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Production of Ammonium Sulfate Fertilizer from FGD Waste Liquors

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Progress Summary

During this quarterly period, an experimental investigation was performed to study the precipitation kinetics and hydrolysis characteristics of calcium imido disulfonate crystals (CaADS). The CaADS crystals were precipitated by a metathetical reaction of lime, supplied by Dravo Lime Co., with flue gas desulfurization (FGD) scrubber waste liquor.

Before approaching for the continuous Double Draw-Off (DDO) crystallization studies, the influence of a Dravo lime slurry on the precipitation characteristics of N-S compounds will be established. A series of N-S compound batch crystallization studies were completed in a wide range of pH (7.0- 9.0), and the influence of pH on the amount of lime required, as well as the amount of precipitate obtained, was investigated. Although the amount of precipitate increased with increase in solution pH, the safe or optimum pH for the precipitation of CaADS lies in the vicinity of 8.2 to 8.3.

For studying the crystallization characteristics of CaADS crystals, a bench scale 7.0 liter DDO crystallizer was built. DDO crystallizer is found to be superior compared to Mixed Suspension Mixed Product Removal (MSMPR) crystallizer. The precipitated crystals were analyzed for elemental composition by chemical analysis. The crystals were also examined under optical microscope for their morphological features.

The present studies confirmed our prediction that N-S compounds in the waste liquor can be precipitated by a reaction with lime slurry. The precipitated crystals were mostly calcium imido disulfonate. The major variables of the DDO crystallizer operation are the DDO ratio and the vessel residence time. The mass mean crystal size was found to be 115 μm at DDO ratio of

10.0 which then increased to 127 μm as the DDO ratio increased to 15.0 at a vessel residence time of 1 hour. This indicates that the filterability of the precipitates can be improved by studying the operating variables. Crystal Size Distribution (CSD) simulation studies have been initiated to predict the steady state and dynamic response of a continuously operated crystallizer using our computer simulator.

Experiments were carried out to investigate the filterability of the N-S compounds precipitated in the DDO crystallizer. The influence of a commercial filtration aid, i.e., diatomaceous earth, on the filtration rate was also examined. Diatomaceous earth is found to improve the filtration rate of product slurry.

Experimental study of the hydrolysis of N-S containing precipitates in an acidic environment required the manufacture of a one liter jacketed glass vessel equipped with a temperature controller. The hydrolysis reaction was carried out in 1M H_2SO_4 solution at 95°C. Under these conditions, the hydrolysis was found to be completed within 12 hours.

One major obstacle for the smooth progress of the present study is the limited supply of waste scrubbing liquor. More waste liquor for experimental study is required.

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1. Introduction

Several integrated processes that remove both SO_x and NO_x simultaneously are proven to be attractive (Sloss et.al. 1992; Sada et.al. 1988; Chang 1986; Martin 1981; Sada et. al. 1980; Faucett et.al. 1977). Nevertheless, these processes are uneconomical and have not yet reached the commercial stages. Research needs to be directed into two broad directions. Namely, total regeneration of waste scrubbing liquor, and continuous process development, in order to overcome the economic obstacles. Removal of the N-S compounds from the scrubbing liquor is the key step for regeneration of waste liquor. One attractive way to remove the N-S compounds of the waste liquor is to use a lime slurry. There is no report in the scientific literature on lime/limestone processes for waste liquor regeneration. However some preliminary work has been performed in Professor Randolph's laboratory (Randolph, A.D., 1993).

2. Project Objective

The goals of the present project are to develop a simple and economical regeneration process for the waste scrubbing liquor using a lime/limestone process, and to convert the calcium salt of the N-S containing compounds into ammonium sulfate which is marketable as fertilizer. A study of the operating conditions for the precipitation of calcium imido disulfonate, and its ultimate conversion to ammonium sulfate, will be conducted. Subsequently, the process design information will be provided. Study of the operating variables for the precipitation of CaADS in the DDO is important, since the filterability of the product slurry is a function of the Sauter mean size of the crystals. In addition, another consideration would be to make the whole regeneration process continuous.

3. The Process

In the lime/limestone process, the N-S containing compounds are precipitated mainly as calcium imido disulfonate. The major N-S compounds in the scrubbing liquor are hydroxylamine disulfonic acid (HADS), hydroxylamine monosulfonic acid (HAMS), amine trisulfonic acid (ATS), amine disulfonic acid (ADS), sulfamic acid (SA), and hydroxylamine (HA). The major reaction pathways of N-S compounds in a wet scrubbing solution, as prepared by Chang(1986), are given in Figure 1. In an aqueous solution, calcium imido disulfonate is the stable phase. During hydrolysis of the precipitated crop, all the N-S containing salts will be converted to ammonium ions, as indicated in Figure 1. The hydrolysis of ATS to ADS is fast (Nickless 1968; Sisler et.al., 1938). However, the conversion of ADS to an ammonium ion in an acidic environment is very slow, and seems to be the rate determining step for the hydrolysis of N-S containing salts (Candlin and Wilkins 1960; Maron and Berens 1950).

During hydrolysis, various N-S compounds of different concentration would be involved in the accompanying side reactions (Figure 1). Hence, it will be difficult to describe the overall hydrolysis in terms of a specific species.

The total process flow diagram is shown in Figure 2. In the process, the scrubber liquor reacts with the lime slurry in a DDO crystallizer. The pH of the mixture is adjusted to 8.2-8.3. The precipitate which forms, due to the reaction with lime, is most likely calcium imido disulfonate, together with Ca and Mg sulfates. The precipitates from the DDO crystallizer then undergo hydrolysis at about 95°C in a 1M H₂SO₄ solution. Subsequently, the filtered hydrolyzed solution is sent to a neutralization unit. Due to the high acidity of the hydrolyzed liquor, the ammonium and magnesium sulfates, and their bisulfates, remain in a soluble form. Next, the

hydrolyzed liquor is neutralized with ammonia gas to yield ammonium sulfate fertilizer (mixed with a small amount of MgSO_4). Note that the neutralizer vessel operates essentially as a reactive crystallizer, and the same DDO configuration could be applied in order to produce larger crystals. For the purpose of improved filtration, the influence of a potential crystal habit modifier, such as a phosphate ion, on the habit of ammonium sulfate crystals, was also studied. The process flow diagram described in Figure 2 is based on our initial observations and has several aspects which require careful study and optimization.

4. Experimental Studies of the Precipitation of N-S Compounds

Experimental investigations were performed to study the precipitation characteristics of N-S compounds in batch and continuous operation. The hydrolysis characteristics of these precipitates were evaluated in the acid hydrolysis experiments. The composition of the waste liquor supplied by Dravo Lime Co., PA is given below. In order to examine the filterability of the N-S compounds precipitated in the DDO crystallizer, standard filtration tests were performed.

4.1 Batch precipitation of N-S compounds

One of the most important characteristics of the precipitation of N-S compounds is probably the influence of the solution pH. A series of batch experiments involving a wide range of pH values were conducted to study the influence of solution pH on both the volume of lime solution required, and the amount of calcium imido disulfonate present in the precipitate.

The batch experiments were carried out in 300 ml Pyrex conical flasks. 150 ml of Dravo waste liquor was mixed with a known volume of 5% (w/v) thiosorbic lime slurry. The mixture

was allowed to set for several hours with constant stirring and then the pH of the solution was measured. The mixture was then filtered, and the precipitate was dried and weighed. In order to determine the CaADS content of the precipitates, a known amount of crystal was heated up to 95°C in a 1M H₂SO₄ solution overnight, and the ammonium ion concentration in the hydrolyzed solution was analyzed. The CaADS content of the crystal was determined, assuming that all the NH₄⁺ ions liberated in the solution originated from CaADS.

4.1.1. Results and Discussion

The pH of the liquor was varied from 6.8 to 9.1. The lime solution was found to increase the pH of the mixture monotonically. The change in pH of the liquor, due to the addition of slaked lime solution, is shown in Figure 3. The dependence of the amount of the precipitated crystals on the pH of liquor is given in Figure 4. As the pH of the liquor increased, the amount of crystal precipitated increased. From the Figure 4, the precipitation profile seems to be divided into two distinct regions, namely region-I and region-II. Below pH 8.5, the amount of precipitate formed in the mixture, due to the change in pH, increased very slowly. This region of initial precipitation, or region-I, is where the precipitates are believed to be composed mainly of calcium sulfate and calcium imido disulfonate. The color of the precipitate is white at pH around 7.5. The precipitate gradually turned to yellowish brown in color as the pH of the mixture approaches 8.5. Above a pH of 8.5, the amount of crystal precipitated in the liquor, due to a rising pH, increased rapidly. Thus, the region above a pH of 8.5 may be termed a region of rapid precipitation, or region-II. In this region, the precipitation of iron is significant, and the precipitates turn more brown in color. To avoid excessive precipitation of iron hydroxide, the optimum pH should be

kept somewhere below a pH of 8.5. During the continuous DDO crystallization experiments, the pH of the slurry was maintained in the neighborhood of 8.3.

Results of the analysis of ammonium ion concentration in the solution, after acid hydrolysis of the precipitates obtained in the pH range of 7.0 to 9.0, indicated that approximately 64% of the precipitated crystals are equivalent to CaADS. The precipitation profile of CaADS, due to reaction with Dravo lime, is given in Figure 5. Although the CaADS content increased with an increasing pH, the plot shows at higher values of pH (>8.5), the fraction of CaADS in the precipitate was found to be lower due to a marked increase of iron hydroxide in the precipitate.

4.2 Continuous Precipitation of N-S Compounds

The continuous crystallization of calcium imido disulfonates from FGD scrubbing liquor is not reported in the literature. For the present investigation, a 7-liter bench scale continuous DDO crystallizer was built. The DDO crystallizer employs the principles of a size dependent residence time, which helps to increase the mean size of the particles, and thereby enhances the filterability of the slurry. The DDO design has many advantages. In a DDO operation, a classified overflow stream is removed from the mixed slurry concurrently with a mixed suspension underflow stream. The overflow stream is classified by an arbitrarily chosen fine cut size. The overflow and underflow streams are then combined together to create the slurry product stream. The process flow diagram of a DDO crystallizer is shown in Figure 6. This crystallizer configuration has been discussed extensively in the literature (White and Randolph, 1989; Randolph et. al., 1990; Chang and Brna, 1986; Hulbert and Stephango, 1969). These studies demonstrated that the mean size from a continuous crystallizer can be significantly increased by using the DDO configuration. The

product size distribution by weight is typically a bimodal distribution. The major advantages of a DDO design are high slurry density, larger crystal size, and less vessel fouling.

4.2.1 Experimental Setup

The experimental setup for the continuous precipitation of calcium imido disulfonate is given in Figure 7. A 7-liter plexiglass crystallizer is included in the setup. The scrubbing liquor is stored in a 50 gallon feed tank, and fed to the crystallizer by the mother liquor feed pump. The pH of the liquor during the reaction is controlled by introducing a pH electrode in the DDO crystallizer vessel. The pH electrode is connected to a controller which regulates the rate of lime addition via the lime feed pump, thus the pH of the crystallization reaction is maintained at the desired set point. A 5% (w/v) thiosorbic lime slurry is made from supplied Dravo lime. The lime slaking process is performed by adding one part lime to five parts deionized water with constant mixing at approximately 300 RPM. The mixture is allowed to stand at a constant temperature for 15 minutes. The slaked lime slurry is then sieved through a 200 mesh screen to remove sand and insoluble matter. The thick slurry is diluted to a 5% solution, and stored in a five gallon lime slurry feed tank. The overflow from the DDO crystallizer is continuously drawn off through an inverted glass cone tube (3.5 cm in diameter and 30 cm in length). The underflow of the crystallizer is set to discharge approximately every 40 minutes at a high flow rate in order to avoid clogging of the underflow line. For the periodic discharge of the underflow, a liquid level probe and controller are incorporated into the operation. During the experiment, samples are drawn from the product line of the crystallizer and filtered. The filter cake crystals are dried, and weighed for estimation of the slurry density. The dry crystals are then sieved for size analysis

using an Allen-Bradley sonic shifter. The crystals are also examined in the optical microscope for their habit.

4.2.2 Results and Discussion

For continuous precipitation of CaADS crystals, the mean residence time, τ , of the crystallizer was fixed at one hour. The pH of the reaction slurry was controlled between 8.2 and 8.3. The DDO ratio was varied. In the first experiment, a DDO ratio [$R = (Q_o + Q_u)/Q_u$] of $R=10$ was used. Here Q_o and Q_u represent the crystallization vessel overflow and underflow flow rates, respectively. In a second experiment, the DDO ratio was adjusted to $R=15$. This was done to examine the influence of the DDO ratio on the product mean size and vessel slurry density.

Plots of the cumulative weight versus crystal size for the precipitation of N-S compounds in a DDO configuration are shown in Figures 8 and 10. Figure 8 describes the results of an experimental run where $\tau = 1$ and $R=10$. The mass average crystal size of the CaADS precipitated in this experimental run was found to be $115 \mu\text{m}$ (Figure 8). When the DDO ratio was increased to $R=15$, the mass average crystal size was observed to increase to $127 \mu\text{m}$ (Figure 10). The result of this experiment indicates that a substantial increase in the Sauter mean size may be achieved by varying the DDO ratio. However, at the higher value of R , mixing is a problem due to the increased slurry density. Also, a lower residence time becomes necessary in order to remove a substantial amount of the underflow slurry. Plots of the population density of the crystalline precipitates versus crystal size are given in Figures 9 and 11. Figure 9 describes the results of the experimental run for $R=10$; likewise Figure 11 describes the results for $R=15$. The

precipitation kinetics of N-S compounds in a DDO configuration can be evaluated from these plots.

To confirm the precipitation of N-S compounds in the DDO, elemental analysis was performed on the samples obtained in the two DDO experiments. The analysis was conducted by the Desert Analytics lab in Tucson, AZ. From the analysis report, the N/S molar ratios were calculated to be 0.44 and 0.48 for the precipitates obtained in the DDO experiment when $R=10$ and $R=15$, respectively. This indicates the precipitation of N-S compounds occurred more as calcium imido disulfonate.

Figure 12 shows the photomicrograph of the precipitated crystals formed by adding a lime slurry to the waste scrubbing liquor using the DDO crystallizer configuration. Figures 12(a), (b), and (c) are the photomicrographs of the precipitated N-S containing crystals in the 115 μm (DDO expt. #1), 127 μm (DDO expt. #2), and 273 μm size range. Both Figures 12(a) and (b) indicated presence of the two different habit forms, namely parallelogram and spherical. Among the two habit forms, the parallelogram like shape was also represented in other photomicrographs [Figure 12(d)]. The crystals in Figure 12(d) are mostly in the 40 μm size range.

In Figure 12(c), it is difficult to pinpoint a certain morphology since the crystals are present in an agglomerated state. However, the shapes suggest an agglomeration predominantly of the parallelogram habit form. This observed parallelogram crystalline morphology also indicates the precipitation of N-S compounds mostly as calcium imido disulfonate.

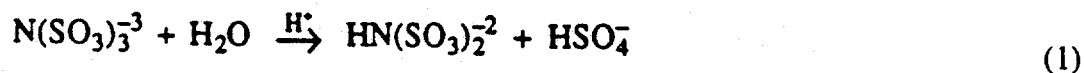
5. Filtration of N-S Containing Compounds

In order to evaluate the filterability of the N-S containing precipitates obtained in the DDO crystallizer, a series of filtration tests were performed with the product slurry. The influence of the commercial filtration aid, diatomaceous earth, on the filtration rate of the slurry was also examined. The result of these standard filtration experiments are given in Table 2. The filtration tests were carried out under vacuum conditions using a Pyrex brand Büchner type funnel with a fritted disc having a pore size of 40-60 μm . The results show the scrubbing liquor, before reaction with lime, took 18 minutes for filtration. This is due to the fine solids contained in the liquor. The filtration time was increased to about 23 minutes following the precipitation of N-S compounds. However, in the presence of diatomaceous earth, the filtration rate was improved noticeably.

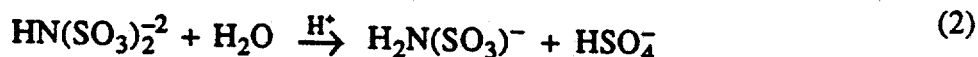
For example, in the presence of 1% diatomaceous earth there is almost a three fold reduction in the filtration time required for the product slurry. The results of these experiments indicate the filterability of the N-S compounds, obtained during the precipitation process in the DDO configured crystallizer, is good and can be improved further with the addition of filtration aids.

6. Hydrolysis of N-S Compounds

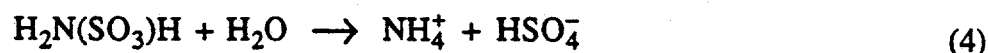
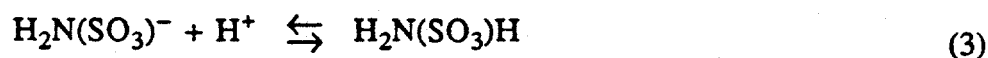
The hydrolysis of N-S containing compounds has been discussed by several authors (Littlejohn and Chang, 1991; Chang et. al., 1982; Nickless, 1968). Noting reaction chemistry, conversion of precipitated CaATS and CaADS to ammonium sulfate may be achieved by the following reaction pathways. ATS is hydrolyzed to ADS by:



This acid-catalyzed reaction occurs rapidly, even under neutral solution conditions, and at 25°C (Sisler and Audrieth, 1938; Chang et. al., 1982; Littlejohn et. al., 1986; Geissler and van Eldik, 1992). ADS is hydrolyzed irreversibly yielding sulfamate as shown below (Doyle and Davidson, 1949).



Sulfamate undergoes hydrolysis to form ammonium and sulfate ions by a mechanism involving a pre-equilibrium between sulfamate ion and sulfamic acid, followed by slow hydrolysis of the acid (Maron and Berens, 1950; Candlin and Wilkins, 1960; Hughes and Lusty, 1977; Littlejohn et. al., 1989):



From the hydrolysis mechanisms, it is difficult to describe the hydrolysis of N-S compounds precipitated from the scrubbing liquor in terms of reagents since the precipitates contain various species of N-S compounds at different concentrations. It is noted that the ammonium ion is an end product which forms only from decomposition of the N-S compounds by hydrolysis. Thus, concentration of the ammonium ion in a hydrolyzed crop can be used as a measure of overall hydrolysis. In order to characterize the progression of hydrolysis, a definition of the extent of hydrolysis, $X_{\text{NH}_4^+}$, is submitted as the ratio of the existing ammonium ion concentration, $C_{\text{NH}_4^+}$, to ammonium ion concentration at completion of hydrolysis, $C_{\text{NH}_4^+}^\infty$. This definition was made since the goal of hydrolysis was to convert the precipitated N-S compounds to ammonium sulfate regardless of formation of intermediate species. Thus, the extent of hydrolysis is calculated as

$$\text{Extent of hydrolysis, } x_{\text{NH}_4^+} = \frac{C_{\text{NH}_4^+}}{C_{\text{NH}_4^+, \infty}} \quad (5)$$

Here, the concentration of ammonium ion at completion of hydrolysis is implicitly related to the total concentration of N-S compounds before hydrolysis.

The extent of hydrolysis of the N-S compounds was found to be insensitive to the initial concentration of the reactant. Thus, the overall kinetics for conversion of N-S compounds to ammonium sulfate, which covers all the steps in equations (1) - (4), may be represented as a first order irreversible reaction in terms of concentration of the N-S compounds:

$$\ln \left(\frac{C_{\text{N-S}}}{C_{\text{NH}_4^+, \infty}} \right) = \ln (1 - x_{\text{NH}_4^+}) = -k f t \quad (6)$$

where $C_{\text{N-S}}$ is the concentration of the N-S compounds, k is a rate coefficient, C_{H^+} is the concentration of hydrogen ions, and f is a function which is mainly dependent on C_{H^+} . It is assumed $C_{\text{NH}_4^+} + C_{\text{N-S}} = C_{\text{NH}_4^+, \infty} = \text{constant}$. The kinetic expression in equation (6) is realistic since previous studies showed that each step of the hydrolysis, given by equations (1)-(4), follows first order kinetics. Assuming that the variation in ionization of sulfuric acid is small enough within the narrow temperature range, f in equation (6) would be nearly constant. The given kinetic expression is then integrated to yield

$$\frac{d}{dt} C_{\text{NH}_4^+} = -\frac{d}{dt} C_{\text{N-S}} = k C_{\text{N-S}} f(C_{\text{H}^+}, \dots) \quad (7)$$

This expression shows that hydrolysis of N-S compounds follows the first order kinetics. Thus, a plot of $\log(1 - x_{\text{NH}_4^+})$ versus time would yield a straight line, with its slope proportional to the rate coefficient.

6.1 Experimental Procedure

The experimental setup for the hydrolysis of N-S compounds is given in Figure 13. A one liter jacketed glass reactor is incorporated in the setup. A temperature probe and controller are used to regulate the temperature of the reaction mixture at the set point. In order to minimize the loss of liquid due to evaporation, a condenser tube is included.

To begin, 500 ml of 1M H_2SO_4 is introduced inside the glass vessel and heated up to 95°C. The hydrolysis reaction is initiated by adding 10 grams of uniform size dry crystalline N-S containing precipitates obtained from the DDO crystallizer. A magnetic stirring bar was used to keep the slurry uniformly mixed. Five ml liquid samples were taken at various times during the reaction. The samples were sent to Copper State Analytical Lab in Tucson, AZ for analysis of ammonia-Nitrogen concentration. The concentration of NH_4^+ in the solution is calculated from the total ammonia-Nitrogen concentration. The ammonia-Nitrogen concentration was calculated according to the EPA method No. 4500-NH3F.

6.2. Results and Discussion

The results of the hydrolysis of N-S compounds are given in Figure 14. It is clear from the figure that at time zero there is no NH_4^+ in the solution. The concentration of NH_4^+ in the solution increased very rapidly at the initial stage of the hydrolysis, and then reached a plateau, indicating the completion of hydrolysis. From Figure 14, it is seen that the hydrolysis reaches completion within 12 hours. This is an attractive feature of the lime/limestone process versus the K_2SO_4 process. The precipitates of N-S compounds obtained by the K_2SO_4 process have been found to require over 20 hours to reach complete hydrolysis. Thus, the lime/limestone process is

more economic than the K_2SO_4 process for regeneration of FGD waste liquor. The concentration of ammonium ion at the completion of hydrolysis was 0.12 moles/liter. Figure 14 indicates that the hydrolysis of N-S compounds obeys first order kinetics.

The progress of the hydrolysis reaction versus time has been plotted in Figure 15. In Figure 15, it is noted that almost 90% of the hydrolysis is completed within 6 hours, this is half the time required for complete hydrolysis. Both the temperature and time required to complete the hydrolysis experiment may be reduced by conducting the experiment under a higher pressure. The plot of $\log(1-X_{NH_4+})$ versus time, shown in Figure 16, indicates that the acid catalyzed hydrolysis is essentially a first order irreversible reaction. The slope of this line is the rate coefficient for the hydrolysis reaction.

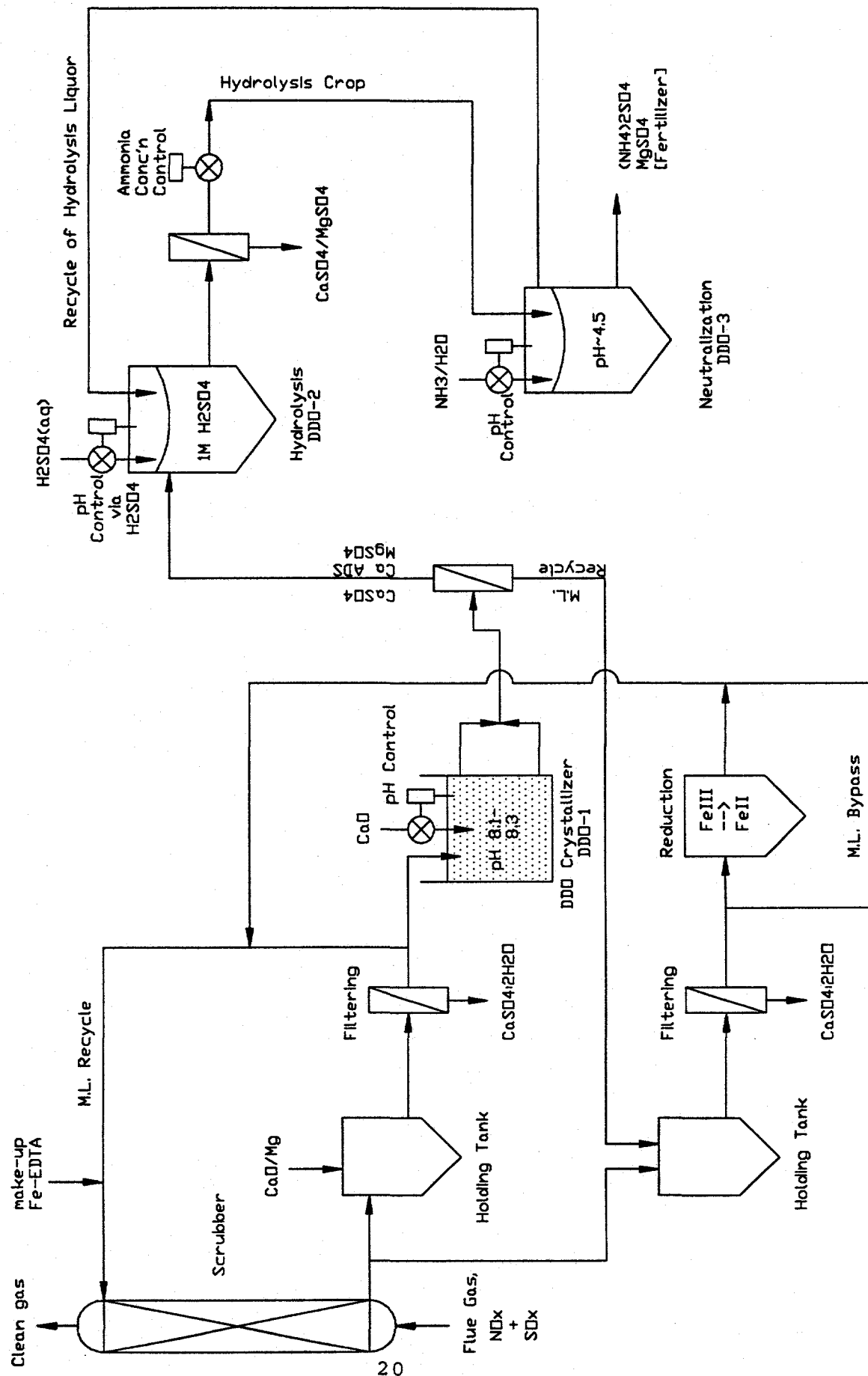


Figure 2. Process Flow Diagram for the lime/limestone process.

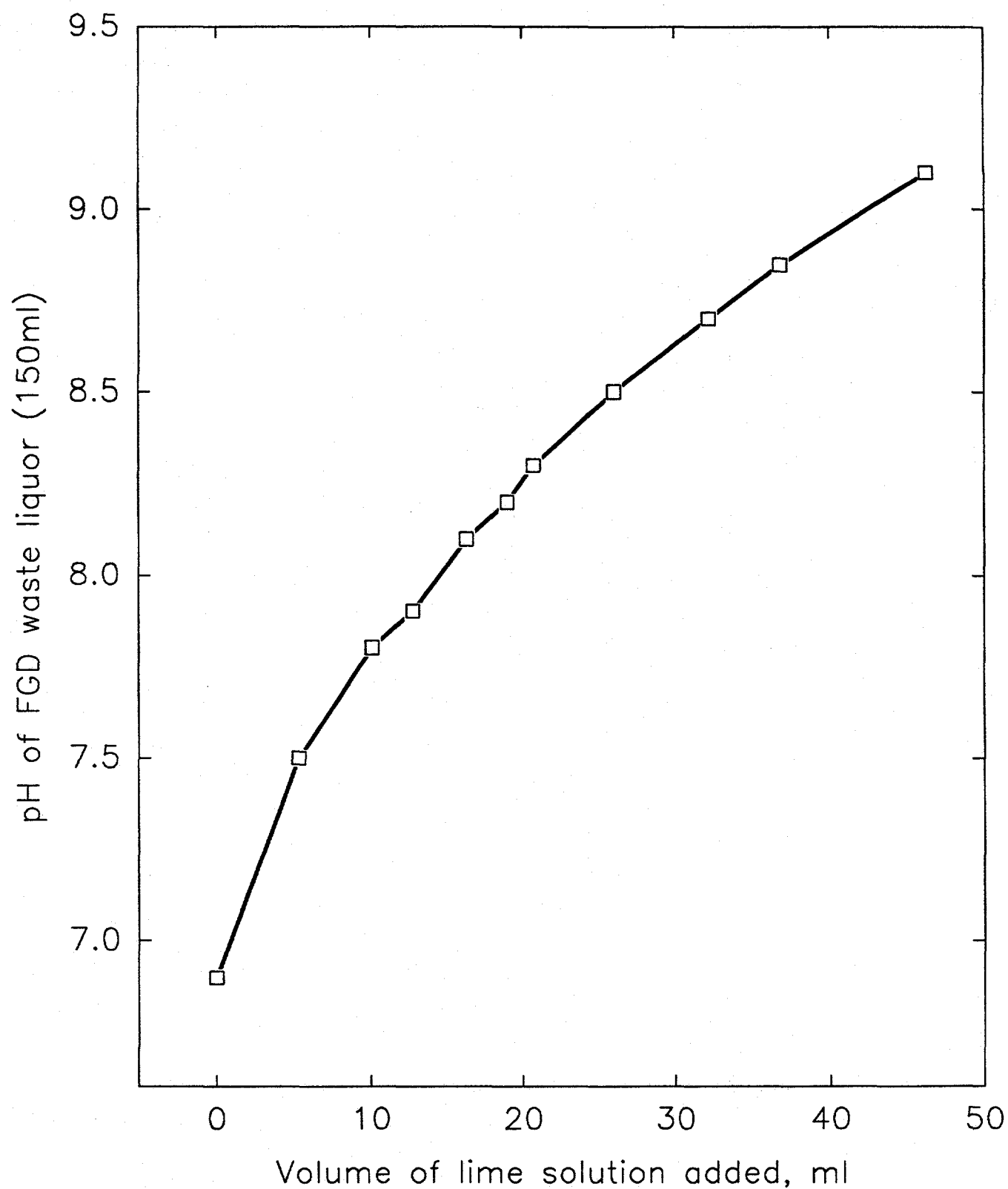


Figure 3. Change in solution pH of FGD scrubbing waste liquor due addition of lime

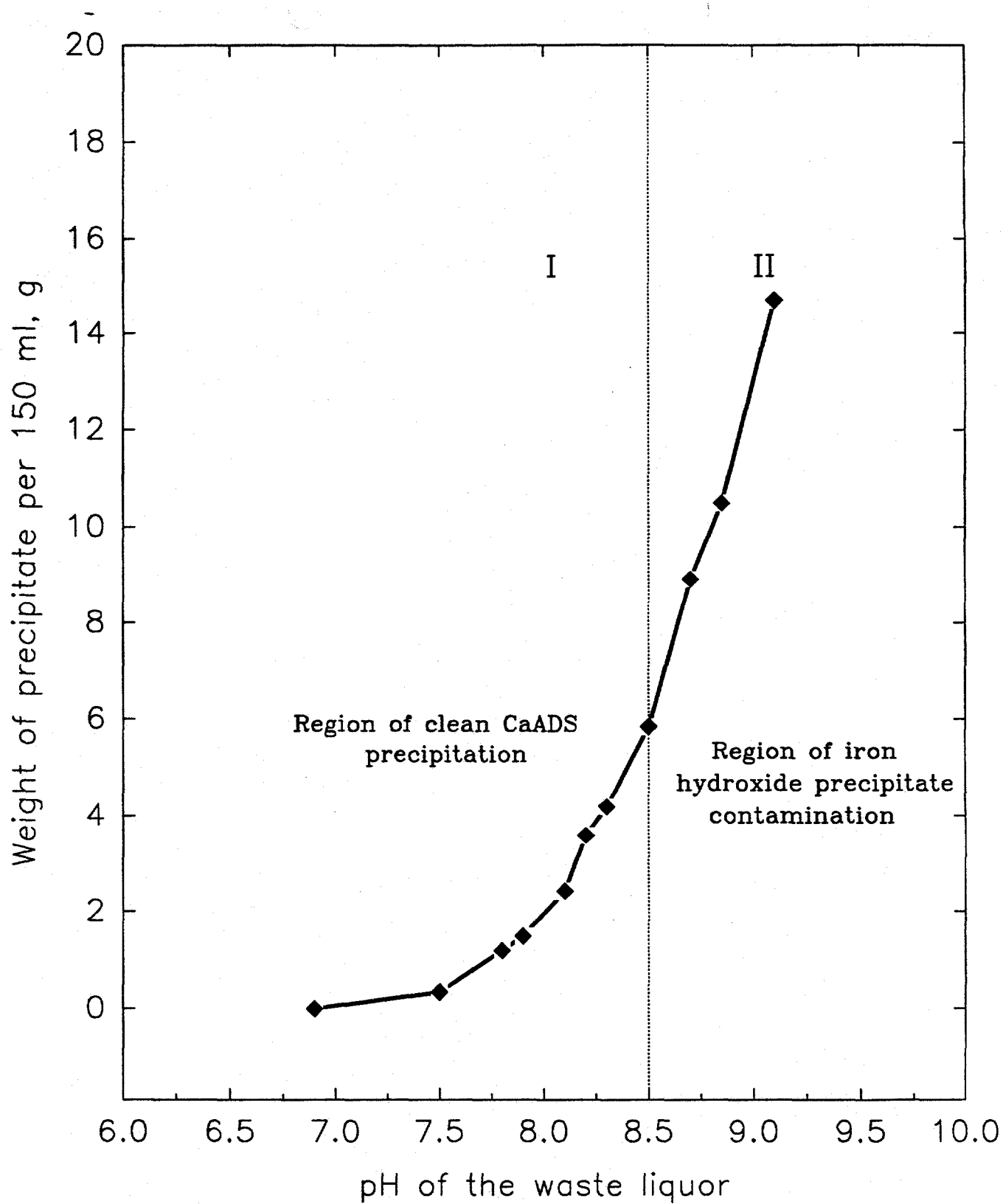


Figure 4. Precipitation profile of FGD waste scrubber liquor in batch operation as a function of pH

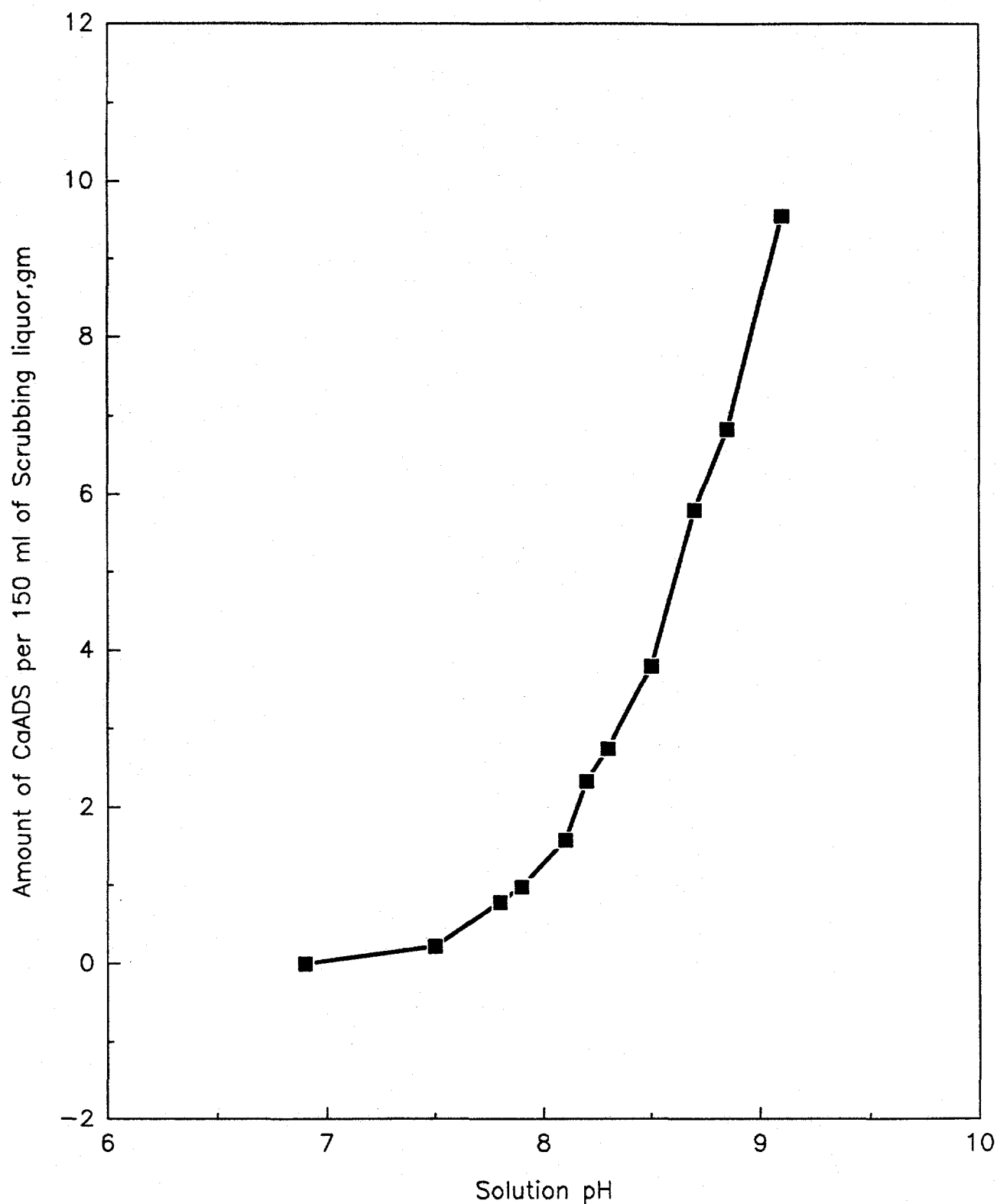
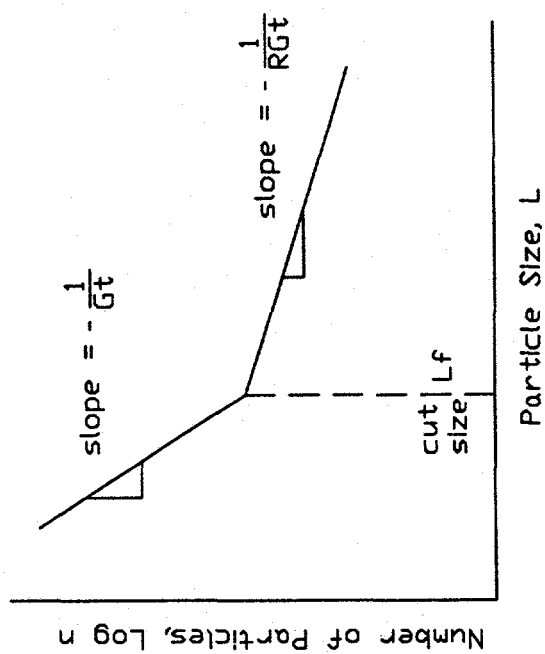
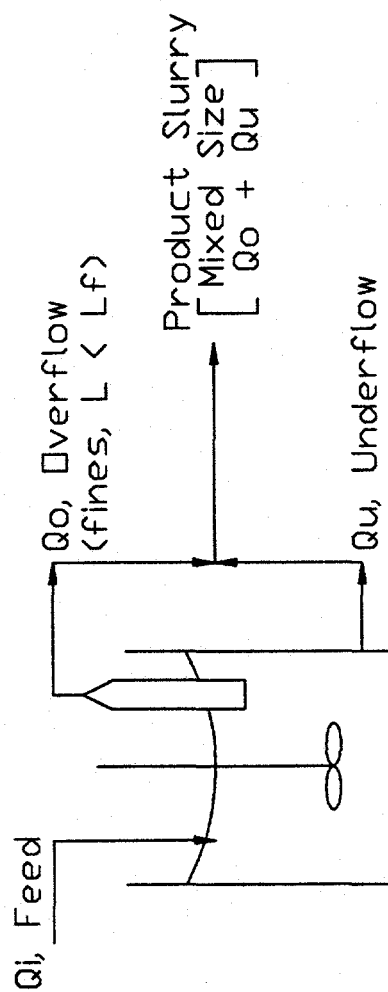
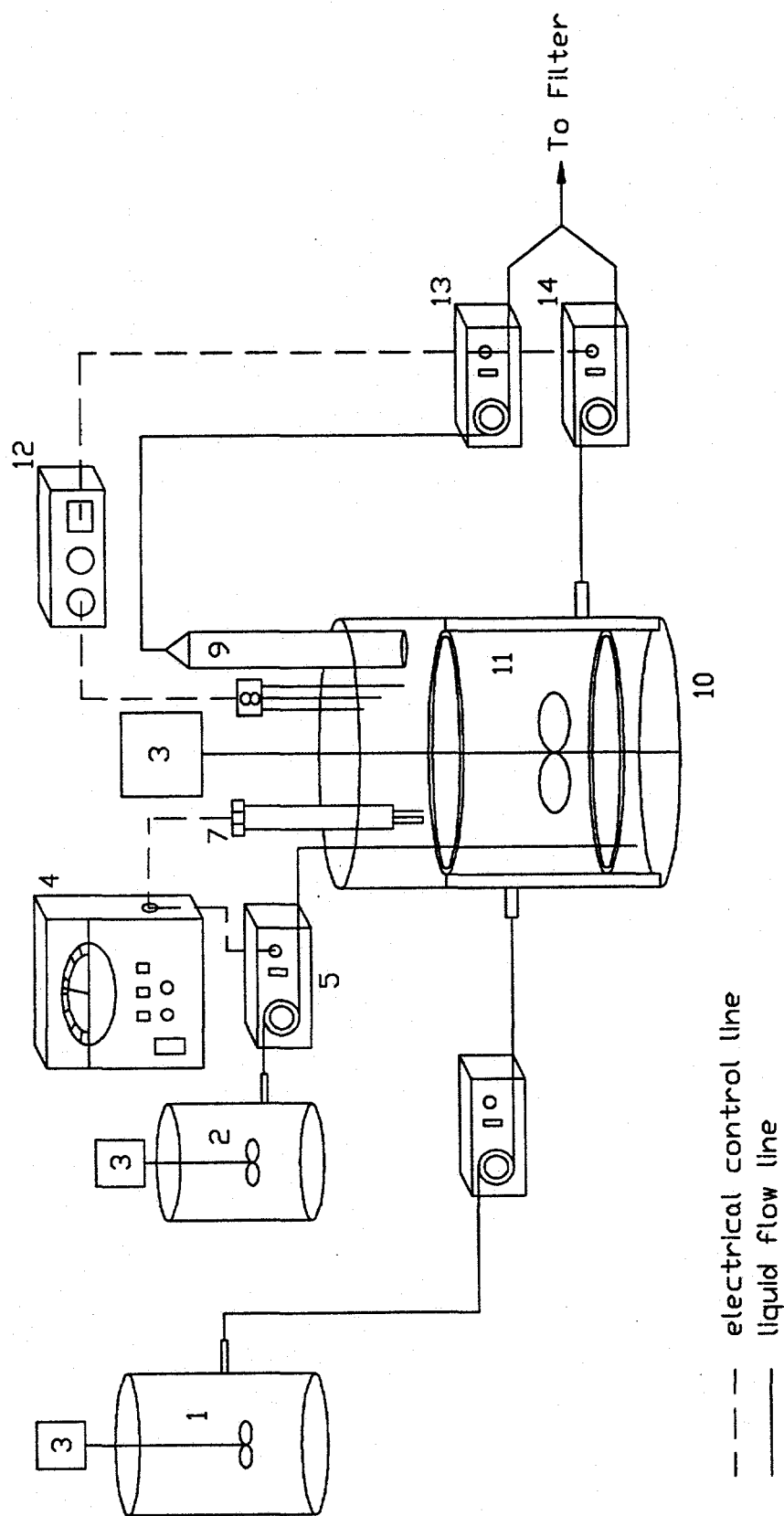


Figure 5. Amount of Calcium imido disulfonate crystals precipitated from FGD waste scrubbing liquor with the addition of Dravo lime expressed as a function of solution pH



G = growth rate of crystals
 t = residence time
 R = DDD ratio = $\frac{Q_o + Q_u}{Q_u}$

Figure 6. Schematic diagram of DDD crystallizer operation.



- | | | |
|--------------------------|--------------------------|-----------------------------|
| 1. M.L. feed tank | 6. M.L. feed pump | 11. Draft tube with baffles |
| 2. Lime slurry feed tank | 7. pH electrode | 12. Liquid level controller |
| 3. Stirrer | 8. Liquid level probe | 13. Overflow pump |
| 4. pH controller | 9. Invert cone tube | 14. Underflow pump |
| 5. Lime slurry feed pump | 10. 7-liter crystallizer | |

Figure 7. Schematic diagram of the experimental setup for continuous precipitation of N-S compounds from Dravo Lime waste scrubber liquor.

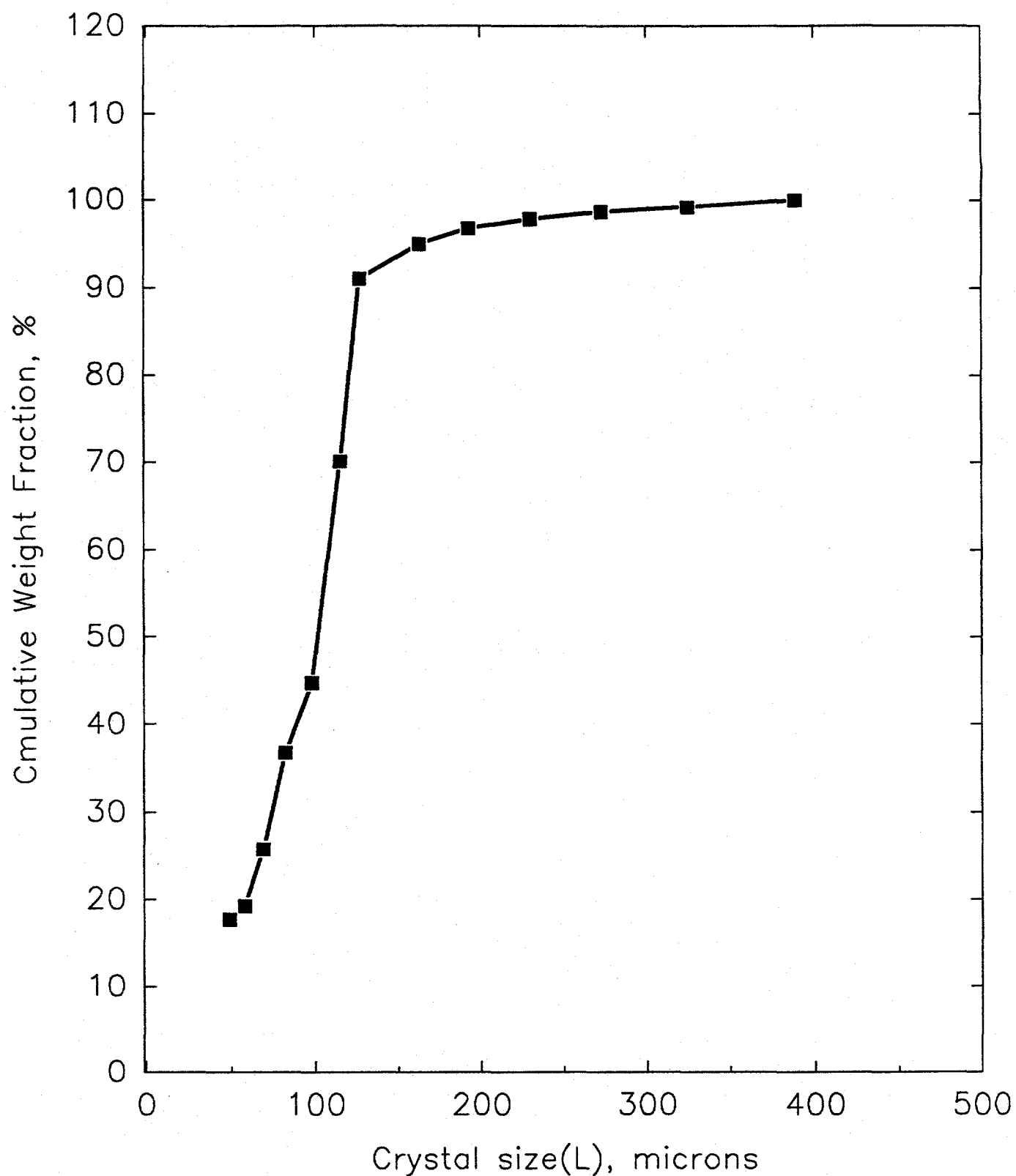


Figure 8. Cumulative weight fraction vs. size of the CaADS crystals obtained from DDO crystallizer operation

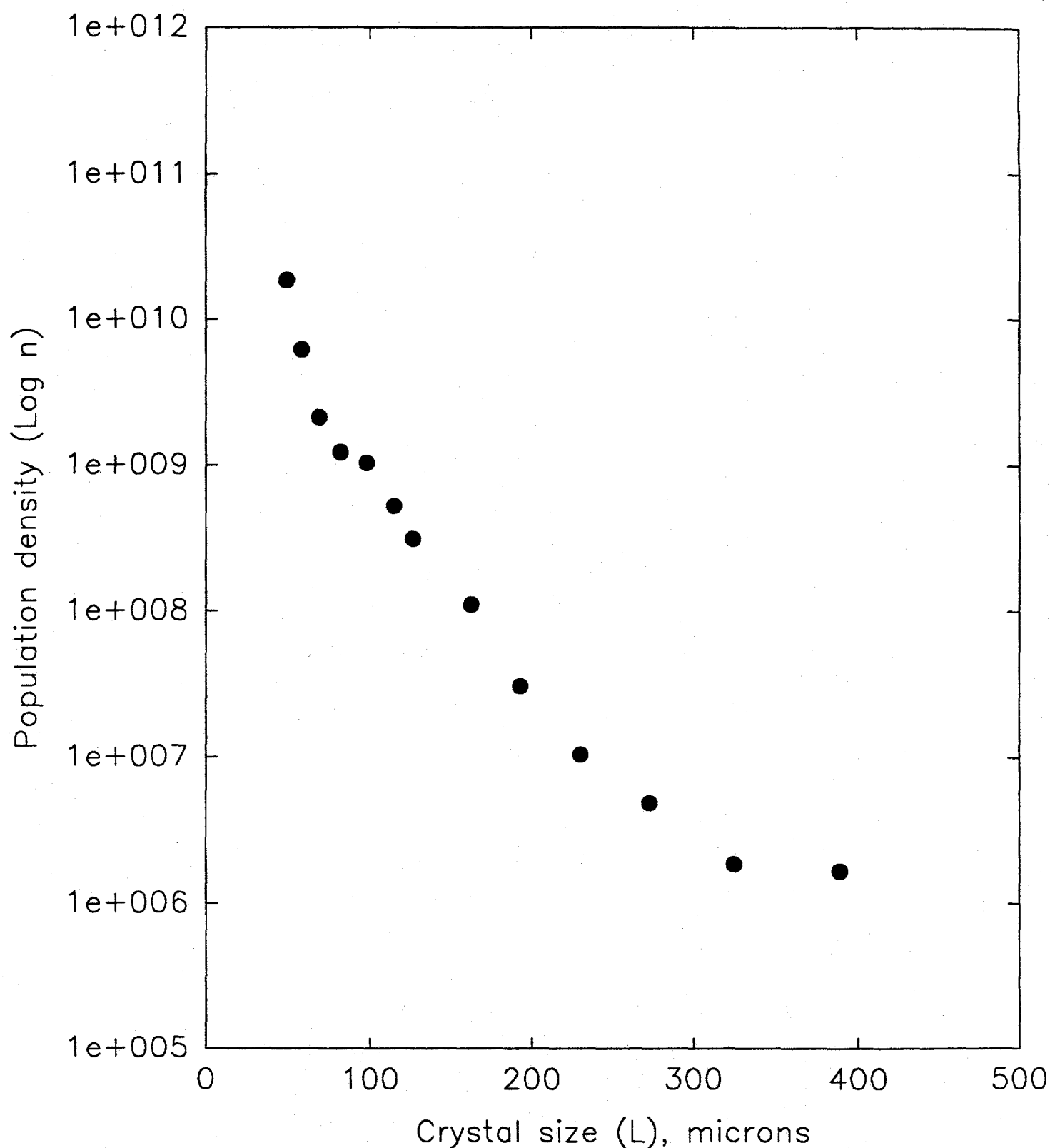


Figure 9. Population density vs. size of CaADS crystals obtained from DDO crystallizer by reaction of FGD waste liquor with Dravo lime

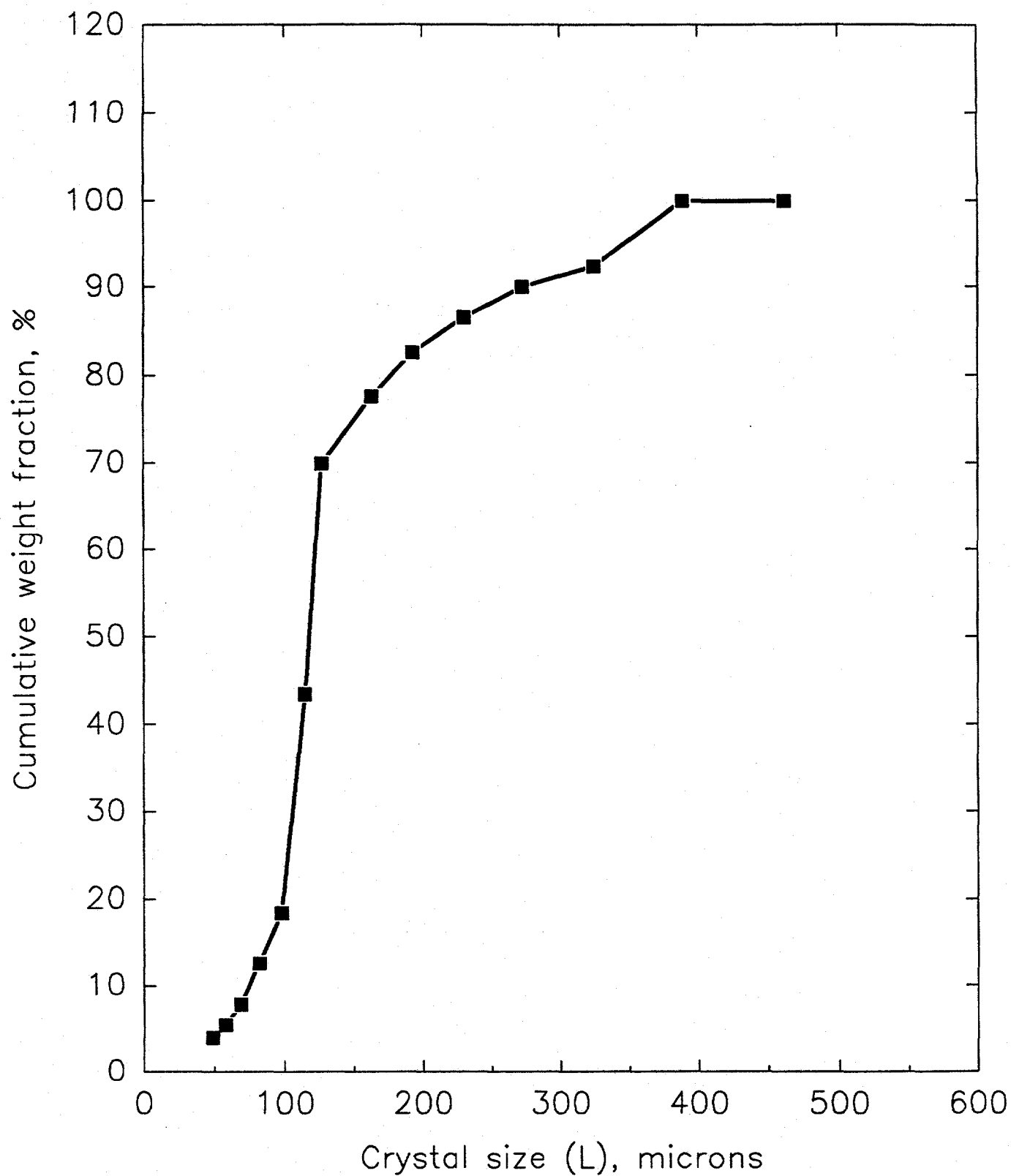


Figure 10. Cumulative weight fraction against the size of calcium imido disulfonate crystals obtained by reaction with lime with FGD waste liquor

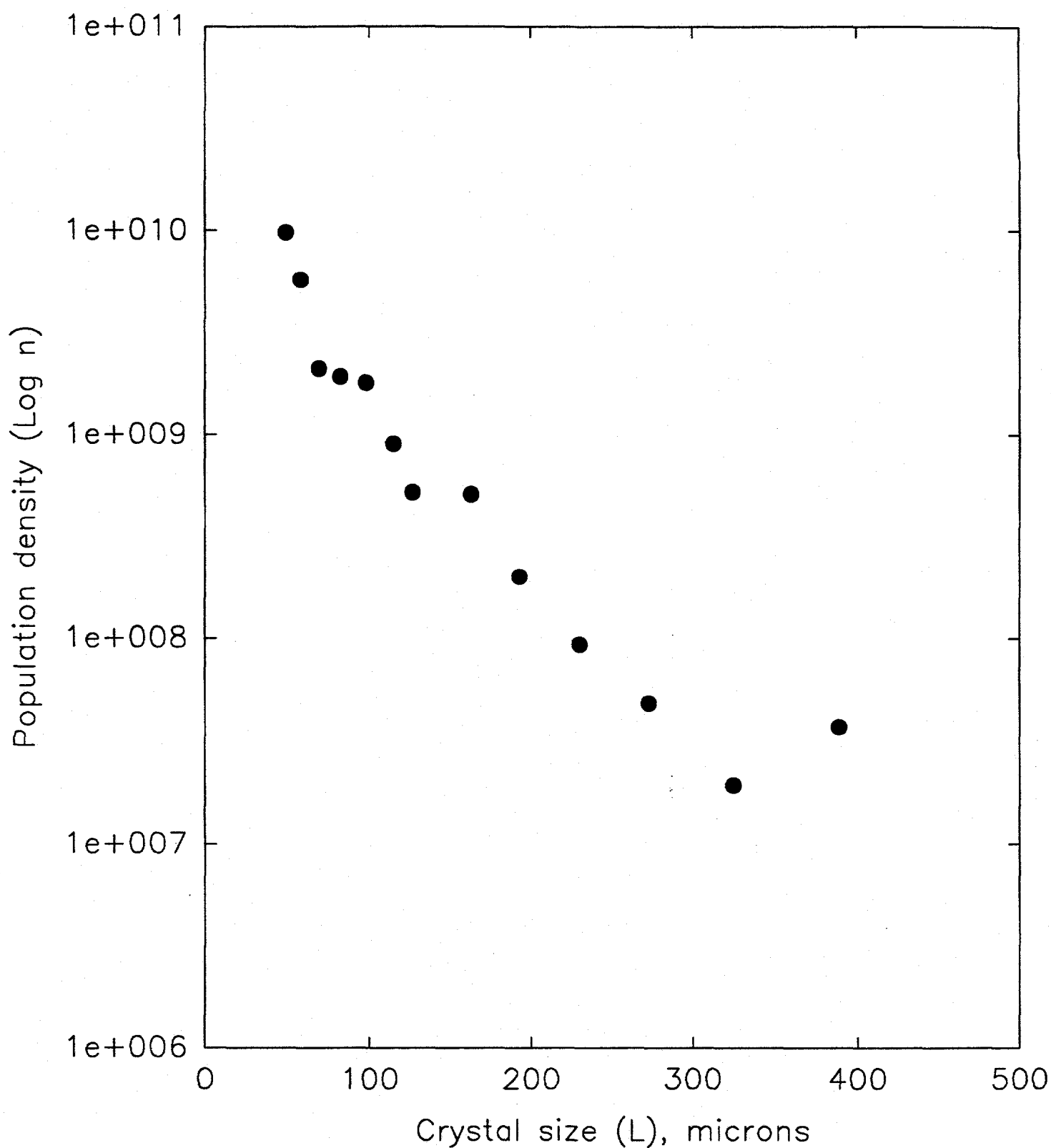


Figure 11. Population density of the crystal precipitates vs. crystal size of the mixed product stream obtained in DDO operation operation



(a)

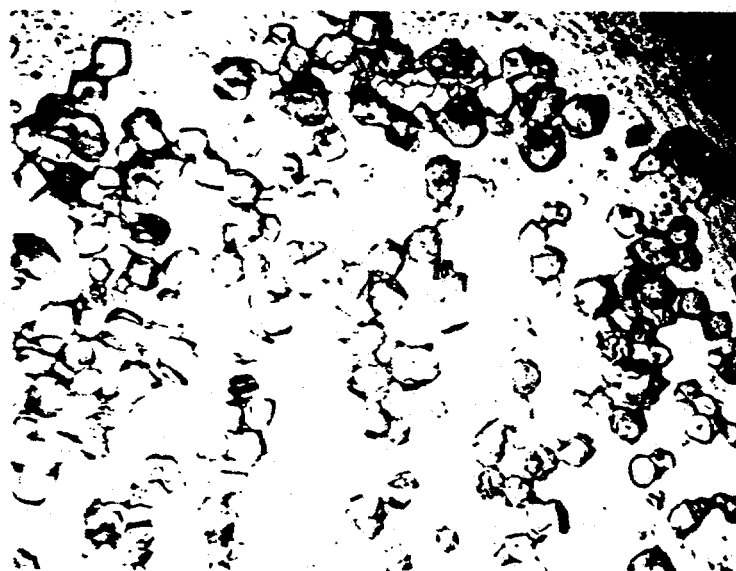


(b)

Figure 12. Photomicrographs of the crystals obtained from the DDO crystallizer
Mass Mean Size of the Crystals are (a) $115\mu\text{m}$: (b) $127\mu\text{m}$

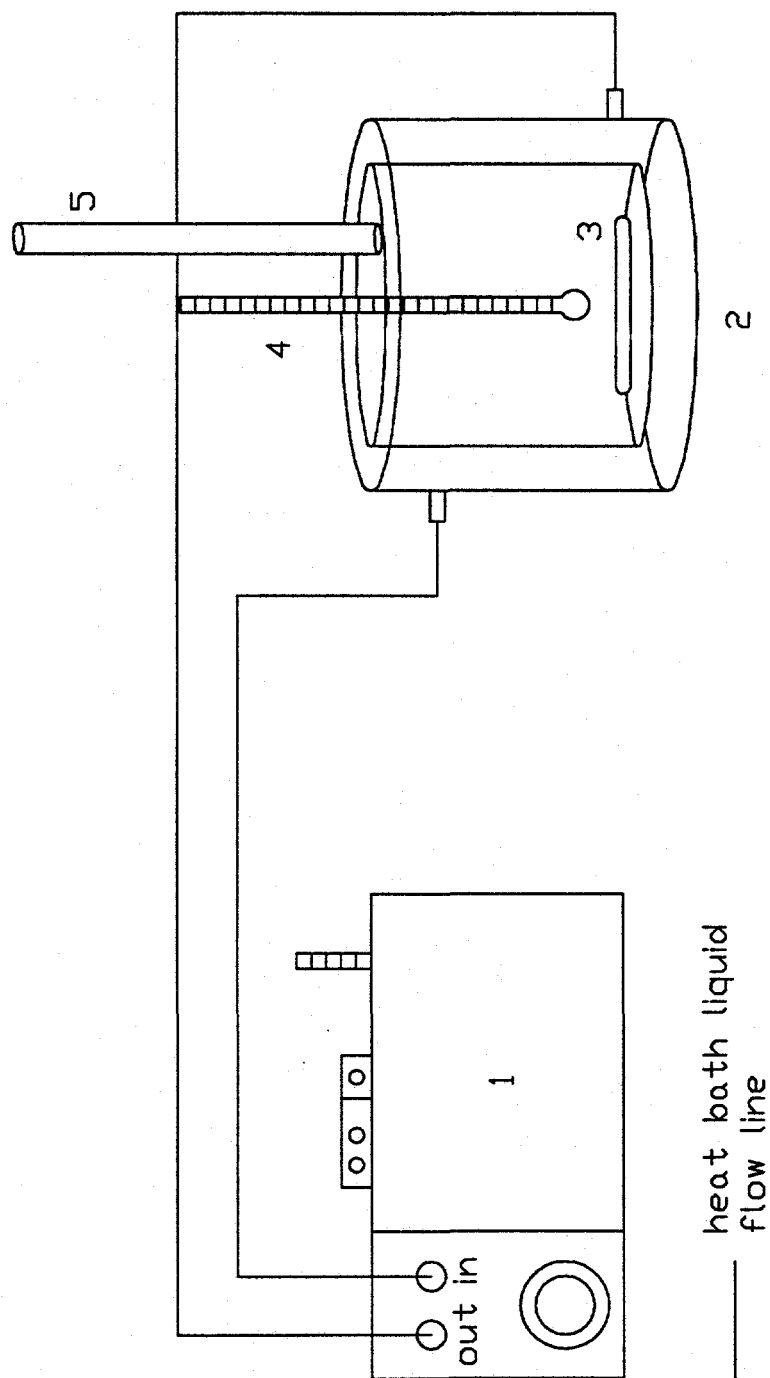


(c)



(d)

Figure 12A. Photomicrographs of the crystals obtained from the DDO crystallizer.
Mass Mean Size of the Crystals are (c) $273\mu\text{m}$; (d) $40\mu\text{m}$



1. Temperature controller and pump
2. Jacketed batch hydrolyzer
3. Stirring rod
4. Thermometer
5. Condenser tube

Figure 13. Experimental setup for the acid hydrolysis of CaADS obtained from the DDD crystallizer.

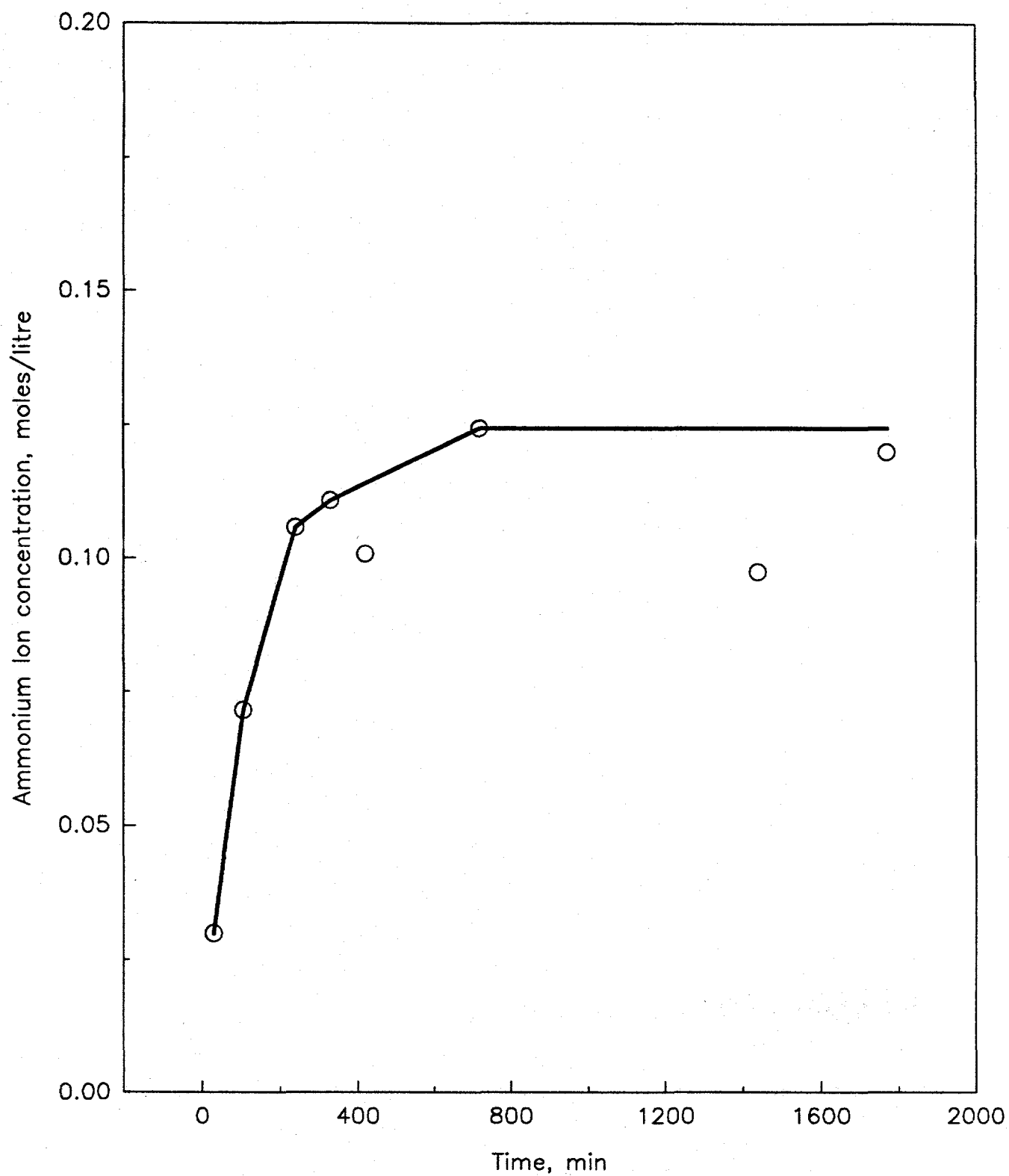


Figure 14. Hydrolysis profile of CaADS in 1M Sulfuric Acid Solution at about 95°C

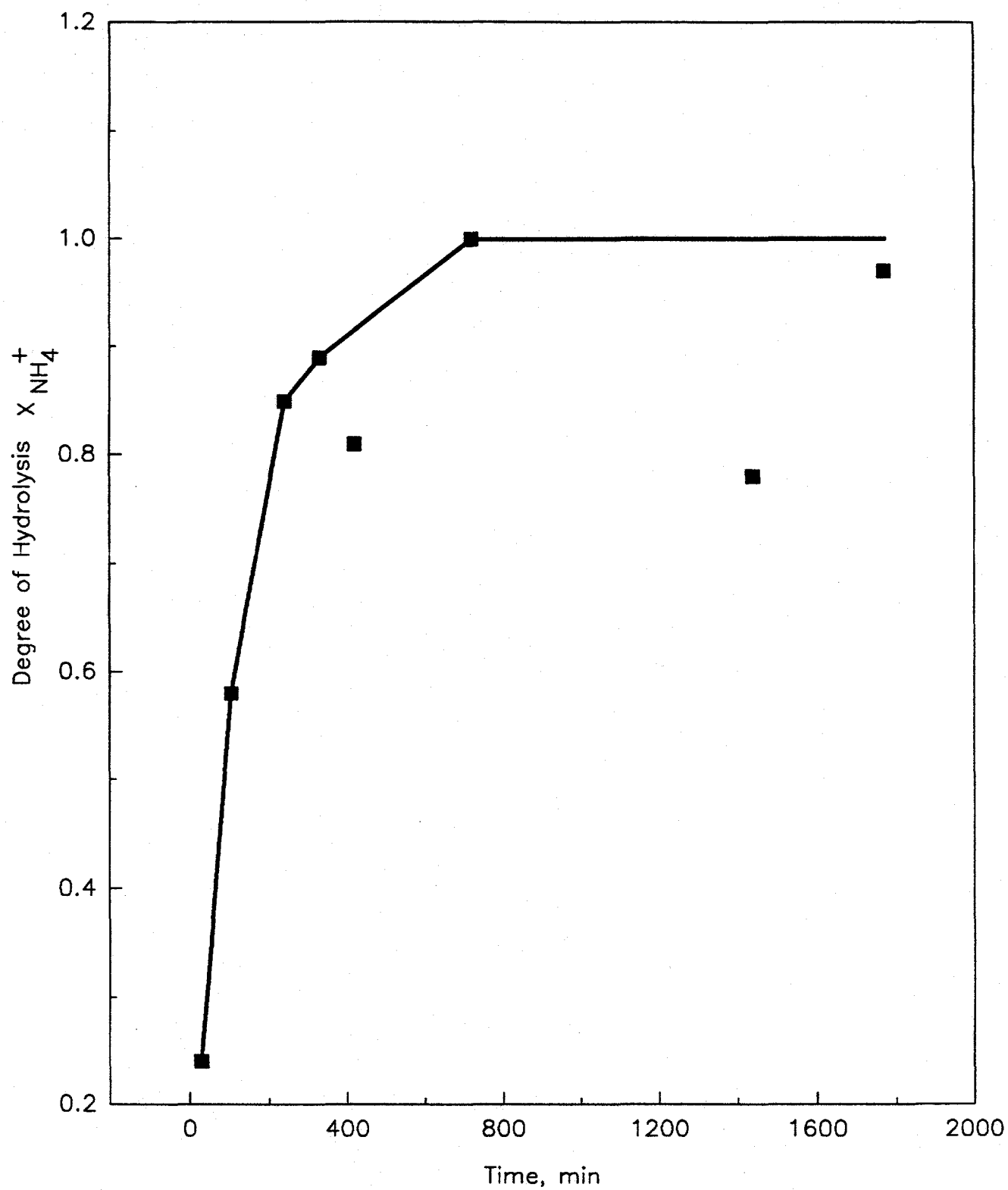


Figure 15. Progress of hydrolysis of CaADS with time in 1M Sulfuric Acid Solution at about 95°C

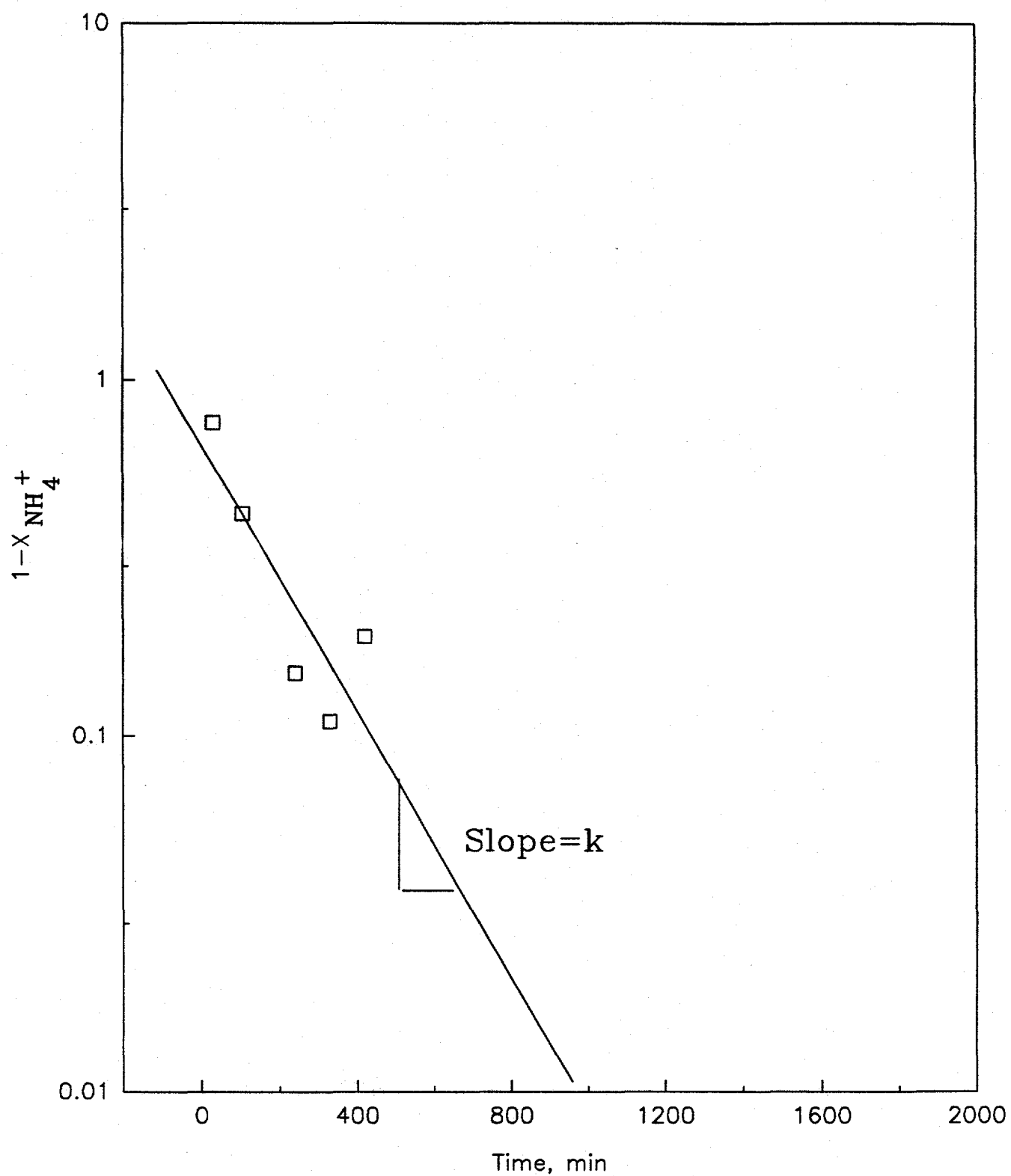


Figure 16. Kinetics of hydrolysis of CaADS in sulfuric acid environment

Table 1. Typical composition and physical properties of the waste liquor provided by Dravo Lime Co.

Compounds	Concentration
MgSO ₄ /MgSO ₃	~10000
N-S Compounds	~5000
CaSO ₄ /CaSO ₃	~1000
Na ₂ SO ₄	~1000
FeSO ₄ /EDTA	~3000
pH	6.5-7.0
Density, g/cm ³	1.11
Viscosity, cP	1.48

Table 2. Results of the Standard Filtration Tests using product slurry from the DDO Crystallizer.

Filtration Area = 50.24 cm²

Pressure Difference, ΔP = 7.3 psi

Filtration Aid = Diatomaceous Earth

Description of Filtration Test	Volume of Product Slurry, ml	Filtration Time, minutes
Scrubbing Liquor before reaction with lime	1000	17.8
Product Slurry after reaction with lime	1000	22.9
Product Slurry in presence of 0.5% (w/v) filtration aid	1000	16.9
Product Slurry with 1% (w/v) filtration aid	1000	8.1
Product Slurry with 2% (w/v) filtration aid	1000	4.5
Product Slurry with 5% (w/v) filtration aid	1000	1.9

References

Candlin, J.P. and R.G. Wilkins, "Sulphur-Nitrogen Compounds. Part I. The Hydrolysis of Sulphmate Ion in Perchloric Acid", *J. Chem. Soc. (London)*, 4236 (1960).

Chang, J.C.S. and Brna, "Gypsum Crystallization for Limestone FGD", *Chem. Engineering Progress*, 51 (1986).

Chang, S.G., Littlejohn, D., Lin, N.H., "Kinetics of Reactions in a Wet Flue Gas Simultaneous Desulfurization and Denitrification System", *Flue Gas Desulfurization*, Hudson, J.L., Rochelle, G.T., Eds., *ACS Symp. Ser.*, No. 188, 127, (1982).

Chang, S.G. "Technical Analyses of a Wet Process for Flue Gas Simultaneous Desulfurization and Denitrification", in *ACS Symp. Ser.*, No. 319, Fossil Fuel Utilization: Environmental Concerns, R. Markuszewsk and B.D. Blaustem, eds., 127 (1982).

Doyle, G.J., Davidson, N., "The Kinetics of the Acid-Catalyzed Hydrolysis of Amine Disulfonate Ion; The Third Ionization Constant of Amine Disulfonic Acid", *J. Amer. Chem. Soc.*, 71, 3491, (1949).

Faucett, H.L., J.D. Maxwell, and T.A. Burnett, Technical Assessment of NO_x Removal Processes for Utility Applications, EPA Report, EPA-600/7-77-127 (November 1977).

Geissler, M., van Eldik, R., "Development of a Gradient Ion-Pair Chromatographic Procedure for the Simultaneous Detection of Nitrogen-Sulfur Oxides Produced During the Reaction of SO_x and NO_y Species in Aqueous Solution", *Anal. Chem.*, 64, 3004, (1992).

Hughes, M.N., Lusty, J.R., "Kinetics of Hydrolysis of Sulfamic Acid in Concentrated Perchloric Acid Solutions", *J. Chem. Soc., Dalton Trans.*, 509, (1977).

Hulburt, H.M. and Stephango, D.G. "Design Models for Continuous Crystallizers with Double Draw-Off", *CEP Symposium Series*, 95, 65:50, (1969).

Kwan, T.M., and Randolph, A.D., "Regeneration of Flue Gas Desulfurization Waste Liquors: Precipitation and Hydrolysis of Nitrogen-Sulfur Compounds", *Ind. Eng. Chem. Res.*, 33, 4, 942, (1994).

Littlejohn, D., Chang, S.G., "Determination of Nitrogen-Sulfur Compounds by Ion Chromatography", *Anal. Chem.*, 58, 158, (1986).

Littlejohn, D., Chang, S.G., "Solubility of the Potassium Salts of Nitrogen-Sulfur Compounds in Aqueous Solution", *Ind. Eng. Chem. Res.*, b, 30, 2350, (1991).

Littlejohn, D., Wizansky, A.R., Chang, S.G., "The Dissociation Constant and Acid Hydrolysis Rate of Hydroxysulfamic Acid", *Can. J. Chem.*, **67**, 1596, (1989).

Maron, S.H. and A.R. Berens, "The Kinetics of Hydrolysis of the Sulfamate Ion", *J. Amer. Chem. Soc.*, **72**, 3571 (1950).

Martin, A.E., Emission Control Technology for Industrial Boilers, Noyes Data Corp., Park Ridge (1981).

Nickless, G., Inorganic Sulphur Chemistry, Elsevier, New York, pp. 607-667 (1968).

Randolph, A.D., Mukhopadhyay, S., Sutradhar, B.C., Kendall, R., "The Double Draw-Off Crystallizer: A Major Player in the Acid Rain Game?", *AIChE Symp. Ser.*, **438**, 115, (1990).

Randolph, A.D., Unpublished Work, (1993).

Sada, E., H. Kumazawa, and Y. Yoshikawa, "Simultaneous Removal of NO and SO₂ by Absorption into Aqueous Mixed Solutions", *AIChE J.*, **34**, 1215 (1988).

Sada, E., H. Kumazawa, I. Kudo, and T. Kondo, "Individual and Simultaneous Absorption of Dilute NO and SO₂ in Aqueous Slurries of MgSO₃ with Fe^{II}-EDTA", *Ind. Eng. Chem. Process Des. Dev.*, **19**, 377 (1980).

Sisler, H. and L.F. Audrieth, "Potassium Nitrilosulfonate", *J. Amer. Chem. Soc.*, **60**, 1947 (1938).

White, E.T. and Randolph, A.D., "Optimum Fines Size for Classification in Double Draw-Off Crystallizers", *Ind. Eng. Chem. Res.*, **28**, 3, pp. 276-284, (1989).