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THE EFFECT OF ADDITIVES ON LIME DISSOLUTION RATES

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by

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EXECUTIVE SUMMARY

In spray dryer flue gas desulfurization, lime slurry is injected into a spray dryer where it contacts with the hot flue gas and desulfurization occurs. This process is complex owing to the heat and mass transfer which must take place. One of the most important fundamental steps in the scrubbing process is the rate at which lime dissolves from the solid particle in the slurry drop and becomes available for reaction with the absorbed sulfur dioxide. This dissolution rate to a large extent controls the degree of reactivity and is the rate controlling step for this process. However, studies on this dissolution rate have been very few and its magnitude under a variety of operating conditions is not well known. This research has as its objective, the study and understanding of the lime dissolution rate. This understanding should lead to a better method of predicting and optimizing spray dryer performance for flue gas desulfurization.

The lime dissolution rate has been successfully measured by means of a spinning disc experimental method. It was found that lime dissolution rate was dependant on the disk rotating speed when the rotating speed was below 300rpm. When the disk rotating speed was greater than 300rpm, lime dissolution rate become constant. Lowering the solution pH increased lime dissolution rate, and lowering the solution temperature reduced lime dissolution rate.

Two groups of additives have been tested for their effects on lime dissolution rate. Among the organic chemicals, sugar and phenol were the most effective in enhancing lime dissolution rate. Glycerin slightly increased the lime dissolution rate, and ethyl-alcohol depressed the lime dissolution.

The most prominent chemical tested was in the inorganic chemicals group. In its 20% by weight solution at 50° C, the NH_4Cl solution increased lime dissolution rate more than a hundred times compared with dissolution in pure water. The other two inorganic chemicals, $(\text{NH}_4)_2\text{SO}_4$ and CaCl_2 , just slightly increased lime dissolution rate.

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INTRODUCTION

In spray dryer flue gas desulfurization, lime slurry is injected into a spray dryer where it contacts with the hot flue gas and desulfurization occurs. This process is complex owing to the heat and mass transfer which must take place. One of the most important fundamental steps in the scrubbing process is the rate at which lime dissolves from the solid particle in the slurry drop and becomes available for reaction with the absorbed sulfur dioxide. This dissolution rate to a large extent controls the degree of reactivity and is the rate controlling step for this process. However, studies on this dissolution rate have been very few and its magnitude under a variety of operating conditions is not well known. This research has as its objective, the study and understanding of the lime dissolution rate. This understanding should lead to a better method of predicting and optimizing spray dryer performance for flue gas desulfurization.

LITERATURE REVIEW

Lime and limestone dissolution rate prediction is an important means to determine the scrubber performance of flue gas desulfurization (FGD) processes. A wide range of studies have been done to investigate the limestone dissolution rate in the typical wet scrubber system, and these studies can be divided into three categories:

- Limestone dissolution rate studies by varying such parameters as Temperature and pH etc.
- Limestone dissolution rate studies under the influence of magnesium, sulfite and

sulfate ions.

- Limestone dissolution rate studies under the influence of other additive ions.

For the first category, The limestone dissolution rate was extensively tested by singly changing such variables as pH, temperature, particle size, magnesium content, and aqueous sulfite and sulfate concentration (Meserole, B.F., B.M. Eklund, K.W. Luke and L.J. Holcombe, 1986). The experimental data were correlated by a best-fit model equation:

$$\ln(\text{DR}) = a + b_1(\text{TP}) + b_2(\text{pH}) + b_3\ln(\text{STIR}) + b_4\ln(\text{TSA}) + b_5\ln(\text{Mg}) \quad \text{Eq. (1)}$$

where, DR = the dissolution rate of calcium or magnesium (mg/g.min)

TP = the inverse of temperature ($^{\circ}\text{K}^{-1}$)

pH = the solution pH

STIR = the stirring rate in the reactor (rpm)

TSA = the total surface area of the test material (cm^2/g)

Mg = the magnesium concentration in the reactor feed solution (mg/l)

a, b_1 , b_2 , b_3 , b_4 , and b_5 are constants.

The sulfite tests indicated that the presence of sulfite produced a significant increase in the dissolution rate of CaCO_3 .

At low pH values (less than 4), there is the consensus that the dissolution rate is approximately proportional directly to the hydrogen ion concentration (Barton, P and T. Vatanatham, 1976, 1979; Berner, A.R. and J.W. Morse, 1974; Plummer, L.N., D.L. Parkhurst, and T.M.L. Wigley, 1979; Wentzler, H.T. and F.F. Aplan, 1972; Uchida, S., C.Y. Wen, and W.J. McMichael, 1974). This means that at low pH, the dissolution rate is controlled by the diffusion of hydrogen ions to the crystal surface.

In the middle pH range (4.5-7), the limestone dissolution rate was originally found to vary linearly with respect to pH, and the rate was considered to be essentially independent of the CO_2 partial pressure (Berner, A.R. and J.W. Morse, 1974; Kim, K.Y., M.E. Deming, and J.D. Hatfield, 1975). Recent studies indicate that the effect of partial pressure of CO_2 on the dissolution rate varies between pH 4 and 5 (Chan, P.K. and G.T. Rochelle, 1982; Toprac, A.J. and G.T. Rochelle, 1982; Noda, K., S. Uchida, and M. Miyazaki, 1989). At a pH above 5, the dissolution rate is controlled by diffusion of OH^- , HCO_3^- , and other species, and by the finite rate of CO_2 reaction. The partial pressure of CO_2 influences the dissolution rate to a lesser extent in the lower pH range. In this range almost all dissolved CO_2 exists in the form of H_2CO_3 and the dissolution rate is considered to be controlled by the hydrogen ion transfer. However, in the range of higher pH the dissolved CO_2 is converted to HCO_3^- and the solubility of CO_2 in molecular and ionic forms is very high compared with that at lower pH. In addition to hydrogen ion transfer, the effect of the other components resulting from dissolved CO_2 on the dissolution rate seems to be significant. At higher pH levels, the dissolution rate is considerably lower and occurs via poorly defined mechanisms (Berner, A.R. and J.W. Morse, 1974; Sjöberg, L.E., 1976). Due to the lack of applicability of the dissolution rate at higher pH, the dissolution of limestone at higher pH (>8) has not received much study.

Though temperature is an important factor affecting limestone dissolution rate, very little effort has been made in determining the correlations under different conditions. Equation (1) indicated the dissolution rate is exponentially related to temperature in the form of

$$DR = c \text{ EXP}(b_1/T)$$

where c is a constant dependent on the other parameters, and b_1 is also a constant related to the type of stone. The value of b_1 ranged from -1700 for Fredonia calcium carbonate to -5670 for Aragonite magnesium carbonate.

The smaller the particle size for a given mass, the higher the dissolution rate. The particle size effect is correlated to total surface area (Meserole, B.F., B.M. Eklund, K.W. Luke, and L.J. Holcombe, 1986), and this is shown in equation 1. For a given weight of limestone, the dissolution rate is directly proportional to the total surface area of the limestone particles, and therefore inversely proportional to particle diameter.

The magnesium ion is considered to be an inhibitor for limestone dissolution. It has been shown that the presence of magnesium ions reduces the dissolution rate of CaCO_3 (Evans, J.T. and M.G. Moseley, 1978; Pesret, F., 1972; Pearson, H.F. and A.J. McDonnell, 1975; Barnes, I. and J.R. O'Neil, 1971). One explanation for this phenomenon is that magnesium ions may absorb onto the limestone surface and slow the dissolution process much the same as many inhibitors. The dissolution study of EPRI (Meserole, B.F., B.M. Eklund, K.W. Luke, and L.J. Holcombe, 1986) shows that at pH values of 5.0 and 5.8, the limestone dissolution rate appears to be independent of the magnesium content in the solids until the MgCO_3 concentration reaches 4 to 5%. Beyond 5%, the magnesium concentration increase results in a decrease of the overall limestone dissolution rate but an increase of magnesium dissolution rate.

The sulfite ion was found to have a dual effect on the dissolution of limestone (Gage, L.C. and G.T. Rochelle, 1992). The sulfite/bisulfite pair acted as a buffer at the limestone

interface by providing hydrogen ion which was consumed during the dissolution reaction. But sulfite also inhibited dissolution by adsorbing on the limestone as calcium sulfite. The presence of sulfite has been shown to increase the dissolution rate of CaCO_3 significantly (Meserole, B.F., B.M. Eklund, K.W. Luke, and L.J. Holcombe, 1986). The most affected, Fredonia stone, showed increase in dissolution rate from 1.8 without sulfite to 11.7 mg/g.min with sulfite. Chan and Rochelle (Chan, P.K. and T.G. Rochelle, 1982) quantified inhibition by sulfite in concentrations greater than 1 mM at conditions far from equilibrium to calcite. Measured rates for reagent calcite were significantly less than values predicted by a mass transfer model which accounted for the buffering effect of sulfite/bisulfite. The experimental data also show that at low concentrations of sulfite and for a given pH, the dissolution rate is enhanced over the rate observed in the absence of sulfite. Jarvis et al (Jarvis, J.B. et al, 1988) studied FGD solution effects on ten different limestone types. Of the species studied, magnesium and adipic acid were found to be minor inhibitors while sulfite and aluminum fluoride complexes were noted to be significant inhibitors to the limestone dissolution rate. The magnitude of sulfite inhibition was found to be dependent on limestone type. The effect of sulfite on limestone mass transfer was modeled with the calcite surface concentrations controlled by a surface kinetics rate involving sulfite at the surface (Gage, L.C. and G.T. Rochelle, 1992). The limestone dissolution rate in the presence of sulfite was found to be controlled by a combined surface kinetics/mass transfer regime.

Sulfate ions have been shown to increase limestone dissolution rate. One study with limestone from Warner Co., in Bellefonte, Pennsylvania (97.15% CaCO_3 , 1.10% MgCO_3 , 1.35% insolubles) showed that the presence of dissolved sulfate ions, at pH values below 5.0,

increased the dissolution rate slightly (Wentzler, H.T. and F.F. Aplan, 1972). The limestone dissolution rate increase was also observed when salts such as Na_2SO_4 and MgSO_4 were added to the solution (Ukawa, N., S. Okino, M. Oshima, and T. Oishi, 1993). The increase of the dissolution rate was thought to be the effect of bisulfate ions coexisting in the solution in equilibrium, thus providing an additional means of diffusing acidity (bisulfate ions) to the limestone surface. Sulfate is a typical species present in scrubbing systems and is a known inhibitor for calcium sulfite crystallization (Gage, L.C. and G.T. Rochelle, 1992), but the presence of sulfate in solution reduces both the dissolution and crystallization rates (Tseng, P.C. and G.T. Rochelle, 1986a and 1986b).

Depending on the type of ions formed, the other additives can have a great effect on the limestone dissolution rates. Jarvis et al (Jarvis, J.B., B.F. Meserole, J.T. Selm, T.G. Rochelle, L.C. Gage, and E.R. Moser, 1988) studied the effects of solution species on limestone dissolution rates. Solution species which were tested included pH, Ca^{2+} , Mg^{2+} , Na^+ , SO_3^{2-} , SO_4^{2-} , CO_3^{2-} , Fe^{3+} , Al^{3+} , F^- , and adipic acid. Of the species studied, magnesium and adipic acid were found to be minor inhibitors while sulfite and aluminum fluoride complexes were noted to be significant inhibitors to the limestone dissolution rates. Dissolution rates decreased with increasing Ca^{2+} and CO_3^{2-} since these species decrease the solubility of CaCO_3 at the limestone surface. No significant effects were noted with changes in the concentrations of Na^+ , SO_4^{2-} , Cl^- , and it was confirmed that sulfate does not inhibit limestone dissolution in a manner analogous to sulfite. The trace metals Fe^{2+} , Fe^{3+} , and Mn^{2+} (at a concentration of 5 ppm) also had no effect on the dissolution rate. Recent studies (Ukawa, N., S. Okino, M. Oshima, and T. Oishi, 1993) indicated that in chloride solutions such as CaCl_2 , MgCl_2 and

NaCl, the limestone dissolution rate decreases when the salt concentration increases. The presence of barium and/or strontium (Pesret, F., 1972) and benzoic acid (Kim, K.Y., M.E. Deming, and J.D. Hatfield, 1975) has been shown to increase the limestone dissolution rate. Barium and strontium only slightly increase the dissolution rate, whereas 0.2% benzoic acid increased the dissolution rate by about 10% at pH 5.5. In the studies of crystal habit (Kelly, B., B. Keough, and A.D. Randolph, 1983), it was found that several crystal habit modifiers, mostly organic acids, significantly reduce crystal growth rate and particle size.

EXPERIMENTAL METHOD

Spray drying processes have different physical and chemical features compared to the wet scrubbing operations. The dissolution rates of lime and limestone could become a critical limiting step for spray drying desulfurization. Spray drying processes contain two phenomena that are totally different from the wet scrubbing. One is the short residence time of the liquid phase in droplets, and the second is the highly concentrated ions in droplets and the ion interactions accompanying the water evaporation. According to the literature review, the second phenomenon has a relationship to the limestone dissolution rate, and because of these phenomena, the lime dissolution rate needs special considerations and studies. Since the dissolution rate can become the limiting step for the overall SO_2 removal in spray dryer (as can be seen by using different sorbents such as NaOH, $\text{Ca}(\text{OH})_2$, and CaCO_3), higher dissolution rate could mean higher sorbent utilization. Based on the above reasons, the objectives of these studies are:

1. Set up experiments to measure the dissolution rate of lime. Study the mechanisms of the sorbent ($\text{Ca}(\text{OH})_2$) dissolution rates and the factors that have the greatest effects on the dissolution rate.

2. Study the influence of additives on lime dissolution rate. These additives may exist as trace compounds in the sorbents, the products of the SO_2 , or other gaseous pollutants reacted with the sorbents or added as artificial additives.

Limestone Test Results

The experimental setup has been postulated and schematically designed as shown in Figure 1. It contains three major blocks. The first block is the sorbent solution container mounted on a temperature controlled hot-plate stir. The sorbent solution in the container is agitated by a magnetic mixer, and its pH and temperature are monitored through a pH probe and a thermocouple, respectively. There is also a gas sparger immersed into the solution for the purpose of saturating the solution with a specific gas. The second block consists of a combination of pH meter and pH stat, a data acquisition system, a cylinder for containing acid solution, a balance for monitoring the weight of acid, and a titration liquid pump. This block works to decrease pH by injecting acid whenever the pH value in the solution gets higher than the upper pH limit value preset on the pH stat. The pH stat controls the titration pump. The third block is composed of a rotation motor and its speed controller. The rotating disk is attached to one end of the shaft which is clamped to the motor. The speed of rotation can be changed by the motor speed controller.

A test of limestone dissolution rate was used to verify the experimental system as the results could be compared to published data. Fisher reagent grade limestone was chosen for the initial dissolution rate test since it was the only type of stone available to us from reported studies.

The overall test results are shown in Figures 2, 3 and 4. Figure 2 gives the recording of two different solution pH values vs time, and Figures 3 and 4 give the loss of the titration acid, HCl, vs time. The pH upper limit was set manually in the pH stat, and for these two cases were 5.6 and 5.2 respectively. The acid was contained in a glass cylinder which sits on a balance, and the balance continuously sends the acid weight signal to the data acquisition system.

From Figure 2, it can be seen that the pH values do not change so quickly at prolonged time intervals; this is probably due to the fact that the overall surface area of the limestone is decreasing. Both the disappearance of smaller particles and the size reduction of larger particles will contribute to the reduction of the overall sorbent surface area. This phenomenon is more clearly seen in Figure 3 and 4 in which the acid consumption rates deviate from a straight line as time passes, i.e. less acid is demanded in order to keep the limestone dissolution at constant pH.

The dissolution rate can be calculated by knowing the slope of the acid vs time and the limestone BET surface area. The formula is as following (and a detailed procedure is given in Appendix I)

ΔW is the acid weight change

Δt is the time change.

$\Delta W/\Delta t = L$ (g/min.) is the acid solution consumption rate.

C_{acid} (mole/liter) is the acid concentration.

W_s (g) is the initial weight of sorbent (limestone).

BET (m^2/g) is the BET surface area of the sorbent to be tested.

ρ (g/cm^3) is the density of the acid solution (the dilute acid density is assumed to be the same as the density of water).

d is the sorbent/acid complete reaction molar ratio (in the case of $CaCO_3/HCl$ $d=1/2$).

The acid consumption rate R in gmole/sec. is :

$$R = \frac{LC_{acid}}{60 \cdot 10^3 \cdot p}$$

The sorbent dissolution rate (flux) R_s in gmole/ cm^2 /sec. is:

$$R_s = \frac{LC_{acid} d 10^{-8}}{6 \cdot BET \cdot W_s \cdot p}$$

The BET surface area of Fisher Scientific reagent limestone was measured as 0.42 m^2/g . The dissolution rates of the limestone under different pH was obtained and compared to the reference (Gage and Rochelle, 1992). It can be seen in Table I that the measured dissolution rates are comparable. In Gage and Rochelle's experiment, N_2 was sparged into the solution while in our experiment there is no gas sparging.

Rotating Disk Technique and Lime Dissolution Rate Experimental Studies

In lime dissolution rate study, it was found that the lime solution pH value is very difficult to control. This is because the reagent lime particles dissolve much faster than the limestone particles. In order to effectively measure the dissolution rate of lime, the surface area of the lime to be measured has to be minimized to consider this effect. Therefore, the idea of using a rotating disk was proposed. A 4cm diameter die was designed to press the Ca(OH)_2 into a solid disk.

The die, which was made of stainless steel, consists of a cylinder and two pistons. The two pistons have a small clearance with the cylinder. When making the Ca(OH)_2 disks, the bottom piston is fit into the cylinder, and then a amount of Ca(OH)_2 is poured into the cylinder. Finally, the upper piston is carefully slid into the cylinder. The die thus mounted is ready to be pressed in a hydraulic compressor. The optimal press force for forming a good Ca(OH)_2 disk is about 6 tons which is equivalent to a pressure of about 48 MPa (Giles et al, 1993). After reaching this pressure, the force is released by turning off the hydraulic valve on the pressor. The die can now be taken out of the pressor, and the bottom piston is slowly turned and removed. Then the die is put into the pressor again to have the disk pushed out, and as soon as the disk is out it is wrapped in wax paper for further processing. The upper piston is also taken out of the cylinder, and all the die components are carefully cleaned using lens papers and methanol.

The disk thus made is not perfectly smooth on the surfaces, especially on its edges. Therefore, surface polishing is necessary. The first step is to use abrasive sand paper 320 (approximately 33 micro grit) to get rid of those major defects on the disk surfaces. The second step is to use abrasive sand paper 600 (approximately 14 micro grit) to make the disk

surface more smooth. The final step is to use polishing cloth with diamond spray of 1 micrometer. The disks are put into glass bottles filled with nitrogen gas for future use.

The compressed lime disk was tested for its chemical composition changes. The major concern was that the pressure might change the water content in the lime. Three TGA dehydration tests showed that from 0 to 48 MPa the lime water content did not change. The TGA results are shown in Figure 6, 7, and 8. Figure 6 is for a dehydration test with lime powder, Figure 7 is for pressed disk lime with 24 MPa pressure, and Figure 8 is for pressed disk lime with 48 MPa.

Before the dissolution rate experiment, a 3mm diameter hole is drilled in the center of disk and it is attached to the tip of a 3/8" diameter shaft by super glue (the diameter of the tip of the shaft is 2mm). The thickness of the disk is measured by a microcalliper, and the surface area of the disk is calculated by adding the two disk face surface areas and the rim surface area, and subtracting the surface area occupied by the hole in the disk center. The disk is then lowered into 450 ml of super-Q water for the dissolution experiment. The pH upper limit is set according to the experiment. The solution temperature is controlled by the temperature controlling hot plate-stir. The acid used is ordered from Fisher Scientific as standardized concentration acid.

Lime Dissolution Rate Under Different Parameters

The dissolution rate of lime vs disk rotating speeds at room temperature is shown in Figure 9 where it can be seen that when the disk rotating speed is above 300 rpm the

dissolution rate is almost independent of the disk rotation. Therefore, a disk rotating speed 300 rpm was chosen as the speed for subsequent experiments.

A series of experiments have also been conducted to test the lime dissolution rate under different pH values. These experiments are conducted by keeping the solution temperature constant at about 50°C in order to simulate the conditions in spray dryer. Figure 10 shows the dissolution rate vs pH, and it shows that under pH 6 the dissolution rate increases with decreasing pH. For a typical measurement, the variation of pH, temperature, and consumption of acid are shown in Figure 11, 12, and 13 respectively. It can be seen in Figure 11 that the pH of solution changed in a wider range than that in limestone test. This is probably due to the fact that the lime rotating disk is a surface source for dissolution while the limestone particles are well mixed in the solution and it is easier for the system to maintain a uniform pH value. Figure 12 gives the solution temperature vs time, and it can be seen that the temperature controlling hot-plate did a good job in keeping the temperature constant. Figure 13 shows that acid consumption rate vs time. Though the consumption rate is not strictly a straight line, it can be considered a line between 5 to 20 minutes. This time period choice is made with the consideration that initially the disk surface may have not be smooth and free of dust which can make the initial dissolution rate slightly greater, and that with time elapse the solution may have a high ion concentration which may result in some deposition on the disk surface to make the dissolution rate decrease.

The Effect of Additives on Lime Dissolution Rate

From solubility studies (Boynton, 1976), it is found that most inorganic salts increase Ca(OH)_2 solubility by 10-15% in 0.1-0.2% salt solutions, but several soluble organic substances markedly increase Ca(OH)_2 solubility far greater than any inorganic chemicals. Glycerol at 25°C yields a steady increase in solubility up to a glycerol concentration of 69%. Ca(OH)_2 solubility at the maximum glycerol level is 3.55g $\text{CaO}/100\text{g H}_2\text{O}$, which is about 22 times greater than Ca(OH)_2 solubility in pure water. Phenol produces an even greater rise in Ca(OH)_2 solubility. At 23°C and 30% phenol concentration Ca(OH)_2 solubility can reach 8.67g $\text{CaO}/100\text{g H}_2\text{O}$, which is an increase of 75 times over pure water. Sugar exerts the greatest influence on lime solubility. At 25°C and 35% sugar concentration Ca(OH)_2 solubility can reach its maximum of 10.1g $\text{CaO}/100\text{g H}_2\text{O}$, which is 100 times more than Ca(OH)_2 solubility in pure water. The solubility of Ca(OH)_2 with respect to the organic additive concentration is shown in Figure 14. It can be seen in Figure 14 that in the additive concentration range of less than 10% by weight the phenol has the greatest effect on increasing the lime dissolution rate. When phenol concentration gets to 20% the lime dissolution rate declines because not all the phenol in water is dissolved. Sugar has enhanced the dissolution rate of lime steadily. The dissolution rate of lime can be related to the sugar weight concentration and fitted as an exponential regression line. Adding glycerin to the solution seems to result in little improvement on lime dissolution over pure water, and an increase in glycerin concentration leads to no further improvement in the lime dissolution rate.

Three inorganic additives were also tested for their effects on lime dissolution rate. They are NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$, and CaCl_2 . It was found that NH_4Cl has the ability to increase

lime dissolution rate tremendously, as can be seen from Figure 16. This phenomenon was first considered a chemical reaction, but the activation energy calculated from further tests on dissolution rate vs temperature indicated that NH_4Cl in some way accelerates the mass transfer process. The lime dissolution rate under 2% NH_4Cl weight concentration vs different temperature is shown in Figure 17. The activation energy is 3.63 kcal/g-mole. The other two inorganic salts improved lime dissolution rate slightly, as shown in Table II.

CONCLUSION

The lime dissolution rate has been successfully measured. It was found that lime dissolution rate was dependant on the disk rotating speed when the rotating speed was below 300rpm. When the disk rotating speed was greater than 300rpm, lime dissolution rate become constant. Lowering the solution pH increased lime dissolution rate, and lowering the solution temperature reduced lime dissolution rate.

Two groups of additives have been tested for their effects on lime dissolution rate. Among the organic chemicals, sugar and phenol were the most effective in enhancing lime dissolution rate. Glycerin slightly increased the lime dissolution rate, and ethyl-alcohol depressed the lime dissolution.

The most prominent chemical tested was in the inorganic chemicals group. In its 20% by weight solution at 50° C, the NH_4Cl solution increased lime dissolution rate more than a hundred times compared with dissolution in pure water. The other two inorganic chemicals, $(\text{NH}_4)_2\text{SO}_4$ and CaCl_2 , just slightly increased lime dissolution rate.

Table I. Comparison of Results for Fisher Reagent Limestone Dissolution Rate

Solution Treatment	pH	Temperature °C	Rate $\times 10^9$ gmol/cm ² -s
With N ₂ Sparging (Gage & Rochelle, 1992)	4.5	25	4.78
	5.0	25	1.36
	5.5	25	0.74
	5.75	25	0.54
	6.0	25	0.36
Without Sparging (This Test)	5.07	23	1.03
	5.51	26	0.30

Table II. Comparison of Different Additives Effects on Lime Dissolution Rate.

Additive Name	Additive % Weight in Solution	pH Stat Upper Limit	Average pH of Solution	Average Temp of Solution °C	Dissolution Rate of Lime gmol/cm ² -sec.
Pure Water	0%	7.00	6.49	49.04	6.05
NH ₄ Cl	2%	7.00	6.97	49.43	30.29
	10%	7.00	7.02	48.56	133.97
	20%	7.00	7.04	51.02	888.84
CaCl ₂	2%	7.00	6.22	53.91	7.56
	10%	7.00	6.38	53.49	9.19
NH ₄ SO ₄	2%	7.00	6.89	47.43	9.04
Sucrose	2%	7.00	6.21	55.52	7.11
	10%	7.00	6.61	51.68	13.86
	20%	7.00	7.18	48.63	37.19
Phenol	2%	7.00	6.71	50.75	12.58
	10%	7.00	6.91	46.99	34.99
	20%	7.00	6.91	44.24	31.07
Glycerin	2%	7.00	6.13	50.97	9.36
	10%	7.00	6.28	51.75	9.72
	20%	7.00	6.42	50.97	10.64
Alcohol	10%	7.00	5.89	54.12	4.98

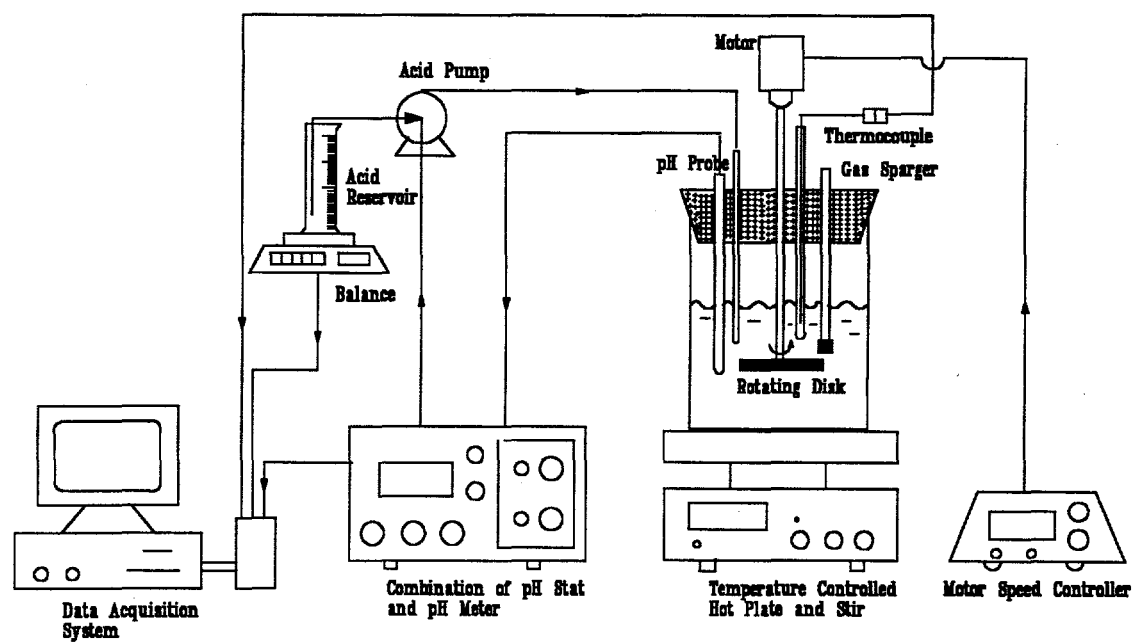


Figure 1. Schematic Diagram of Experimental Setup for Dissolution Rate Study.

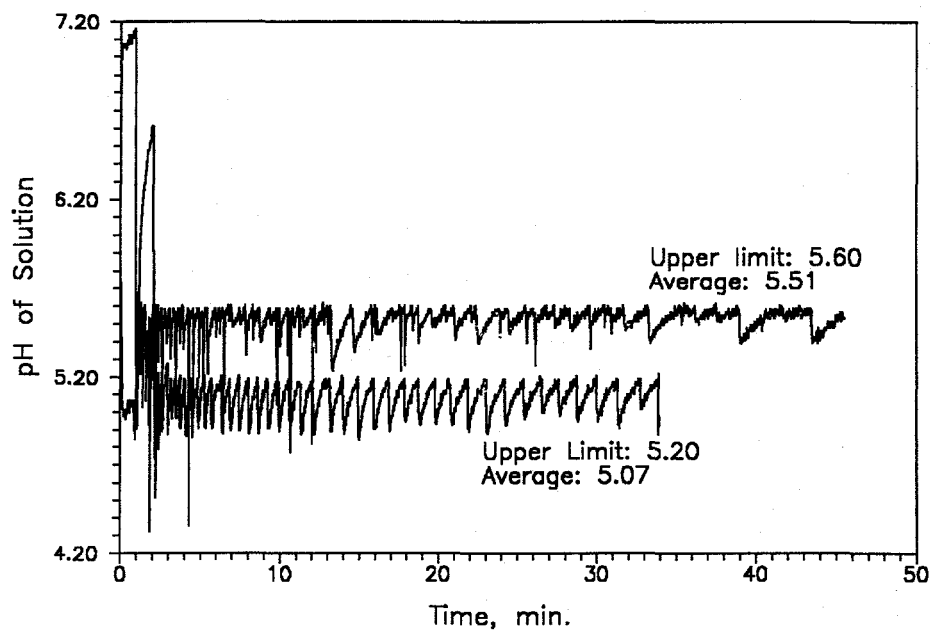


Figure 2. Variation of Solution pH vs Time at Different pH Upper Limit in the Fisher Reagent Limestone Dissolution Tests.

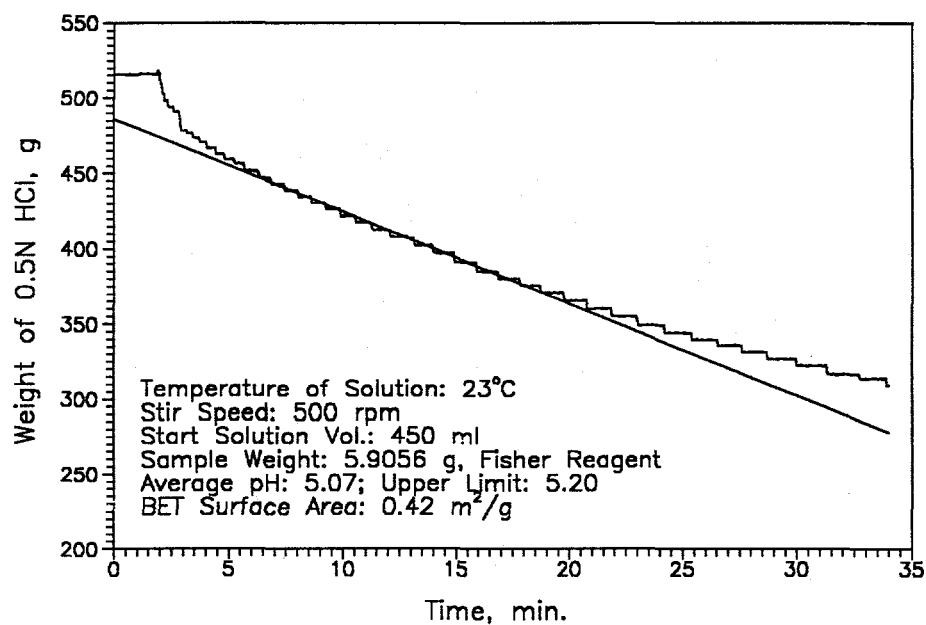


Figure 3. Acid HCl Weight in the Reservoir vs Time at pH Upper Limit 5.2 in the Fisher Reagent Limestone Dissolution Test.

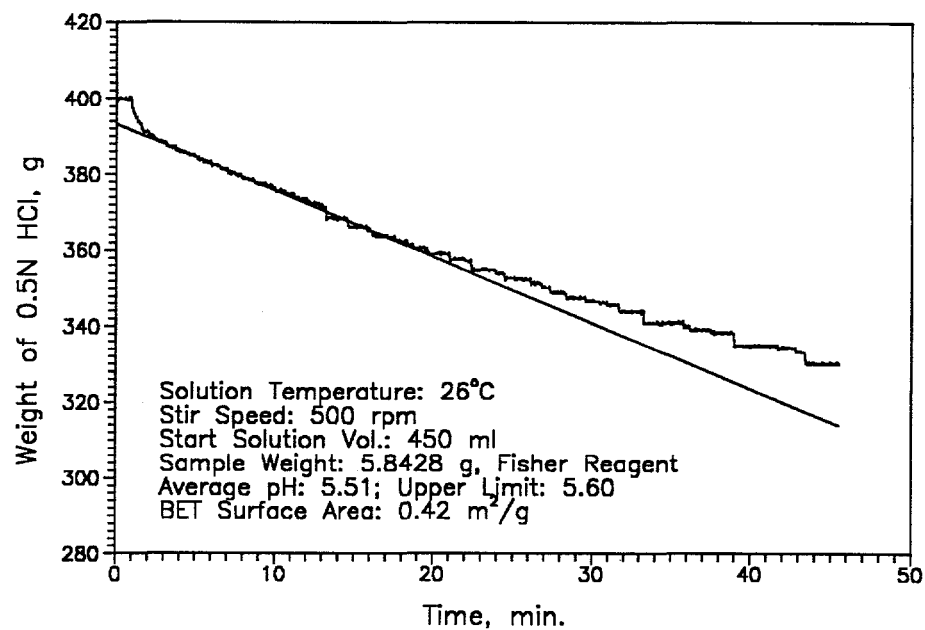


Figure 4. Acid HCl Weight in the Reservoir vs Time at pH Upper Limit 5.6 in the Fisher Reagent Limestone Dissolution Test.

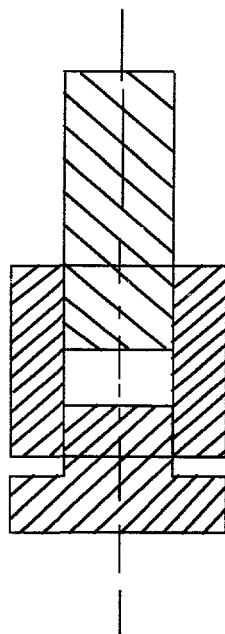


Figure 5. Drawing of the Die for Making Lime Disk.

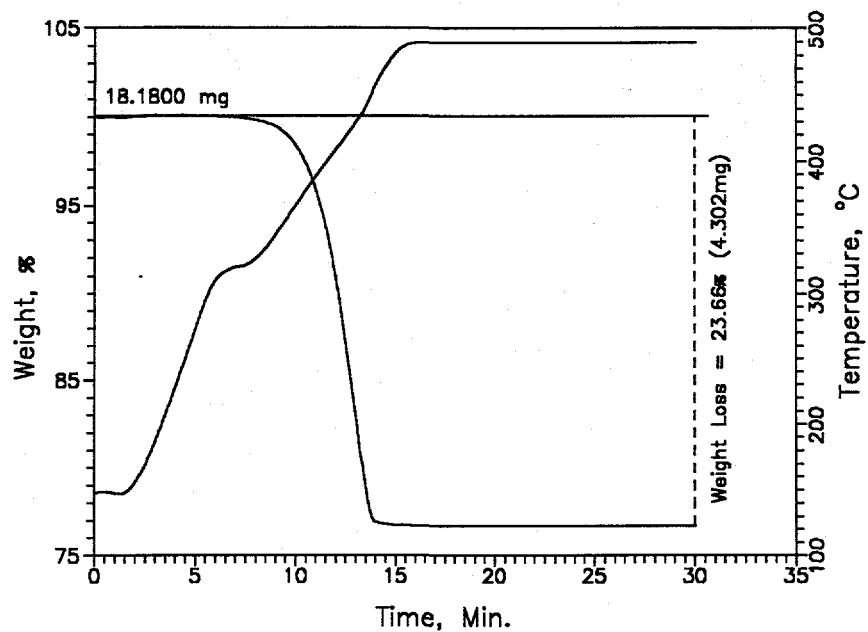


Figure 6. TGA Dehydration Test for Lime Powder.

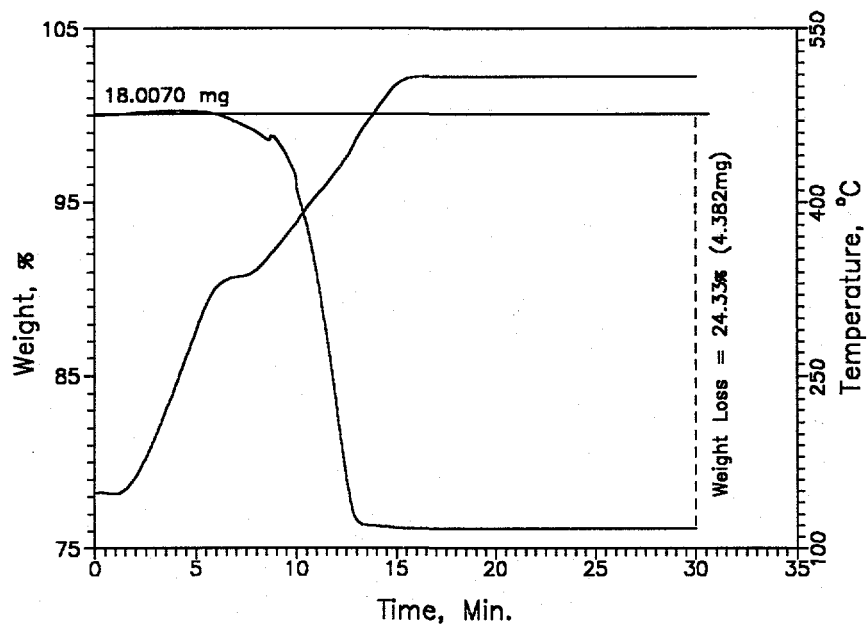


Figure 7. TGA Dehydration Test for 24 MPa Pressed Lime.

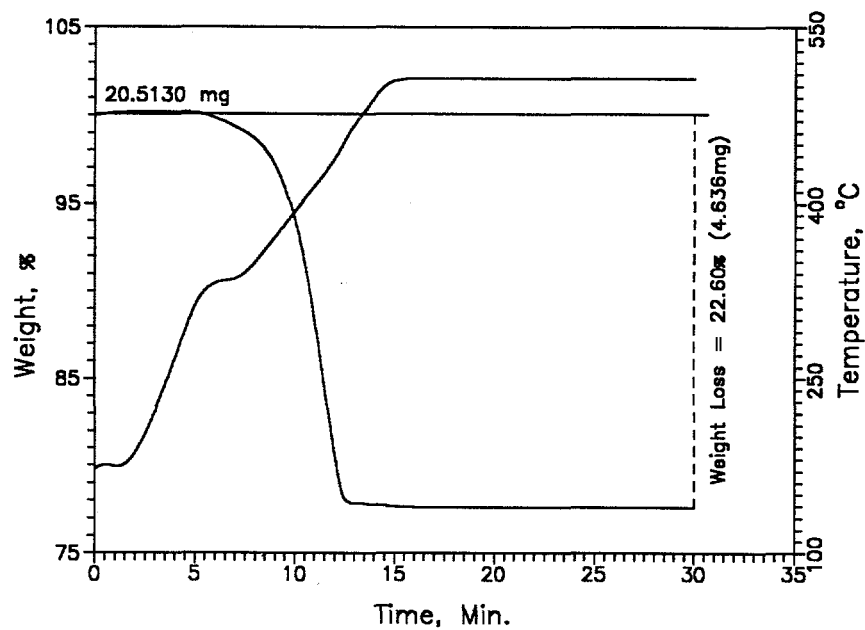


Figure 8. TGA Dehydration Test for 48 MPa Pressed Lime.

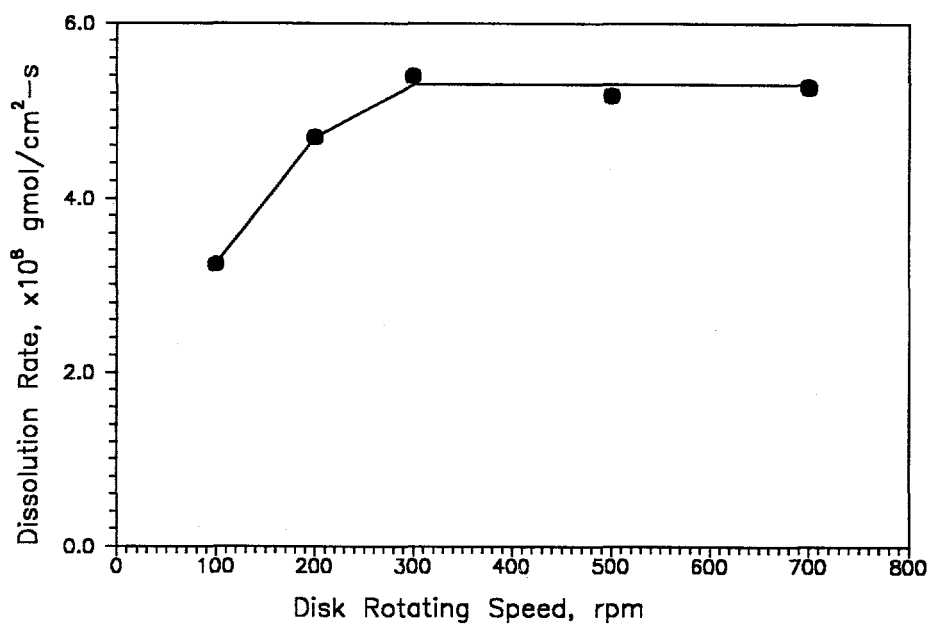


Figure 9. Lime Dissolution Rate vs Disk Rotating Speed.

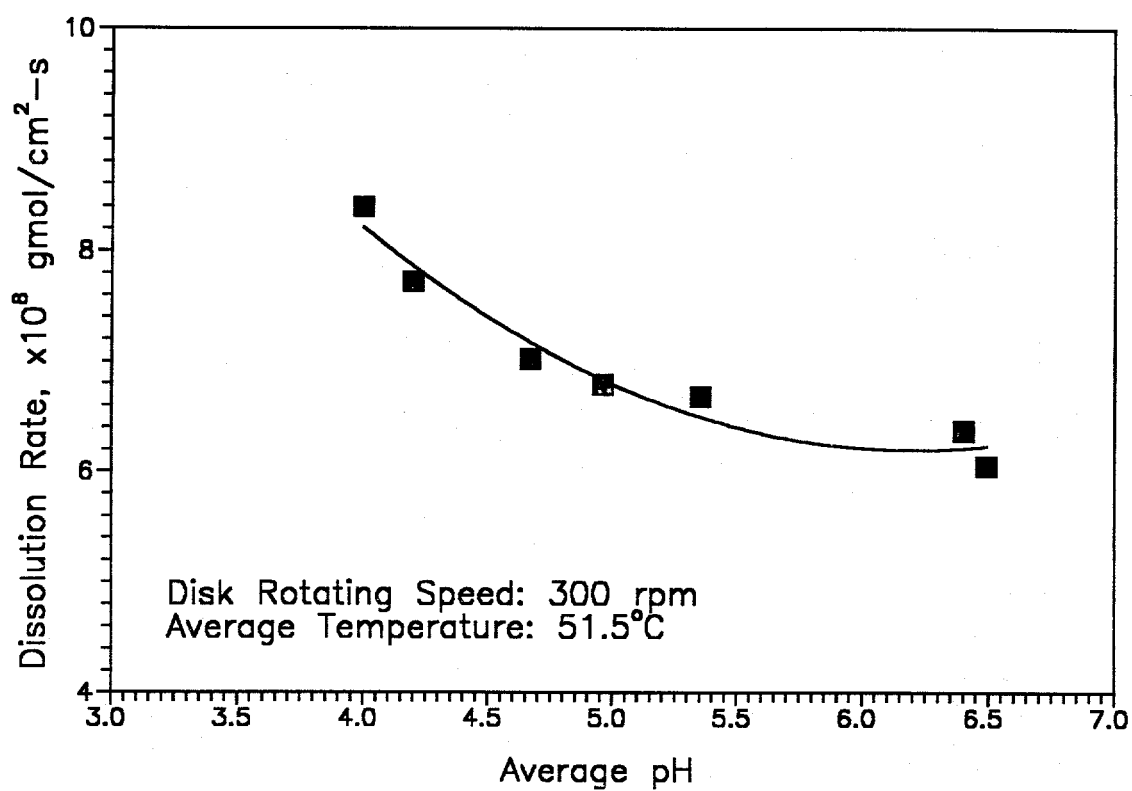


Figure 10. Lime Dissolution Rate vs Solution pH.

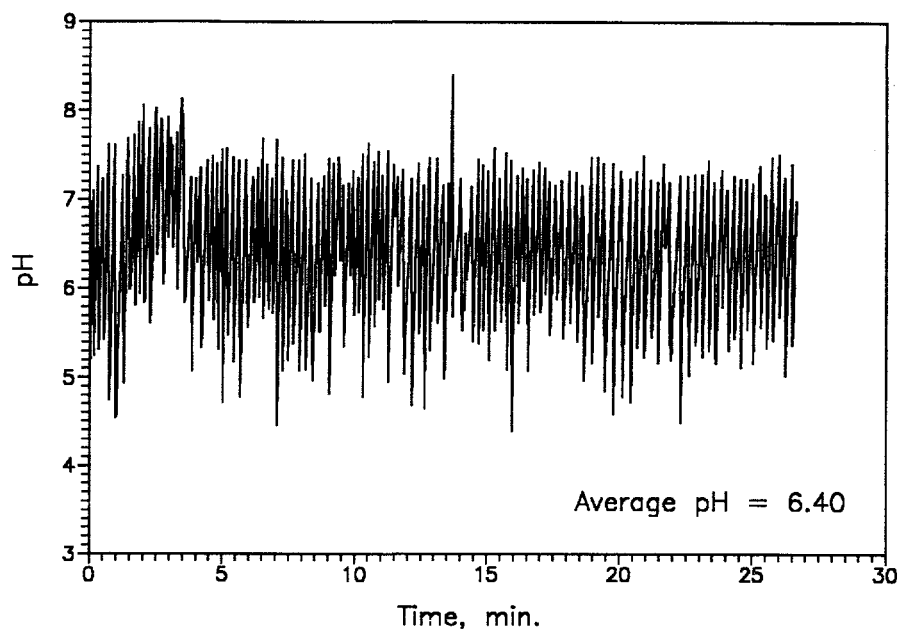


Figure 11. Measured Solution pH vs Time for Lime Dissolution Study.

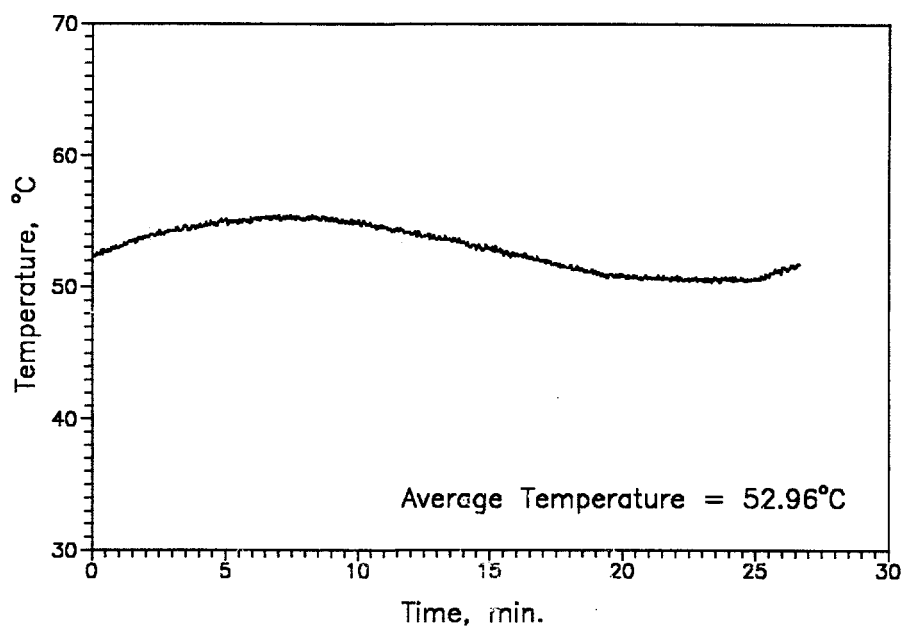


Figure 12. Solution Temperature vs Time for Lime Dissolution Study.

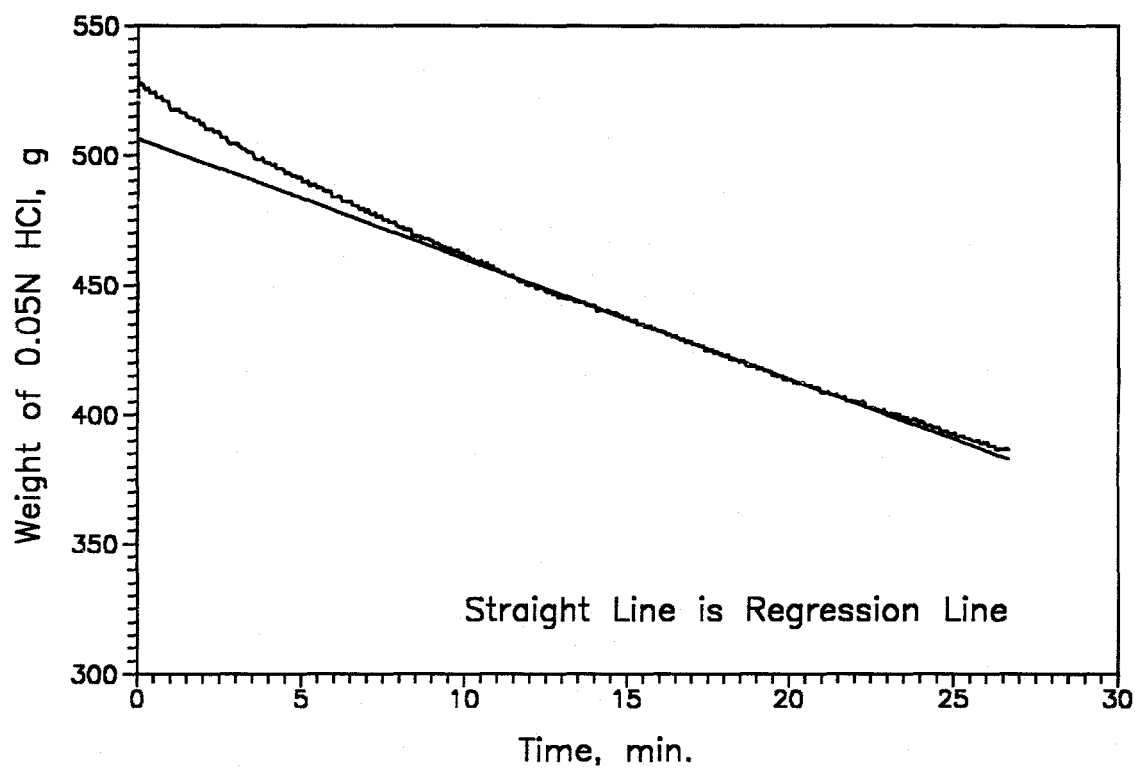


Figure 13. Acid HCl Weight in Reservoir vs Time for Lime Dissolution Study.

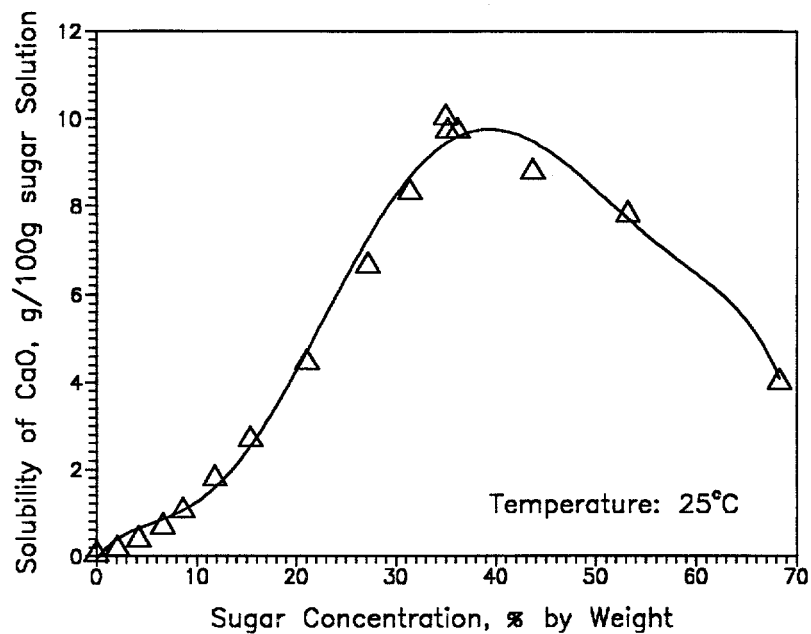


Figure 14. $\text{Ca}(\text{OH})_2$ Solubility in Sugar Solution (data from Boynton, 1976)

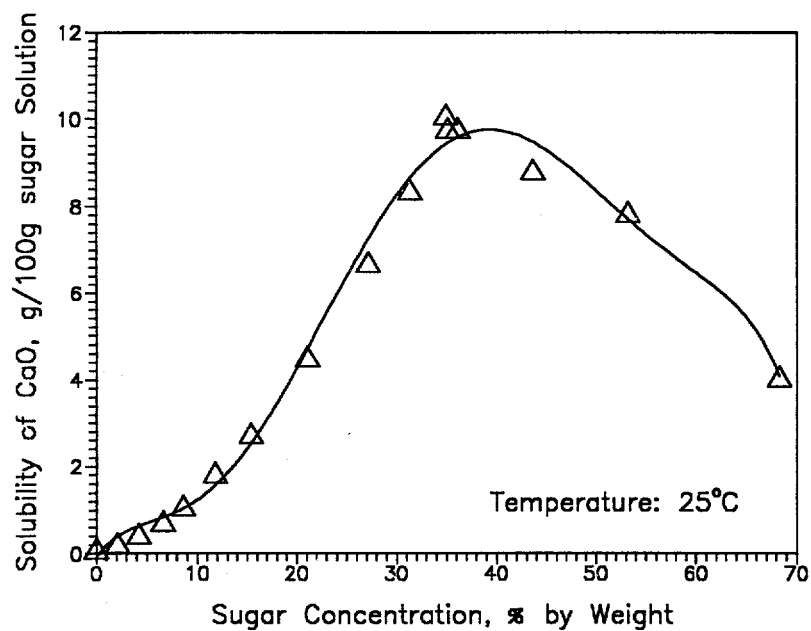


Figure 15. Lime Dissolution Rate Under Different Additive Solutions as a Function of Additive Concentrations.

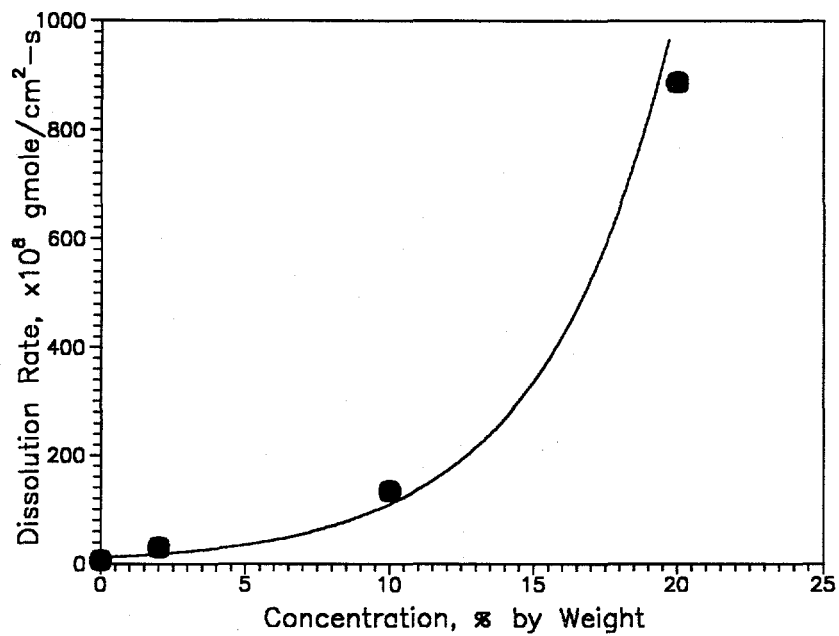


Figure 16. Lime Dissolution Rate vs NH_4Cl Weight Concentration.

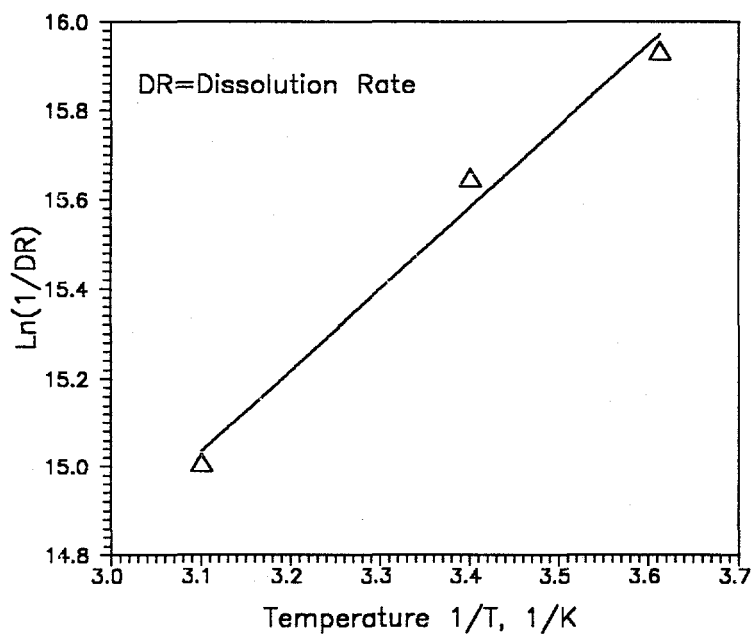


Figure 17. Lime Dissolution Rate vs Temperature as Derived From Activation Energy Formula.

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APPENDIX: DETAILED DETERMINATION OF THE DISSOLUTION RATE FORMULA

ΔW is the acid weight change

Δt is the time change.

$\Delta W/\Delta t = L$ (g/min.) is the acid solution consumption rate.

C_{acid} (mole/liter) is the acid concentration.

W_s (g) is the initial weight of sorbent (limestone).

BET (m^2/g) is the BET surface area of the sorbent to be tested.

ρ (g/cm^3) is the density of the acid solution (the dilute acid density is assumed to be the same as the density of water).

d is the sorbent/acid complete reaction molar ratio (in the case of CaCO_3/HCl $d=1/2$).

Since the acid solution consumption rate is $\Delta W/\Delta t = L$ (g/min.), and the density of the solution is ρ (g/cm^3), the volume flow of the acid solution is then L/ρ ($\text{cm}^3/\text{min.}$).

Since the concentration of the acid is C_{acid} (mole/liter), considering the units of the volume, the pure acid mole flow rate (consumption rate) R is $10^{-3}C_{\text{acid}} L/\rho$ (mole/min.), i.e. $10^{-3}C_{\text{acid}} L/(60\rho)$ (mole/sec.).

Because the solution pH is kept constant, this means that all the acid flow is neutralized by the sorbent dissolution. If the sorbent/acid mole ratio for complete reaction is d , then the sorbent dissolution rate should be $10^{-3}C_{\text{acid}} Ld/(60\rho)$ (mole/sec.).

Since the BET surface area is measured in m^2/g and the total amount of sorbent added to one test is W_s (g), the dissolution rate in flux ($\text{gmole}/\text{m}^2/\text{sec.}$) is $10^{-4}C_{\text{acid}} Ld/(6\text{BET } W_s \rho)$. In terms of $\text{gmole}/\text{cm}^2/\text{sec.}$, the dissolution rate (flux) is $10^{-8}C_{\text{acid}} Ld/(6\text{BET } W_s \rho)$ $\text{gmole}/\text{cm}^2/\text{sec.}$