alpha/2)(n_X+n_Y-2)}$.

The value of $t_{(\alpha/2)(n_X+n_Y-2)}$ is the (1 - α/2) = 0.975 quartile of the t-distribution with $(n_X + n_Y - 2) = 24$ degrees of freedom.

$t_{(1-\alpha/2),(n_X+n_Y-2)} = t_{(0..975),(24)} = 2.0639$ from Iman and Conover 1983, Table A3

Since $T < t_{(\alpha/2)(n_X+n_Y-2)}$ (0.2643< 2.0639), the null hypothesis is not rejected at $\alpha = 0.05$.

That is, $\mu_X = \mu_Y$ at $\alpha = 0.05$, a conclusion that supports combining HY and HY2 results for ERDA-6 brine.

Similar tests were done for GWB brine. The test based on the F-distribution applied as described above showed that the HY and HY2 samples are not likely to be samples from populations with the same σ^2.

Let $s_X = s_{HY} = 0.0043$, from Table 1.

$(s_X)^2 = 1.849 \times 10^{-5}$

Let $s_Y = s_{HY2} = 0.0348$, from Table 1.

$(s_Y)^2 = 1.211 \times 10^{-3}$

n = number of observations taken to be equal to the number of input results used for the regression calculation (See SUMMARY OUTPUT tables in Excel filename "hydration kinetics Q & HY2 & HH djc 5-1-07.xls."

Let $n_X = n_{HY} = 12$

Let $n_Y = n_{HY2} = 7$

Use the approximation that the population variances σ_X^2 and σ_Y^2 are estimated by the sample variances s_X^2 and s_Y^2.

The null hypothesis H_0 is $\sigma_X^2 = \sigma_Y^2$. That is to say, if H_0 is rejected, then results HY and HY2 are samples from populations with different variances. That is, $\sigma_X^2 \neq \sigma_Y^2$.

Choose the level of significance, $\alpha = 0.05$. That is, the maximum probability of erroneously rejecting the null hypothesis when it is true is 0.05.

The test statistic, F = the larger of the two sample variances divided by the smaller of the two sample variances.

Since $(s_Y)^2 > (s_X)^2$,
$F = 1.211 \times 10^{-3} / 1.849 \times 10^{-5}$
$F = 6.549 \times 10^1$
k = degrees of freedom = $n - 1$, and
since $(s_Y)^2 > (s_X)^2$, then
set $k_1 = n_Y - 1 = 6$, and
Set $k_2 = n_X - 1 = 11$
Reject H_0 at level of significance α if $F \geq F_{\alpha/2,k_1,k_2}$.
$F_{\alpha/2,k_1,k_2}$ = is the value of F in a tabulated distribution for values $\alpha/2$, k_1, and k_2.
Then, $F_{\alpha/2,k_1,k_2} = F_{0.025,6,11}$.
Values of F in Iman and Conover 1983, Table A5, pp. 445-450 are tabulated for $F_{1-(\alpha/2),k_1,k_2}$,
Therefore, choose $F_{0.975,6,11} = 3.881$ from Iman and Conover 1983, Table A5.
Reject the null hypothesis H_0 at $\alpha = 0.05$ if $F \geq F_{0.975,6,11}$.
Recall that $F = 6.549 \times 10^1$.
Since $F > F_{0.975,15,11}$ ($6.549 \times 10^1 > 3.881$), the null hypothesis is rejected at $\alpha = 0.05$.
That is, $\sigma_X^2 \neq \sigma_Y^2$ at $\alpha = 0.05$,

With that conclusion about variances, the two-sample t-test for populations with unequal variances can be used next, given that the populations are assumed to be normal.

Next, a test based on the Student's t-distribution and the above conclusion (unequal variances) showed that HY and HY2 results sets for GWB brine are likely to be samples from populations that do not have the same mean value. See, for example, Iman and Conover 1983, pp. 276-278. Calculations for the test were done as follows:

Values of s_X, $(s_X)^2$, s_Y, s_Y^2, n_X, and n_Y for GWB are the same as used above for the test for equality of variances based on the F distribution

Let $\bar{X}$ = the sample mean value of K_R derived from HY results = 0.0660 year^{-1} from Table 1.

Let $\bar{Y}$ = the sample mean value of K_R derived from HY2 results = 0.2314 year^{-1} from Table 1.

Use the assumption that the population variances σ_X^2 and σ_Y^2 are unequal, as demonstrated above.

Let μ = the population mean.
μ_X = the population mean value of K_R sampled by HY results.
μ_Y = the population mean value of K_R sampled by HY2 results.

The null hypothesis H_0 is $\mu_X = \mu_Y$. That is to say, if H_0 is rejected, then results HY and HY2 are samples from populations with different means. That is, $\mu_X \neq \mu_Y$.

Choose the level of significance, $\alpha = 0.05$. That is, the maximum probability of rejecting the null hypothesis when it is true is 0.05.

The test statistic is T, calculated as follows:

$$T = \frac{\bar{X} - \bar{Y}}{\sqrt{s_X^2/n_X + s_Y^2/n_Y}}$$

$$T = \frac{0.0660 - 0.2314}{\sqrt{\left(1.849\times10^{-5}\right)/12 + \left(1.211\times10^{-3}\right)/7}}$$

$T = -1.2519 \times 10^1$

Calculate approximate degrees of freedom, f as follows:

$$f = \frac{\left(s_X^2/n_X + s_Y^2/n_Y\right)^2}{\frac{\left(s_X^2/n_X\right)^2}{n_X - 1} + \frac{\left(s_Y^2/n_Y\right)^2}{n_Y - 1}}$$

$$f = \frac{\left(1.849\times10^{-5}\right)/12 + \left(1.211\times10^{-3}\right)/7)^2}{\frac{\left(\left(1.849\times10^{-5}\right)/12\right)^2}{12-1} + \frac{\left(\left(1.211\times10^{-3}\right)/7\right)^2}{7-1}}$$

$$f = \frac{3.0465\times10^{-8}}{\frac{2.3742\times10^{-12}}{11} + \frac{2.9929\times10^{-8}}{6}} = \frac{3.0465\times10^{-8}}{2.1584\times10^{-13} + 4.9882\times10^{-9}}$$

$f = 6.107$

Reject the null hypothesis H_0 at $\alpha = 0.05$ if $T < -t_{\alpha/2,f}$

The value of $-t_{\alpha/2,f}$ is the (1 - α/2) = 0.975 quartile of the t-distribution with f = 6.107 degrees of freedom.

6.107 degrees of freedom is not in Iman and Conover 1983, Table A3, so approximate f with degrees of freedom = 6.

$-t_{(1-(\alpha/2)),6} = -2.4469$ from Iman and Conover 1983, Table A3

Since $T < -t_{(0.005)(6)}$ ($-1.2519 \times 10^1 < -2.4469$),

Therefore, reject H_0 ($\mu_X = \mu_Y$) at $\alpha = 0.05$,

That is, $\mu_X \neq \mu_Y$ at $\alpha = 0.05$, a conclusion that supports the decision not to combine HY and HY2 results for GWB brine.

Clayton, Daniel James

From: Nowak [ejnowak@hawaiiantel.net]
Sent: Sunday, September 02, 2007 3:57 PM
To: Clayton, Daniel James
Subject: signature authorization

To Whom It May Concern,
I hereby authorize Daniel J. Clayton to sign "Analysis of MgO Hydration Laboratory Results and Calculation of Extent of Hydration and Resulting Water Uptake versus Time under Postulated WIPP Conditions" for me.
Edwin J. Nowak