



Measurement of Acid Reaction Rates with the Rotating Disk Apparatus

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This paper is to be presented at the Petroleum Society's 8th Canadian International Petroleum Conference (58th Annual Technical Meeting), Calgary, Alberta, Canada, June 12 – 14, 2007. Discussion of this paper is invited and may be presented at the meeting if filed in writing with the technical program chairman prior to the conclusion of the meeting. This paper and any discussion filed will be considered for publication in Petroleum Society journals. Publication rights are reserved. This is a pre-print and subject to correction.

Abstract

The authors have published several papers on the rotating disk apparatus (RDA) in recent years. The RDA is used to measure acid reaction rates, reaction order and activation energy of acidizing fluids with carbonate reservoir rock. This paper summarizes the different ways that acid reaction rates are measured, the factors that affect the results and why this is important when modelling acid stimulation treatments in the field.

In particular, experimental procedures used to obtain acid reaction rates vary widely and can produce very different results. These procedures are often not well-documented in the literature. The validity of different experimental procedures are carefully compared in this paper.

In addition to experimental concerns, the reactivity of reservoir rock can also vary widely. It was recently reported that the reactivity of reservoir rock toward acid is strongly affected by mineralogy and by mineral impurities. In particular, clay impurities in calcite rock were found to reduce the dissolution rate by nearly an order of magnitude. Some calcite rocks containing small amounts of clay particles showed acid reactivity similar to that of 100 wt% dolomite.

Acidizing additives such as polymers and corrosion inhibitors have been shown to significantly affect the way that acid reacts with the reservoir rock.

Introduction

The rotating disk instrument is widely used in the petroleum industry for kinetic studies of the reaction of acidic fluids and chelating agents with reactive rock⁽¹⁻¹¹⁾. This system allows the determination of rock dissolution rate, reaction rate constants, reaction order, and diffusion coefficients^(1,12).

Taylor et al.⁽¹³⁾ examined the effects of acidizing additives on acid reaction rates of calcite and dolomite rock. These additives were quaternary amines, polymer, surfactant, mutual solvent, iron chelating agents and dissolved iron (III).

Taylor et al.^(14,15) examined in detail the relationship between acid reaction rates and rock mineralogy for a deep, dolomitic gas reservoir. Their results showed that mineralogy significantly affected acid reaction rate, and that clay contents as low as 1 wt% could reduce the apparent reaction rate of limestone reservoir rock by up to a factor of 25.

There has been significant variability in acid reaction rate data of reservoir rocks⁽¹¹⁾. These variations have often been

attributed to activation energies lower than obtained for pure calcite or dolomite rock⁽¹¹⁾. However, several detailed studies have contradicted this claim^(8,16).

Alkattan et al.⁽⁸⁾ showed that the dissolution rates of calcite crystals, limestones, and compressed calcite powders were the same within experimental error in the bulk solution pH range of -1 to 3 and at temperatures of 25, 50, and 80°C. The limestones contained less than 1 vol% clays, but one type of limestone (St. Maximin) did contain 16 vol% quartz. This shows that the dissolution rates of pure forms of calcium carbonate are not significantly affected by different mineralogy.

Herman and White⁽¹⁶⁾ showed that dissolution rates of pure forms of dolomite are not significantly affected by mineralogy. The dissolution rates of dolomites in the form of a single crystal, microcrystalline sedimentary rock, and coarse-grained marble in aqueous carbonate solutions were also found to be similar⁽¹⁶⁾. The single crystal of dolomite was of hydrothermal origin. The sedimentary dolomite was from the upper Bellefonte formation, Pennsylvania, U.S. It was composed of 80 wt% microcrystalline dolomite (grain size approximately 10 μm), 20 wt% interstitial quartz, and traces of feldspar. The coarse-grained dolomite marble (grain size approximately 100 μm) was from the Fauske formation in Norway and was composed entirely of dolomite.

The purpose of this paper is to examine the different ways that acid reaction rates are measured with the RDA and the factors that affect the results. It is proposed that measurement procedures, rock porosity and clay impurities can have a significant effect on RDA measurements.

Experimental Studies

The rotating disk apparatus used in this work was the RDA-100 manufactured by CoreLab Instruments Ltd. All experiments were made under a nitrogen pressure of 6.9 MPa so that carbon dioxide would remain in solution. Separation of carbon dioxide out of solution will adversely affect the way the acid reacts with carbonate rocks, especially when organic acids are used.

The HCl solutions were prepared from concentrated hydrochloric acid (ACS reagent grade) and distilled water. An auto-titrator (METTLER DL70ES) was used to accurately measure the HCl concentration of the prepared samples. The titrant, 0.1 M sodium hydroxide, was standardized using potassium hydrogen phthalate (KHC₈H₄O₄).

Calcium and magnesium determinations were made using inductively coupled argon plasma emission spectroscopy. Sulfate concentrations were determined using turbidity measurements after mixing with 0.1 N barium chloride solutions.

The Reynolds number, Re, for flow at the surface of the rotating disk was calculated for rotational speeds up to 1,000 rpm⁽⁴⁾. Re was well below the transition value of 3×10⁵ indicating that the measurements were made in the laminar flow regime^(3,17).

Rock from reservoir K was obtained from Well A as core plugs that were 1.5 in. in diameter and approximately 5 in. in length. Core properties are shown in Table 1. Core plugs in Table 1 were cut into disks that were approximately 1.5 in. in diameter and 0.5 in. thick. Each surface of the disk was highly polished. Disk preparation was identical for all experiments and the procedure of Fredd⁽⁵⁾ and Taylor et al.⁽¹³⁾ was followed, since disk surface preparation has an effect on results.

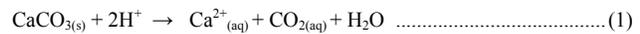
During reaction of the acid with the reservoir rock, samples (10 mL) of the reacted acid were taken every 2 minutes for 20 minutes. Acid concentration was calculated from the calcium

and magnesium concentrations of the collected samples and corrected for the decrease in the total sample volume, using the method of Fredd⁽⁵⁾ unless stated otherwise. From the decrease in acid concentration vs. time and the initial surface area of the rock disk, the dissolution rate was calculated in units of mol/s·cm².

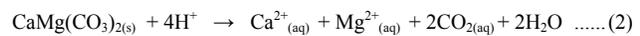
Discussion

RDA Method Overview

The reaction of calcite with HCl in the rotating disk instrument is given in Equation (1).



The reaction of dolomite with HCl proceeds according to Equation (2).



Newman⁽¹⁸⁾ showed that for Newtonian fluids, the rate of mass transfer, J_{mt} , to the rotating disk instrument in a laminar flow regime is given by:

$$J_{mt} = \frac{0.62048 \text{ Sc}^{-2/3} (\nu\omega)^{1/2}}{1 + 0.2980 \text{ Sc}^{-1/3} + 0.1451 \text{ Sc}^{-2/3}} * (C_b - C_s) \dots\dots(3).$$

- J_{mt} = Rate of mass transfer of HCl to a rotating disk, moles/s·cm²
- ν = Kinematic viscosity, cm²/s
- ω = Disk rotational speed, rad/s
- C_b = Bulk concentration of acid, moles/cm³
- C_s = Surface concentration of acid, moles/cm³
- Sc = Schmidt Number = ν/D
- D = Diffusivity of HCl, cm²/s

Lund et al.⁽³⁾ described the rate of the surface reaction dependence on concentration by the power-law expression shown in Equation (4):

$$-r_{\text{HCl}} = kC_s^n = J_{mt} \dots\dots(4)$$

- $-r_{\text{HCl}}$ = Rate of dissolution of dolomite (or calcite) in HCl, moles of HCl/s·cm²
- k = Specific reaction rate (moles HCl/cm²·s)(mole/cm³)⁻ⁿ
- n = Reaction order at the solid surface, dimensionless

It is important to note that the surface reaction rate in Equation (4) is expressed in terms of the reactant HCl.

The mass transfer limited regime and the surface reaction limited regime are important features of the rotating disk instrument and have been described in detail⁽¹⁵⁾. Fluid-solid reactions can be described by the sequence of diffusion of H⁺ to the surface, surface reaction and diffusion of reaction products to the bulk phase. The slowest step is considered the rate-determining step. If the slowest step is the diffusion of the reactants or the products to and from the rock surface, then the reaction is mass transfer limited. If the slowest step is the surface reaction itself, then the reaction is surface reaction limited. In the rotating disk instrument, both of these regimes can occur. At low rotational speeds, the acid dissolution rate increases as disk rotational speed increases. This is the mass transfer limited regime. Acid dissolution rate increases because

the thickness of the diffusion boundary layer of the rotating disk decreases at high rotating speeds⁽¹²⁾. At high rotating speeds, the acid dissolution rate is constant. This occurs because the reaction rate in this regime is limited by the surface reaction rate.

The single most important experimental measurement with the rotating disk instrument is the determination of the rate of dissolution of the rock, $-r_{\text{HCl}}$, expressed in terms of the reactant, HCl. All subsequent calculations build from this measurement.

Figure 1 shows a plot of acid concentration versus time for a disk of reservoir dolomite. Acid concentration is determined by periodically withdrawing a small acid sample from the rotating disk instrument and measuring the calcium and magnesium concentration. Calcium and magnesium represents dolomite that has reacted with the initial acid present in the vessel. The surface area of the disk is known, and so $-r_{\text{HCl}}$ can be calculated from the slope and is equal to 1.10×10^{-6} moles of HCl/s·cm². Figure 1 shows an excellent correlation coefficient, and there is high confidence in the value obtained.

Using Equation (3) and the value of $-r_{\text{HCl}} = J_{\text{mt}}$ from Figure 1, the surface concentration of acid, C_s , can be determined as 0.000908 moles/cm³ (0.908 moles/L). All other values in the equation are known⁽¹⁴⁾.

This value of C_s is for a single acid concentration, a single disk rotational speed and a single temperature. A minimum of three different C_s values are required at a single temperature to calculate the reaction rate and reaction order using Equation (4). A typical plot is shown in Figure 2.

Reaction rate values from a minimum of 3 different temperatures are then required to calculate the activation energy, E_a , which can be obtained by plotting the specific reaction rate from Equation (4) as a function of the reciprocal of the absolute temperature in Kelvin⁽³⁾. This is done using the Arrhenius' equation and an example is shown in Figure 3.

This means that a minimum of 27 measurements (3x3x3) are required to obtain a value of E_a . In practice this is very difficult to achieve, and short-cuts are often taken.

The most common short-cut is making multiple measurements on a single rock sample in the RDA. For instance, acid samples may be taken at one rotational speed, then the speed is increased and another set of samples is taken. Multiple measurements can introduce a high degree of error into the results as will be shown in the next section.

Another method that has been used is normalizing the reaction order to compare results^(10,11). For instance different results will be normalized to a reaction order of 0.4. This procedure appears to ignore the quality of the data. Reaction rate reduction caused by clays will be discussed in this paper that can explain the results reported by Gdanski and van Domelen^(10,11).

Single versus Sequential Measurements

Figure 4 clearly shows a non-linear dissolution behaviour of a reservoir rock in contact with 1M HCl at 85°C. The data in the first 500 seconds is linear and can be used to calculate the dissolution rate. As the reaction progresses, the apparent dissolution rate increases. This is because the surface area of the rock surface increases as shown in Figure 5. In this case, sequential measurements would give erroneously high values of $-r_{\text{HCl}}$ after nearly 500 seconds from the initial acid-rock contact.

This effect is more likely to occur at high acid concentrations or at high temperatures, and this nonlinear effect was clearly shown by Taylor et al.⁽¹⁴⁾

Effect of Rock Porosity

Rock porosity is seldom discussed when measuring acid reaction rates. However, it has a significant effect on measurements and results. The rock samples used in these experiments were chosen to cover a range of reservoir depths and dolomite contents, but with low porosity as shown in Table 1. High porosity acts to increase the surface area of the reacting rock disk. Because the acid dissolution rate depends on the surface area of the rock disk, the dissolution rate will appear to increase as the porosity of the rock increases. A low-porosity rock minimizes this effect. Correction factors could be used for surface area of the disk. But a secondary problem is that surface porosity will disrupt laminar flow at the disk surface, and this may affect the validity of Equation (3).

Rock Composition – Sulfate Minerals

Gypsum can be dissolved during acidizing and this is clearly shown in Figure 6. A reservoir rock containing 37 wt% anhydrite was rotated at 800 rpm in 1M HCl at 85°C. Sulfate concentration increased with time. Calcium concentration increases due to reaction with acid and dissolution of gypsum. Dissolution of anhydrite must be taken into account when calculating the amount of acid that has reacted with the rock. This calculation will directly affect the determination of the rate of dissolution of the rock in the RDA instrument.

Effect of Rock Mineralogy

It is generally assumed that the reaction of acid with limestone reservoir rock is much more rapid than acid reaction with dolomite reservoir rock. Taylor et al.^(14,15) were the first to show this assumption to be false in some cases, because of mineral impurities commonly found in these rocks. Trace amounts of clay impurities in limestone reservoir rocks were found to reduce the acid dissolution rate by up to a factor of 25, to make the acid reactivity of these rocks similar to that of fully dolomitized rock. A rotating disk instrument was used to measure dissolution rates of reservoir rock from a deep, dolomitic gas reservoir in Saudi Arabia (135°C, 85 MPa).

More than 60 experiments were made at temperatures of 23 and 85°C and HCl concentration of 1.0 M (3.6 wt%). Eight distinctly different rock types that varied in composition from 0 to 100% dolomite were used in the study (Figure 7). In addition, the mineralogy of each rock disk was examined before and after each rotating disk experiment with an environmental scanning electron microscope (ESEM) using secondary and backscattered electron imaging and energy dispersive X-ray (EDS) spectroscopy. Acid reactivity was correlated with the detailed mineralogy of the reservoir rock. It was also shown that bulk anhydrite in the rock samples was converted to anhydrite fines by the acid at 85°C, a potential source of formation damage.

Effect of Additives

The effect of common acidizing additives on RDA reaction rates were examined by Taylor et al.⁽¹³⁾ 1.5 vol% of a cationic acrylamide copolymer decreased the calcite and dolomite dissolution rates significantly. Polymer changed the acid-rock reaction from mass transfer limited to surface reaction limited with both calcite and dolomite. This is a surface effect possibly due to polymer adsorption. The presence of 5,000 mg/L iron (III) resulted in surface deposition of iron (III) hydroxide for both calcite and dolomite. At low rotational speeds, this surface layer had an inhibiting effect on the rock dissolution rate. Citric acid at 12 g/L decreased the dissolution rate of calcite by an

average of 9%, possibly due to the formation of calcium citrate at the surface⁽¹⁹⁾.

Nasr-El-Din and co-workers⁽²⁰⁻²²⁾ examined the reaction kinetics of non-Newtonian fluids (gelled acid and surfactant gelled acid) with calcite. The impact of acid-soluble polymers and viscoelastic surfactants on the etching patterns on the rock surface, dissolution rate of calcite, and diffusion coefficient of H⁺ in these acids was studied. In another investigation, Nasr-El-Din et al.⁽²³⁾ examined the reaction of regular cement with HCl. The impact of surface reaction and precipitation of reaction products was addressed.

Conclusions

- Sequential measurement of dissolution rate can introduce a very large error in calculation of reaction rate and activation energy.
- Reservoir rock mineralogy has a significant effect on acid dissolution rates.
- Clay concentrations as low as 1 wt% can significantly reduced measured dissolution rates in reservoir rocks.
- The effect of acidizing additives on acid reaction rates was summarized.

Acknowledgements

The authors thank Saudi Aramco for permission to publish and present this work.

NOMENCLATURE

C_b	= Bulk concentration of acid, moles/cm ³
C_s	= Surface concentration of acid, moles/cm ³
D	= Diffusivity of HCl, cm ² /s
E_a	= Activation energy, cal/mole
J_{mt}	= Rate of mass transfer of HCl to a rotating disk, moles/s·cm ²
K	= Specific reaction rate, (moles HCl/cm ² ·s) (mole/cm ³) ⁻ⁿ
N	= Reaction order at the solid surface, dimensionless
Re	= Reynolds number, dimensionless
$-r_{HCl}$	= Rate of dissolution of dolomite in HCl, moles of HCl/s·cm ²
Sc	= Schmidt Number = ν/D
ν	= Kinematic viscosity, cm ² /s
Ω	= Disk rotational speed, rad/s

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Adjusted Depth, feet	Zone	Core / Tray	Porosity, vol%	Air Perm., mD	Grain Density, (g/cm ³)	Bulk Density, (g/cm ³)
11,173.3	K-B	C2/T23	1.47	<0.1	2.72	2.68
11,181.5	K-B	C2/T20	4.04	<0.1	2.72	2.61
11,192.7	K-B	C2/T16	0.73	<0.1	2.75	2.73
11,555.7	Base K-B	C3/T9A	0.71	<0.1	2.83	2.81
11,556.0	Base K-B	C3/T9B	1.7	0.2	2.83	2.78
11,562.8	Base K-B	C3/T7	2.8	0.1	2.83	2.75
11,564.0	Base K-B	C3/T6C	2.7	0.3	2.86	2.78
11,565.5	Base K-B	C3/T6B	0.8	0.1	2.88	2.86
11,565.8	Base K-B	C3/T6A	0.72	<0.1	2.78	2.76
11,576.7	Base K-B	C3/T1	0.74	<0.1	2.72	2.7
11,637.6	K-C	C4/T2	1.1	<0.1	2.80	2.77

TABLE 1: Well-H59, Core Sample Properties.

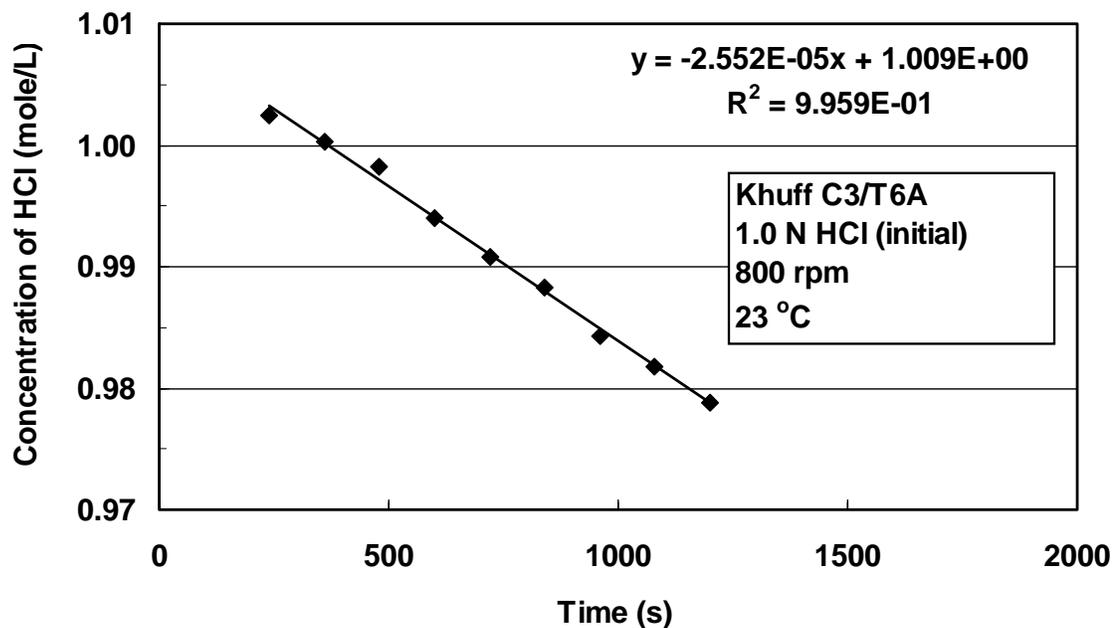


Figure 1: Rate of Dissolution – Ideal Case. (from Taylor et al.⁽¹⁴⁾)

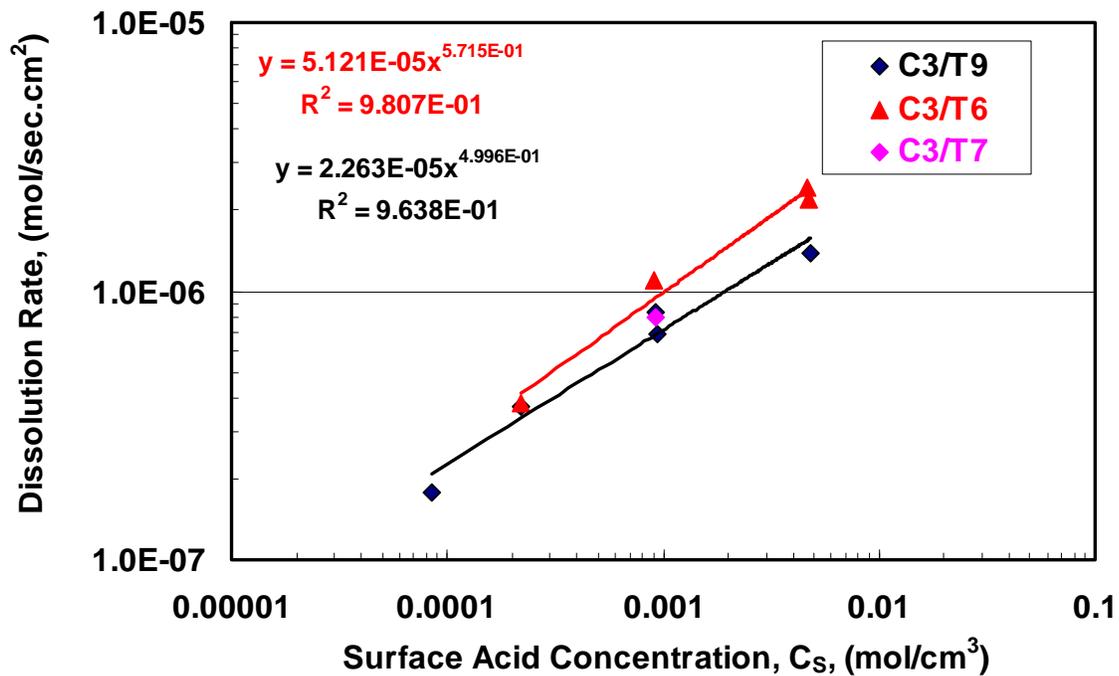


FIGURE 2: Specific Reaction Rate at 23 °C. (from Taylor et al.⁽¹⁴⁾)

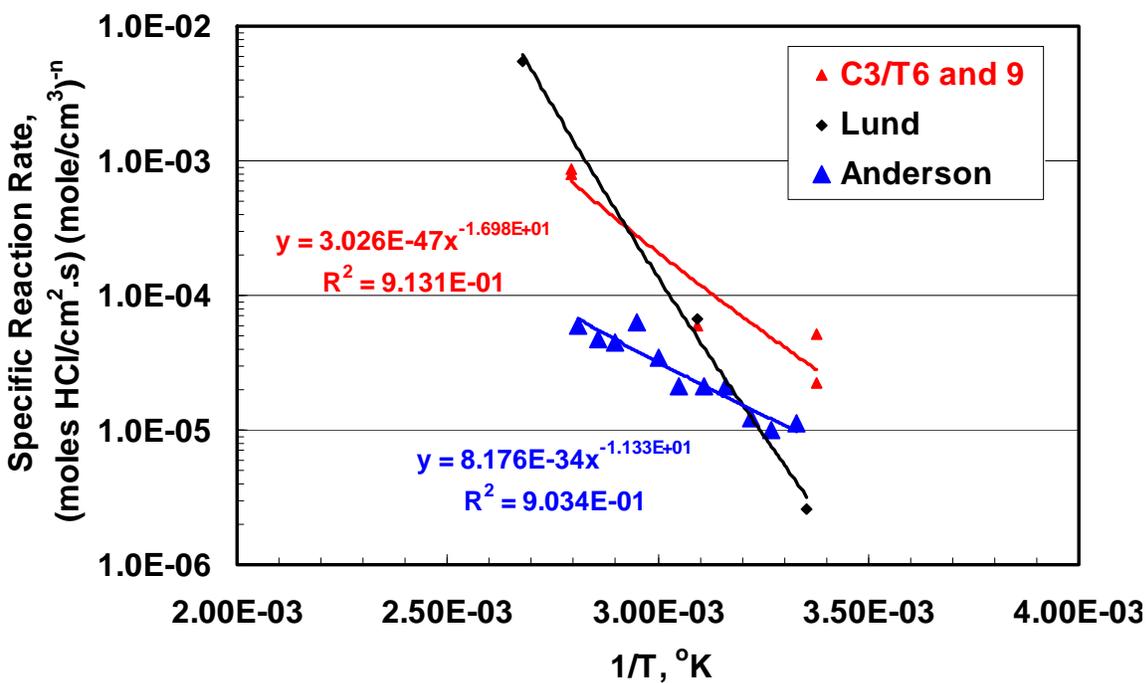


FIGURE 3: Arrhenius Plot. (from Taylor et al.⁽¹⁴⁾)

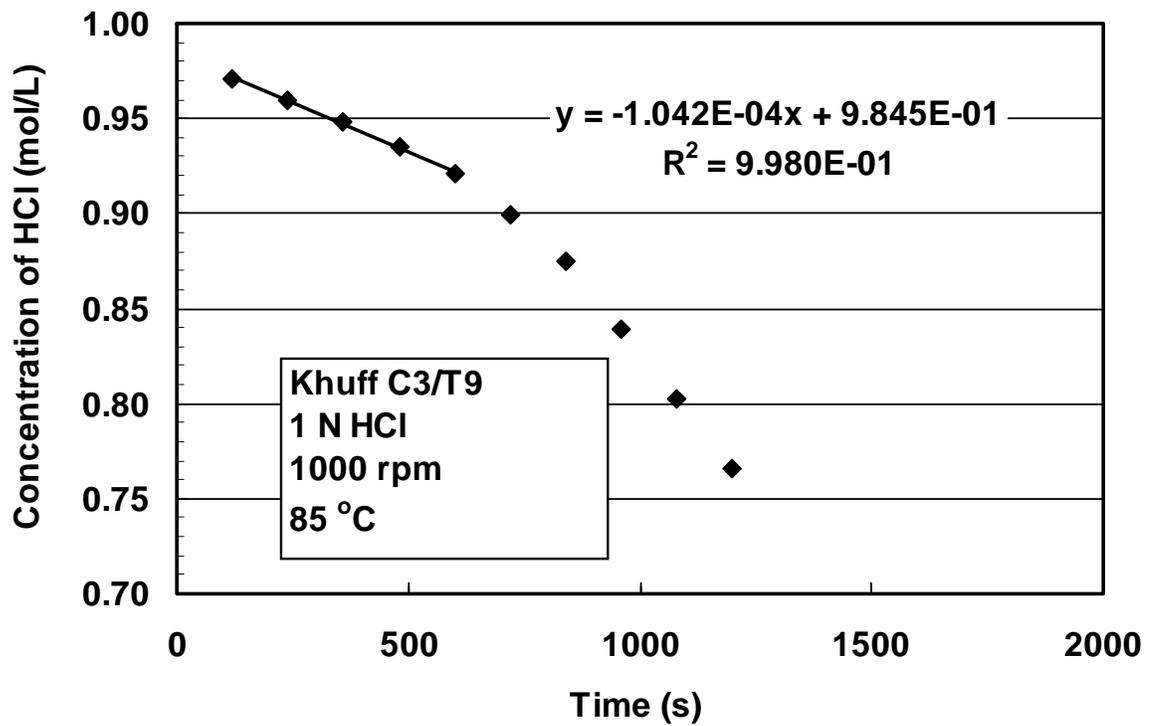


Figure 4: Non-linear Dissolution Behaviour. (from Taylor et al.⁽¹⁴⁾)



Figure 5: C3/T9 After Reaction

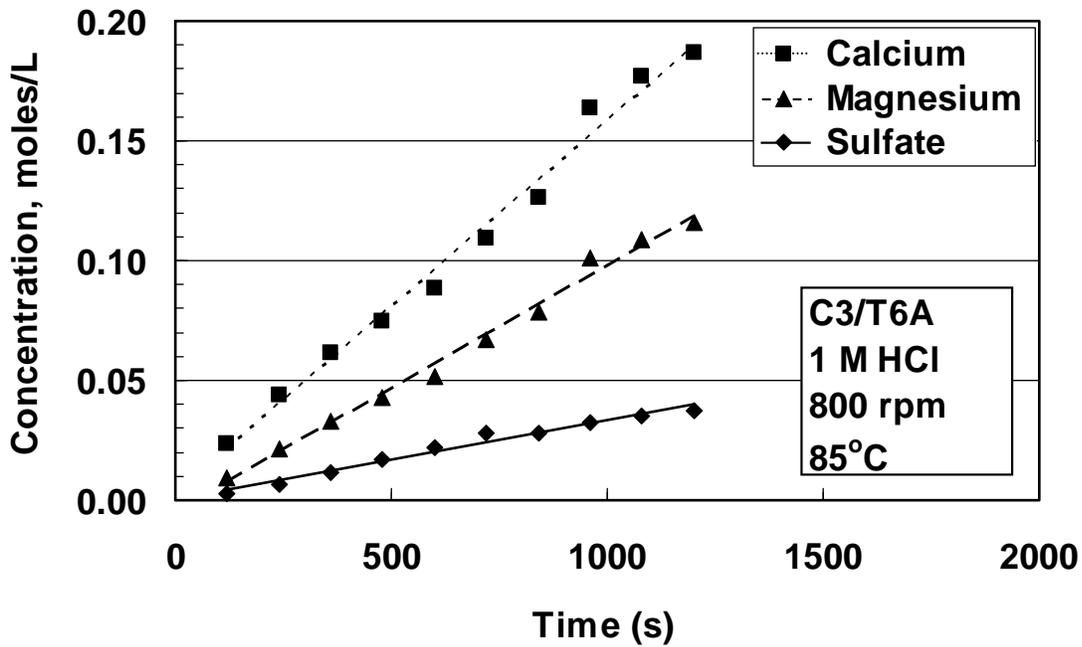


Figure 6: Concentrations of calcium, magnesium and sulfate in samples collected during reaction of C3/T6A with 1 M HCl at 85°C.

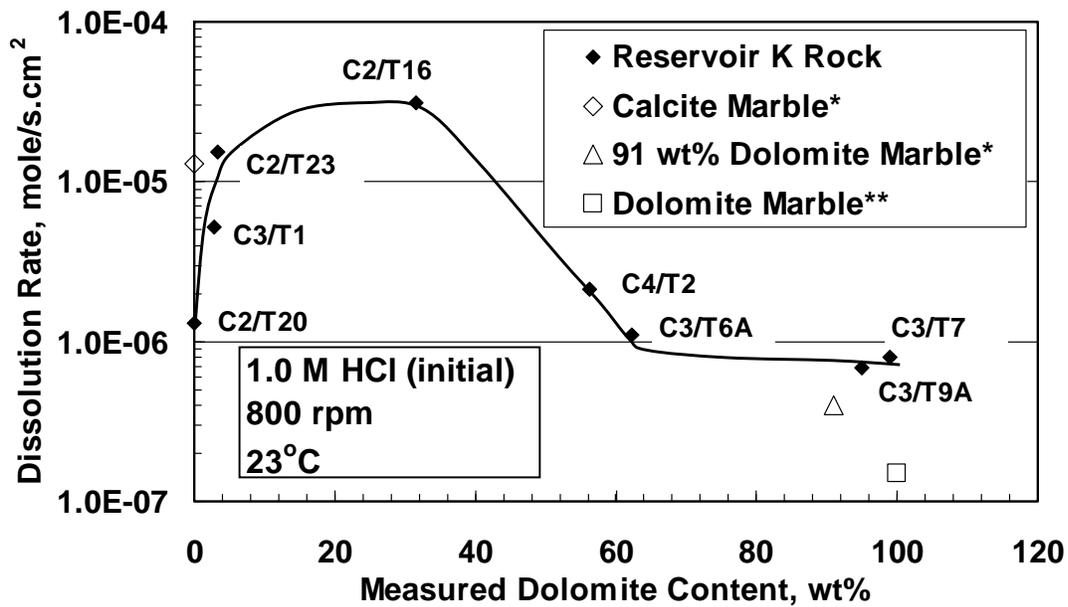


FIGURE 7: Effect of Measured Dolomite Content on Dissolution Rate.

*Taylor et al.⁽¹³⁾ **Lund et al.⁽³⁾