

Felleslab RE-8 / ST-1
Crystal Growth Rate Determinations of
Calcium Carbonate
Group B-16

Yngve Mannsåker Hereide Åge Johansen
yngvemh@stud.ntnu.no agej@stud.ntnu.no

November 13, 2013

Abstract

In this experiment the growth rate constant and the growth order has been calculated for calcium carbonate (aragonite) for two parallels with a solution of 70wt% MEG at 50°C, in a batch reactor, by measuring the change of concentration of calcium ions over time. The growth rate constant was found to be 9.03 and 7.77 nm s^{-1} . The growth rate order was found to be 0.77 and 0.55, for the two parallels respectively.

Contents

1	Introduction	1
2	Theory	1
2.1	Crystal structures of calcium carbonate	1
2.2	Growth rate	2
2.3	Supersaturation	3
2.4	EDTA-titration	4
2.5	Chemical handling and attention (HSE)	4
3	Experimental	4
3.1	Preparation of reactant solutions	5
3.2	Growth experiment	5
4	Results	7
4.1	Calcium concentration	7
4.2	Growth rate	7
4.3	Growth rate constant and growth order	10
4.4	Comparison to master thesis	10
5	Discussion	10
6	Conclusion	12
A	Preparing reactant solutions	14
B	Growth rate	16

1 Introduction

Crystallisation is an important reaction in many chemical processes. Crystallisation can be exploited to produce or extract a product, or it can lead to formation of by-products, which can sometimes be unwanted. In this experiment the crystallisation growth rate and growth order of calcium carbonate (CaCO_3) has been calculated for a given temperature in a solution of 30%_{wt} water and 70%_{wt} mono ethylene glycol (MEG). MEG has been chosen since it is a common antifreeze additive in petroleum pipelines, where crystallisation of calcium carbonate can plug the pipes and make heat exchangers less efficient.

2 Theory

2.1 Crystal structures of calcium carbonate

A crystal is a collection of constituents (e.g. atoms, ions or molecules) arranged in a lattice forming large sections of similar parts. A crystal can be shaped in many different ways. This is called the crystal's structure and different crystal structures give rise to different crystal polymorphs. Calcium carbonate forms three different structures or polymorphs: The least stable vaterite, the more stable aragonite and the most stable one, calcite. Vaterite and aragonite can dissolve and re-crystallize to calcite over time. Figure 1 shows pictures of the three different polymorphs of calcium carbonate taken with a scanning electron microscope (SEM).

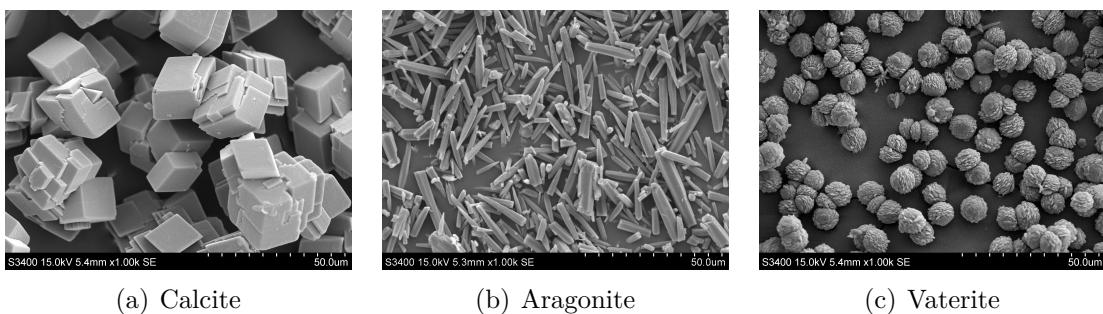


Figure 1: The Figure is gathered from Nergaard's Script: Brief fundamentals of crystallization of calcium carbonate [1] and shows the three different polymorphs of calcium carbonate, from left to right: Calcite, aragonite and vaterite.

2.2 Growth rate

The growth rate (G) is by definition the change of the crystal dimensions over time. By neglecting the nucleation (formation of new particles), agglomeration (combining two or more particles into one) and particle breakage the growth rate can be measured from decrease in calcium concentration. This decrease is linked to the change of particle volume by Equation (2.1),

$$\Delta V = \frac{-\Delta c M_W}{\rho N m_N} \quad (2.1)$$

where ΔV is the change in volume of the crystal(s), Δc is the change in concentration, M the molecular weight, m is the weight of seed crystals, ρ is the aragonite density and N is the number of seed particles. In this experiment the geometrical relation between the cylindrical aragonite particles is approximated by Equation (2.2),

$$r = H/6 \quad (2.2)$$

where r is the radius and H the height of the particle. In order to calculate the growth rate the volume change is linked to the particle height by equation (2.3).

$$\begin{aligned} V &= \pi r^2 H \\ V &= \pi(H/6)^2 H \\ V &= \pi H^3 / 36 \\ \Delta V &= \frac{\pi \Delta H^3}{36} \end{aligned} \quad (2.3)$$

The characteristic dimension h is needed to find the growth rate. As a crystal grows in two directions, h corresponds to half the height ($H/2$) and is given by Equation (2.4)

$$h = H/2 \quad (2.4)$$

Solving (2.3) with respect to h gives Equation (2.5).

$$h = 2 \cdot \sqrt[3]{\frac{36 \Delta V}{\pi}} \quad (2.5)$$

The growth rate is given by Equation (2.6),

$$G = \frac{\Delta h_{i+1}}{\Delta t_{i+1}} \quad (2.6)$$

where G is the growth rate and t is the change in time. The overall growth rate is calculated by Equation (2.7),

$$G = k_g(S - 1)^g \quad (2.7)$$

where k_g is the growth rate constant, S the supersaturation ratio, and g is the growth order.

The mass growth rate can be calculated by Equation (2.8),

$$R_M = \frac{\Delta m_c}{Ac\Delta t} \quad (2.8)$$

where R_M is the mass deposition rate, Δm the change in mass of calcium carbonate, Ac the surface area and Δt the time interval. Note that mass is calculated by Equation (2.9).

$$m_c = c_{\text{Ca}^{2+}} \cdot V_{\text{sol}} M_W \quad (2.9)$$

2.3 Supersaturation

Supersaturation is the driving force of crystallisation. Supersaturation occurs in cases where the ionic activity product (IAP) in a solution is exceeded. The supersaturation of a system is measured by the ratio between the IAP and the solubility product constant (K_{sp}). The K_{sp} is the ion activity product of the ions in a solution when the ions are in thermodynamic equilibrium. The ratio then gives some information of how far beyond the equilibrium condition the supersaturated solution is. For calcium carbonate, the supersaturation ratio is expressed through (2.10):

$$S = \sqrt{\frac{a_{\text{Ca}^{2+}} \cdot a_{\text{CO}_3^{2-}}}{K_{\text{sp}}(\text{CaCO}_3)}} \quad (2.10)$$

In (2.10), the supersaturation ratio has been calculated using the activity, a_i , instead of the concentration, c_i , of the ions. The activity is a measure of how "active" ions behave in a solution, and it is expressed as the product of the concentration and an activity coefficient, γ_{\pm} , as shown in Equation (2.11).

$$a_i = c_i \gamma_{\pm i} \quad (2.11)$$

In other words, the activity coefficient is the ratio between the activity and the concentration:

$$\gamma_{\pm i} = \frac{a_i}{c_i}$$

In the ideal case, the activity is equal to the concentration and the activity coefficient is 1.

As solubility often changes quite drastically as a function of temperature and depending on the solvent, the properties of the supersaturation ratio will also vary as a function of temperature and the solvent composition.

2.4 EDTA-titration

The concentration of calcium carbonate can be calculated from EDTA titration. EDTA consume Ca^{2+} in a 1mol:1mol relationship and by knowing the concentration and volume of the EDTA as well as the volume of the calcium carbonate solution the calcium concentration can be calculated from Equation (2.12),

$$c_{\text{Ca}_2^+} = \frac{c_{\text{EDTA}} V_{\text{EDTA}}}{V_{\text{Ca}_2^+}} \quad (2.12)$$

where C is the concentration and V the volume. The volume of the calcium solution is obtained from Equation (2.13),

$$V_{\text{sol}} = m_{\text{sol}} / \rho_{\text{sol}} \quad (2.13)$$

where ρ is the density of the solution and m is the mass. By combining (2.12) and (2.13), Equation (2.14) is obtained.

$$c_{\text{Ca}_2^+} = \frac{c_{\text{EDTA}} V_{\text{EDTA}}}{m_{\text{sol}} / \rho_{\text{sol}}} \quad (2.14)$$

The mass and the density of the calcium solution is given in Table 3 in [2]. Weight sample of calcium solution: 5 g. Density of titrated solution: 1000 g cm^{-3} .

2.5 Chemical handling and attention (HSE)

Only chemicals in Table 1 will be used in the experiment. Due to low concentrations only glykol needs extra attention. According to the Safety sheet [3], glykol is harmful if swallowed. This is however easy to avoid.

3 Experimental

The experiment was conducted twice with the same parameters: The reaction temperature was 50°C , and the solvent consisted of 70%_{wt} mono ethylene glycol (MEG) and 30%_{textwt} Water.

Table 1: The different chemicals used in the experiment and their concentration.

Chemical	Concentration
$\text{Ca}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	0.1 mol kg^{-1}
NaOH	1 mol kg^{-1}
CO_2	[$-$]
Glykol (MEG)	100%
HCl	1 mol kg^{-1}
$\text{NH}_3 / \text{NH}_4\text{Cl}$	1 mol kg^{-1}
EDTA	0.01 mol kg^{-1}

3.1 Preparation of reactant solutions

From mother solutions of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \times 4 \text{H}_2\text{O}$, 0.1 mol kg^{-1}) and sodium hydroxide (NaOH, 1.0 mol kg^{-1}), 0.375 kg of each reactant solution were prepared by mixing the components by the ratios described in Table 2 so that the reaction mixture ideally would contain Ca^{2+} -ions at a level of 5 mmol kg^{-1} and OH^- -ions at a concentration level of 31 mmol kg^{-1} . The actual mixing ratios are given in Table 3, resulting in the actual concentrations given in Table 4.

*Table 2: Mixing ratios in preparation of the reactant solutions.
 The method for computing the ratios is described in appendix A.*

	Ca^{2+} -solution	OH^- -solution
Mother solution	37.50 g	23.25 g
Water	75.00 g	89.25 g
MEG	262.5 g	262.5 g
Total	375.0 g	375.0 g

The prepared solutions were placed in a water bath (50°C) and bubbled with carbon dioxide (CO_2) for some 20 to 30 minutes until the pH-values had stabilised.

3.2 Growth experiment

The saturated reactant solutions were mixed in a carbon dioxide bubbled reactor with constant stirring, and then the aragonite seed crystals (1.194 g and 1.201 g in the first and the second parallel respectively) were added at $t = t_0$. Then, the calcium concentration was

Table 3: Actual mixing ratios of chemicals in the two parallels.

Solution species	Chemical	Parallel 1	Parallel 2
Ca ²⁺	Mother solution	37.55 g	37.73 g
	Water	75.14 g	75.35 g
	MEG	262.57 g	262.74 g
	Total	375.26 g	375.82 g
OH ⁻	Mother solution	23.31 g	23.26 g
	Water	89.82 g	89.24 g
	MEG	262.51 g	262.56 g
	Total	375.64 g	375.06 g

Table 4: Actual concentrations of components in the reaction mixtures in experiment parallel 1 and 2. Clearly, the chemicals have been measured out quite precisely.

Ion	Concentration in Parallel 1 [mmol kg ⁻¹]	Concentration in Parallel 2 [mmol kg ⁻¹]	Theoretical concentration [mmol kg ⁻¹]
Ca ²⁺	5.001 mmol kg ⁻¹	5.025 mmol kg ⁻¹	5 mmol kg ⁻¹
OH ⁻	31.04 mmol kg ⁻¹	30.98 mmol kg ⁻¹	31 mmol kg ⁻¹

measured as a function of time by taking out small samples (approximately 5 mL each) for analysis using a syringe with a 0.22 mL Millipore filter in order to filter out the calcium carbonate particles so that the crystal growth in the samples would halt. 16 and 18 samples were gathered in the first and second parallel respectively, the sampling being more frequent shortly after the time had started.

The samples were weighed individually and then diluted with distilled water to a volume of ca. 50 mL each before being analysed by titration with EDTA. Before titration, each sample had hydrochloric acid (HCl, 1M, about 1 mL) and an ammonium/ammonia buffer solution (about 1 mL) added in order to stabilise the pH-value of the solution to avoid precipitation of calcium carbonate.

After the experiment had run for a while (62 min for the first parallel and 92 min for the second), the reactor content was filtered and the product washed twice with both water (about 30 mL) and ethanol (about 30 mL) to remove the MEG, which is an organic solvent.

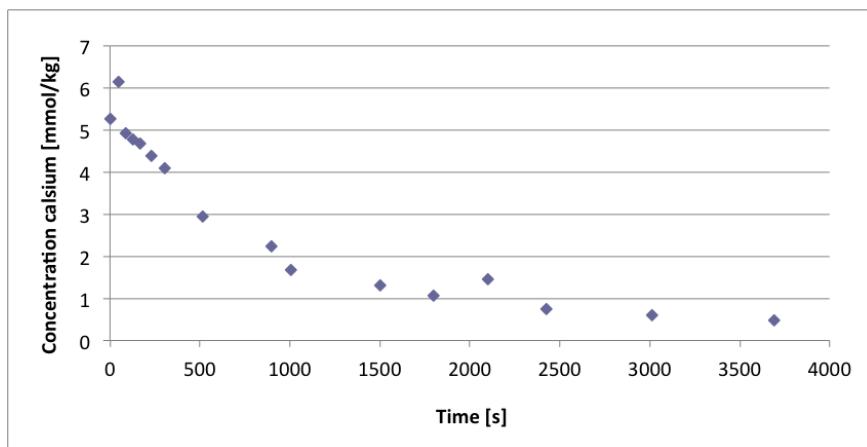


Figure 2: The plot shows the calcium concentration in mmol/kg plotted against time in s for Parallel 1.

The reactor was finally washed with diluted hydrochloric acid and water.

4 Results

4.1 Calcium concentration

The calcium concentration in the solution decreases as more crystals grow. The calcium concentration was found using titration with EDTA and then calculated from Equation (2.14). The results are found in Figures 2 and 3 where the calcium concentration is plotted against time.

4.2 Growth rate

The expression of the supersaturation ratio was found using EXCEL's trendline tool, the plot used to calculate this is given in 5. The expression for the supersaturation ratio was found to be:

$$S = 0,0102c_{\text{Ca}^{2+}}^3 - 0,1174c_{\text{Ca}^{2+}}^2 + 0,9085c_{\text{Ca}^{2+}} + 0,4689$$

The growth rate was found using (2.6). And the results are presented in table 5 and table 6.

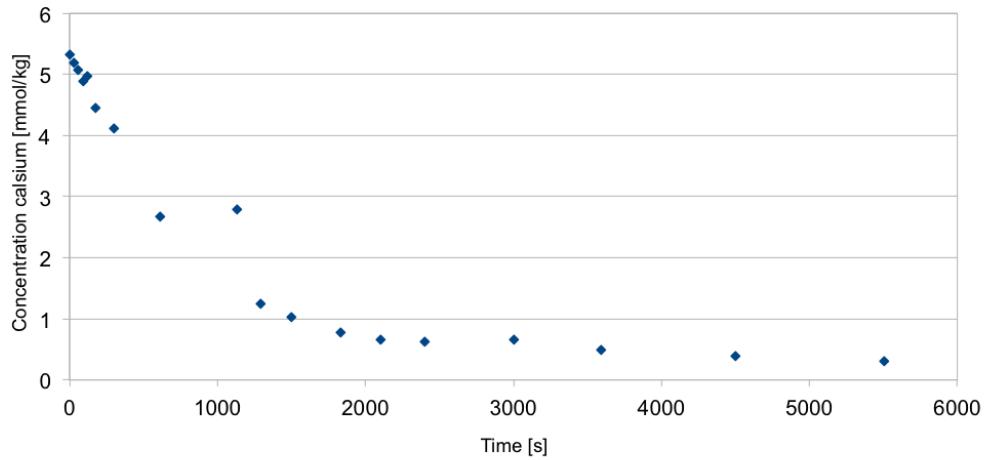


Figure 3: The plot shows the calcium concentration in mmol/kg plotted against time in s for Parallel 2.

Table 5: The table is showing the results from the growth rate expression, for the first parallel.

$c_{\text{Ca}^{2+}}$ [mmol L $^{-1}$]	G [nm s $^{-1}$]
6,152	136,279
4,927	80,210
4,767	10,438
4,673	6,052
4,380	12,510
4,080	10,119
2,945	13,276
2,245	4,363
1,684	11,784
1,319	1,674
1,063	1,920
1,448	8,472
0,745	4,594
0,598	0,526
0,482	0,355

Table 6: The table is showing the results from the growth rate expression for the second parallel.

$c_{\text{Ca}^{2+}}$ [mmol L ⁻¹]	G [nm s ⁻¹]
5,187	13,264
5,076	12,589
4,894	16,793
4,793	10,509
4,458	19,959
4,113	7,908
2,664	12,858
2,308	1,854
1,254	17,064
1,021	2,801
0,779	1,802
0,664	1,074
0,620	0,360
0,496	0,509
0,486	0,038
0,391	0,257
0,299	0,223

4.3 Growth rate constant and growth order

The growth rate constant and growth order was found using Equation (2.7) to the form of Equation (4.1).

$$\ln G = g \cdot \ln(S - 1) + \ln k_g \quad (4.1)$$

The results are found in table 7.

Table 7: The table is showing the linear growth rate and the growth order for both parallels.

Parallel #	Growth rate constant, k_g	Growth rate order g .
1	9,025	0,765
2	7,768	0,549

4.4 Comparison to master thesis

Table 8 shows the results in this experiments compared to the results in the master thesis. The results in the master thesis is gathered from [2]. Only relevant geometries, MEG concentrations and temperatures are included.

Table 8: Growth rate constant , k_g and growth order, g for aragonite growth experiments

Source	MEG [wt%]	T [°C]	g	k_g [nm s ⁻¹]
Master thesis	70	40	1.63 ± 0.03	0.20 ± 0.02
Master thesis	70	70	0.8 ± 0.0002	4.21 ± 0.32
Parallel 1	70	50	0.77	9.03
Parallel 2	70	50	0.55	7.77

5 Discussion

The first results showed some data points where the concentration increased. This should not have happened, and is most likely caused by inaccuracy in either the titration or in the weighing of the sample glasses. Especially the process of weighing was quite inaccurate during the experiment. In order compensate of the increased concentration, a 4th grade polynomial trend line was found for the concentration and

for the specific tests, the actual test results was exchanged with the approximation in order to calculate the change in specific height Δh and growth rate G . The actual results was plotted in Figures 2 and 3.

A large source of error which causes wrong crystal volume (and in the end, wrong growth rate) occurred for the first parallel when a large amount of the seed crystals was blown out of the reactor due to to high pressure inside the reactor. This was corrected in the second parallel. This means that the second parallel should give more accurate results.

The growth rate G shows as expected a decreasing trend over time, but with some increase for some samples. However, small inaccuracies in the change of concentration give a great impact on the growth rate, so again, inaccuracies in the weight measurement and the titration is the most likely cause of this error, but due to a quite large number of data points this should not affect the calculation of the growth rate constant and the growth order.

It was expected that the results from the different parallels should lie between the results from the master thesis in Table 8. However both parallels give a lower growth order and a higher growth rate constant than expected. This is again caused by inaccuracies in the growth rate, however the error may not be as large as the number suggest, due to the logarithmic calculations of the growth order and growth rate constant. As mentioned earlier in this section, the second parallel should give better results. As seen in Table 8, this seems to be the case with growth rate constant, but not with the growth order. A possible explanation for this is that the other sources of error had a greater impact of the final results than the spilled seeds.

From the results in the master thesis given in Appendix 2 in [2], it looks like an increase in temperature yields a large increase in the growth rate constant as well a large decrease in growth order. Increase in MEG concentration made both the growth rate constant and the growth order decrease. The results from the conducted experiment do not correspond with the results found in the master thesis, and are therefore not used in the discussion of changes in parameters.

The desired combination of parameters in separation depend on the wanted results. If the purpose of the reaction is to extract crystals from the liquid, for instance by using filtration, a low growth order that gives larger particles (mononuclear growth) is desirable, as well as high growth rate. A combination that gives this is higher tem-

perature and lower concentration of MEG. If the purpose is to avoid growth inside pipelines or heat exchangers, the desired growth order is high which gives polynuclear growth (smaller crystals that don't stick to each other) and the growth rate constant should be low so that fewer crystals form. A combination for this is lower temperature and higher concentration of MEG.

6 Conclusion

In this experiment the growth rate constant and the growth order has calculated for calcium carbonate (aragonite) and has been found for two parallels with a solution of 70wt% MEG at 50 °C. The growth rate constant was found to be 9.03 and 7.77 nm s^{-1} . This was higher than the values found in the master thesis. The growth rate order was found to be 0.77 and 0.55, for parallel 1 and 2 respectively. This was lower than the values found in the master thesis. This means that the growth mechanism is possibly controlled by the mass transport to the growing surface (diffusion). However this can not be concluded finally as no theory is given for the case with $g < 1$.

Trondheim, November 13, 2013

Signatures: _____

References

- [1] Nergaard, Margrethe *Script: Brief fundamentals of crystallization of calcium carbonate*
- [2] Nergaard, Margrethe *Script: Crystal growth rate determinations of calcium carbonate: The polymorph aragonite in water/mono ethylene glycol mixtures*
- [3] Safety sheet; etylenglykol, Sigma-Aldrich
http://app.ecoonline.com/documents/msds/1000472/285_6354716.pdf, visited:19th October 2013

A Preparing reactant solutions

The reactant solutions are prepared by mixing mother solution, water and MEG (Mono Ethylene Glycol) in the ratios described in Table 2. The numbers in Table 2 have been calculated through the following procedure:

The reactant solutions must be mixed so that one contains calcium ions at a concentration level of 5 mmol kg^{-1} and the other contains hydroxide ions at a concentration level of 31 mmol kg^{-1} . Knowing that each solution must have a total weight of 0.375 kg and contain 70 wt% MEG, it is possible to calculate how much of each component is needed using the mother solutions in Table 9.

Table 9: Mother solutions for preparation of reactant solutions.

Reactant	Chemical	Concentration in reaction mixture (0.750 kg)
Ca^{2+}	CaCO_3	$0.1 \left[\frac{\text{mol}}{\text{kg}} \right]$
OH^-	NaOH	$1.0 \left[\frac{\text{mol}}{\text{kg}} \right]$

The mass needed of each mother solution can be calculated through the number of molecules needed in the total volume of the reaction mixture of 0.750 kg :

$$m_{i\text{-solution}} = \frac{n_{i\text{-solution}}}{c_{i\text{-solution}}} \quad (\text{A.1})$$

$$n_i = c_{i\text{-reactant solution}} \cdot V_{i\text{-reactant solution } i} \quad (\text{A.2})$$

$$n_{\text{Ca}^{2+}} = 5 \cdot 10^{-3} \frac{\text{mol}}{\text{kg}} \cdot 0.750 \text{ kg} = 3.750 \cdot 10^{-3} \text{ mol}$$

$$n_{\text{OH}^-} = 31 \cdot 10^{-3} \frac{\text{mol}}{\text{kg}} \cdot 0.750 \text{ kg} = 2.325 \cdot 10^{-2} \text{ mol}$$

$$m_{\text{Ca}^{2+}\text{-solution}} = \frac{3.750 \cdot 10^{-3} \text{ mol}}{0.1 \frac{\text{mol}}{\text{kg}}} = \underline{\underline{37.50 \text{ g}}}$$

$$m_{\text{OH}^-\text{-solution}} = \frac{2.325 \cdot 10^{-2} \text{ mol}}{1.0 \frac{\text{mol}}{\text{kg}}} = \underline{\underline{23.25 \text{ g}}}$$

The amount of MEG is supposed to be 70wt% for both the reaction solutions, so the amount of MEG will be the same in each solution:

$$m_{\text{MEG}} = 0.70 \cdot 0.375 \text{ kg} = 262.5 \text{ g} \quad (\text{A.3})$$

The mother solutions are aqueous, and so the contribution from these have to be taken into consideration when calculating the amount of water in the reactant solutions.

$$m_{\text{water}} = m_{\text{reactant solution}} - m_{\text{mother solution}} - m_{\text{MEG}} \quad (\text{A.4})$$

$$\text{Ca}^{2+} : m_{\text{water}} = 0.375 \text{ kg} - 0.03750 \text{ kg} - 0.2625 \text{ kg} = 75.00 \text{ g}$$

$$\text{OH}^- : m_{\text{water}} = 0.370 \text{ kg} - 0.02325 \text{ kg} - 0.2625 \text{ kg} = 89.25 \text{ g}$$

B Growth rate

Table 10: The table is showing the dummy data given to find an expression for the supersaturation as well as the alkalinity based on calcium concentrations. The table is valid for a 70% MEG, at 40°C.

#	Ca	A	SR	S
1	5	31	20,081	3,34
2	4,5	30	17,455	3,12
3	4	29	14,968	2,89
4	3,5	28	12,62	2,65
5	3	27	10,41	2,41
6	2,5	26	8,33	2,15
7	2	25	6,403	1,89
8	1,5	24	4,603	1,6
9	1	23	2,938	1,28
10	0,5	22	1,603	0,94
11	0,25	21,5	0,76	0,65

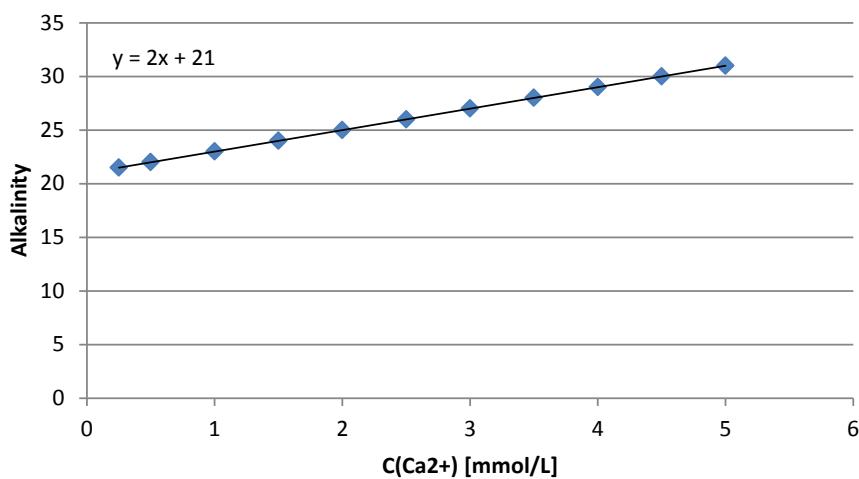


Figure 4: The Figure is showing the plot of the Calcium concentration and the alkalinity values in 10. A linear regression line is included using EXCEL's trendline tool

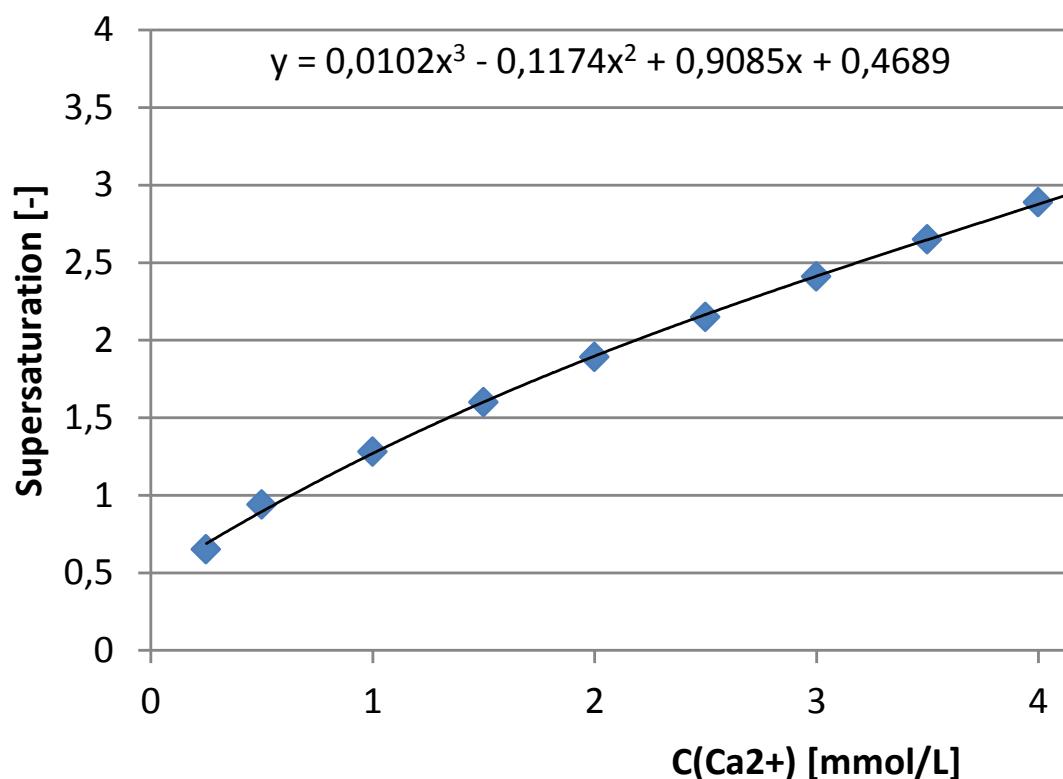


Figure 5: The figure is showing the supersaturation for the dummy data