Production of Ammonium Sulfate Fertilizer from FGD Waste Liquors

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

First Quarterly Technical Report, 1995

Submitted to

U. S. Department of Energy
Pittsburgh Energy Technology Center
P. O. Box 10940
Pittsburgh, PA 15236-0940

by

A. D. Randolph, S. Mukhopadhyay and E. Unrau
Department of Chemical and Environmental Engineering
University of Arizona
Tucson, AZ 85721

RECEIVED
JSDOE/PETC
95 MAY -5 AM 8:58
ACQUISITION & ASSISTANCE DIV.

US/DOE Patent clearance is ^{not} required prior to the publication of this document

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Table of Contents

Progress Summary	3
List of Figures	5
List of Tables	6
1. Introduction	7
2. Physical-Chemical Analysis of Nitrogen-Sulfur Containing Compounds	7
3. Hydrolysis of Nitrogen-Sulfur Containing Compounds	8
3.1. Experimental Procedure	9
3.2. Results and Discussion	9
4. Crystallization of $(\text{NH}_4)_2\text{SO}_4$ from the Hydrolyzed Liquor	10
4.1. Batch Crystallization of $(\text{NH}_4)_2\text{SO}_4$ from the Hydrolyzed Liquor	11
4.2. Results and Discussion	12
5. Optimization of Process Variables by Computer Simulation	13
References	17

PROGRESS SUMMARY

During this reporting period the hydrolysis experimentation was extended. Hydrolysis of Nitrogen-Sulfur Containing Compounds (N-SCC) was carried out at high temperature and pressure with varying sulfuric acid concentration. The purpose of these experiments was to determine the influence of temperature and acid concentration on time required for complete hydrolysis of N-SCC.

An autoclave (Hirayama Model #HA-MII) was employed for the high temperature/pressure hydrolysis experiments. An ammonia specific electrode (gas sensing) was purchased to determine the concentration of ammonium ion in the hydrolyzed liquor.

The result of the hydrolysis experiment indicated a large reduction in time for complete hydrolysis of the Ca salt of N-SCC. However, the varying acid concentration was not found to influence the rate of hydrolysis of the N-SCC. The physical-chemical analysis of the N-SCC obtained by re-liming the waste scrubbing liquor (containing the Fe-EDTA complex) was found to contain a high quantity of sodium. Hence, the N-SCC is believed to be a double salt of calcium and sodium.

The final product, $(\text{NH}_4)_2\text{SO}_4$, was obtained in experimentation using an evaporative crystallizer. The clean hydrolyzed liquor was neutralized with a strong NH_3 solution before the final crystallization of $(\text{NH}_4)_2\text{SO}_4$. The size of the ammonium sulfate crystals was found to be very large ($\sim 400 \mu\text{m}$).

Theoretical crystal size distribution studies were performed by computer simulation techniques. The results of these studies indicate the ratio (DDO to MSMR) of the mass mean crystal size distribution could be increased by at least a factor of three. Also, the slurry density

ratio (DDO to MSMPR) could be increased by a factor of more than 20. To increase the accuracy and completeness of these simulations, further DDO and MSMPR crystallizer runs are necessary.

One obstacle for smooth progress of the present study is the limited supply of waste scrubbing liquor. No DDO or MSMPR experimentation was conducted due to the lack of waste scrubbing liquor. To study the influence of many process variables on the optimum mean crystal size, it is necessary to conduct further tests using the scrubbing liquor.

List of Figures

Figure 1. Scanning electron photomicrograph of the calcium salt of N-S compounds	20
Figure 2. Surface element analysis for SEM photograph 1	21
Figure 3. X-ray mapping of elements present on the surface of N-S containing compounds	22
Figure 4. Calibration curve for estimation of NH_4^+ ion concentration in hydrolyzed liquor	23
Figure 5. Plot of the high temperature/pressure acid hydrolysis at 0.5 M H_2SO_4	24
Figure 6. Plot of the high temperature/pressure acid hydrolysis at 1.0 M H_2SO_4	25
Figure 7. Plot of the high temperature/pressure acid hydrolysis at 2.0 M H_2SO_4	26
Figure 8. Comparison of the acid hydrolysis at 95°C and 115°C in 1 M H_2SO_4	27
Figure 9. Process Flow Diagram for the production of $(\text{NH}_4)_2\text{SO}_4$	28
Figure 10. Solubility of $(\text{NH}_4)_2\text{SO}_4$ in an aqueous sulfuric acid solution	29
Figure 11. Photomicrograph of gypsum crystals obtained from the hydrolyzed liquor	30
Figure 12. Crystallization of $(\text{NH}_4)_2\text{SO}_4$ from the neutralized hydrolyzed liquor	31
Figure 13. Cumulative Weight Fraction vs. Size of $(\text{NH}_4)_2\text{SO}_4$ crystals obtained by evaporative crystallization	32
Figure 14. Population Density vs. Size of $(\text{NH}_4)_2\text{SO}_4$ obtained in batch crystallization	33
Figure 15. Photomicrograph of $(\text{NH}_4)_2\text{SO}_4$ crystals at initiation of crystallization; magnification = 40X	34
Figure 16. Photomicrograph of $(\text{NH}_4)_2\text{SO}_4$ crystals at initiation of crystallization; magnification = 100X	34
Figure 17. Photomicrograph of sieved $(\text{NH}_4)_2\text{SO}_4$ crystals; size = 420 μm ; 40X	35
Figure 18. Mass Mean Size vs. X_f ; $j = 0.5$	36

Figure 19. Mass Mean Size vs. X_f ; $j = 0.7$	37
Figure 20. Mass Mean Size vs. X_f ; $j = 0.8$	38
Figure 21. Mass Mean Size vs. X_f ; $j = 1.0$	39

List of Tables

Table 1. Element analysis for the crystals obtained by re-liming the Dravo waste liquor	18
Table 2. Comparison of the molar ratios for the theoretical and present experimental salt	18
Table 3. Element analysis of final crystalline product obtained by evaporative crystallization of the hydrolyzed liquor.	19

1. INTRODUCTION

The final goal of this project is to develop an economical process for making ammonium sulfate from waste scrubbing liquor. The work performed to date has been concentrated on the experimental investigation of N-SCC which are then converted to ammonium sulfate. The time required for complete hydrolysis of the N-SCC is usually high (Randolph, Mukhopadhyay and Unrau) which could be a disadvantage. The present report studies the usefulness of high temperature/pressure hydrolysis. Currently, there is no literature reporting on high temperature/pressure acid hydrolysis of N-SCC. Hydrolysis at a temperature slightly above the boiling point may be required to increase the attractiveness of the process. The precipitate obtained by re-liming the scrubber liquor containing Fe-EDTA chelate, was found to be a double salt of calcium and sodium.

Contrary to previous understanding, simple cooling of the hydrolyzed liquor to room temperature or ice point was found not to yield any $(\text{NH}_4)_2\text{SO}_4$ crystal due to low concentration of NH_4^+ ion (typically 0.1M) in the hydrolyzed liquor. In order to obtain $(\text{NH}_4)_2\text{SO}_4$, the hydrolyzed liquor need to be enriched in NH_4^+ ion by evaporation.

2. THE PHYSICAL-CHEMICAL ANALYSIS OF NITROGEN-SULFUR CONTAINING COMPOUNDS

The waste scrubbing liquor (containing Fe-EDTA) from the Fort Miami, Ohio plant (Dravo Lime Co.) was allowed to react overnight at room temperature at a slurry pH of 8.3. The slurry was filtered, and the solids were washed repeatedly with deionized water to eliminate all possible impurities. The bright yellowish-white crystals, characteristic of N-S containing salt,

were isolated and dried. The salt was then sent to Desert Analytics (Tucson, AZ) for chemical analysis. The analysis report is given in Table 1. The molar ratios of the various elements present in the salt were calculated based on the assumption that all elemental nitrogen comes from the N-S containing salt of the solid crystalline mixture. Following a comparison of the analysis report presented by Divers and Haga (1892), the experimental salt (the N-SCC precipitated during experimentation) is believed to be closer to the double salt. However, a new salt cannot be ruled out. Significantly higher Ca/S and N/S molar ratios were obtained for the experimental salt than can be explained theoretically. The molar ratios of experimental and theoretical salts are given in Table 2.

The suspected calcium amine disulfonate crystals were subjected to X-ray mapping, which also indicated the presence of sodium on the crystal surface. The SEM photographs and corresponding X-ray mapping of the selected elements of the N-S containing crystals are shown in Figures 1-3. The SEM photographs and X-ray analysis were provided by Dravo Lime Co. Both the chemical and physical analysis confirmed that the N-SCC obtained during the DDO operation at a pH of 8.3 are predominantly a double salt of calcium and sodium.

3. HYDROLYSIS OF NITROGEN-SULFUR CONTAINING COMPOUNDS

The chemistry of hydrolysis has been discussed in the previous DOE report (Randolph, Mukhopadhyay and Unrau, 1994). The present hydrolysis experiments were designed to determine the influence of a higher temperature (in excess of 100°C) and sulfuric acid concentration on the time required for complete hydrolysis.

3.1. Experimental Procedure

High temperature-pressure hydrolysis of N-SCC were carried out using an autoclave (Hirayama Model #HA-MII). Two grams of uniformly sized N-SCC crystals were placed in a set of 500 ml Erlenmeyer flasks with 100 ml of sulfuric acid. Three sulfuric acid concentrations (0.5 M, 1.0 M, 2.0 M) were used for the present study. The flasks were closed with autoclavable silicon sponge closures, which allow alleviation of pressure while reducing evaporation and preventing the passage of aerosols. The flasks were then placed in the autoclave to hydrolyze the N-SCC at 115°C (0.75 Kg/cm² gauge pressure). The experimental run time ranged from 0.5 to 8 hours. A total of fifteen experiments were conducted to accommodate the study. The hydrolyzed samples were cooled to room temperature, filtered, and then analyzed for the ammonia nitrogen concentration.

3.2 Results and Discussion

The concentration of NH_4^+ ion in the hydrolyzed liquor was calculated by monitoring the dissolved ammonia in aqueous solution with a gas-sensing Orion ammonia electrode (Model No. 95-12). This gas-sensing electrode measures the ammonium ion concentration in solution after converting it to NH_3 by the addition of alkali. For accurate measurement of ammonium ion concentration, a blue color indicator was used to indicate the correct solution pH.

Before calculating the concentration of NH_4^+ ion in the hydrolyzed solution, a calibration line was established for the electrode by measuring the mV reading at some known concentrations of "ammonia N" (e.g. 10-1000 ppm N). Figure 4 shows the calibration curve for the estimation of the NH_4^+ ion concentration in hydrolyzed liquor. To measure the concentration of NH_4^+ ion, the

hydrolyzed liquor was diluted to bring down the concentration of N to between 10-1000 ppm. 100 ml of the diluted hydrolyzed liquor was placed in a 150 ml beaker, and 2 ml of Ionic Strength-Adjustor (ISA, Orion Cat. #951211) was added to correct the pH. A blue color developed at this stage. The solution mixture was then placed on a magnetic stirrer and stirred gently. The NH_3 electrode was rinsed with distilled water before being placed in the solution. The millivolt (mV) value was recorded when a stable reading was reached. The concentration of the NH_4^+ ion in the hydrolyzed liquor was calculated from Figure 4.

The results of the hydrolysis experiments are given in Figures 5 through 8. Comparison of Figure 5 with Figures 6 and 7 indicate that the rate of hydrolysis does not depend on the sulfuric acid concentration. Thus, for all concentrations (0.5 M, 1.0 M, 2.0 M) in Figures 5 through 7, 90% of the hydrolysis was achieved in approximately 2.5 hours. It is interesting to note that the temperature has a large effect on the rate of hydrolysis. Figure 8 provides a comparison of the hydrolysis profile for N-SCC at 95°C and 115°C in 1 M H_2SO_4 . At 115°C (0.75 Kg/cm² gauge pressure), hydrolysis proceeds at a much faster rate than at 95°C. Although the initial rates are very different at these two temperatures, with time the difference in the rate of hydrolysis diminishes. About 90% of hydrolysis was accomplished within 2.5 hours at 115°C, while it took almost 6 hours to attain the same degree of hydrolysis at 95°C (Figure 8).

4. CRYSTALLIZATION OF AMMONIUM SULFATE FROM THE HYDROLYZED LIQUOR

Hydrolyzed liquor contains the NH_4^+ ion which can be precipitated as $(\text{NH}_4)_2\text{SO}_4$. First however, the liquor, which has a very low pH (0.1-1.0), needs to be neutralized partially up to a

pH of approximately 5.5. Next, to initiate $(\text{NH}_4)_2\text{SO}_4$ crystallization, the NH_4^+ ion concentration in the liquor need to be raised at least to the saturation level by evaporation. The process flow diagram for the production of $(\text{NH}_4)_2\text{SO}_4$ from Dravo waste liquor is given in Figure 9.

4.1. Batch Crystallization of Ammonium Sulfate from Hydrolyzed Liquor

The typical concentration of NH_4^+ ion in the hydrolyzed liquor is around 0.1-0.2 M. The solubility of $(\text{NH}_4)_2\text{SO}_4$ at room temperature is approximately 43 grams per 100 grams of saturated solution as shown in Figure 10 (Seidell, 1940). Therefore, severe evaporation of the hydrolyzed liquor is required before crystals of $(\text{NH}_4)_2\text{SO}_4$ could be precipitated.

500 ml of hydrolyzed liquor is filtered to obtain clean liquor. The solids contain mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The photomicrograph of these solids is shown in Figure 11. The pH of the liquor was then adjusted to approximately 5.5 using a 27% strong ammonia solution. The clean hydrolyzed liquor of pH ~5.5 is then transferred into an evaporative crystallizer shown in Figure 12. About 1% (w/V) phosphoric acid is added to the hydrolyzed liquor in order to obtain crystals of favorable habit. Next, the mixture was heated up to $\sim 80^\circ\text{C}$ under vacuum to increase the NH_4^+ ion concentration in solution. A magnetic stirrer bar was used to keep the solution gently agitated. At the first sign of precipitation, the agitation was stopped in order to minimize secondary nucleation. The evaporated, concentrated hydrolyzed liquor was subsequently cooled -down to room temperature slowly. The white crystalline ammonium sulfate was then dried.

4.2 Results and Discussion

The dried $(\text{NH}_4)_2\text{SO}_4$ crystals were sieved for size analysis using an Allen-Bradley sonic sifter, and the average crystal size was found to be high. Figure 13 shows the cumulative weight percent of ammonium sulfate crystals in various size ranges. From this plot, the mass average size of the product crystals was $420\ \mu\text{m}$ (Figure 13). The results of this ammonium sulfate crystallization experiment are satisfactory in terms of the average product crystal size, however, further study of the continuous precipitation of $(\text{NH}_4)_2\text{SO}_4$ from hydrolyzed liquor is needed. The population density of the ammonium sulfate crystals in various size ranges is shown in Figure 14.

At the same time, these crystals were analyzed for chemical composition. The chemical analysis of the ammonium sulfate crystals obtained by evaporation and cooling of the hydrolyzed liquor is given in Table 3. This analysis was done by Desert Analytics in Tucson, AZ. The product composition calculated from the element analysis was 89.7% $(\text{NH}_4)_2\text{SO}_4$ (assuming all nitrogen in the analysis originated from $(\text{NH}_4)_2\text{SO}_4$), the residual was gypsum and magnesium sulfate.

A sample of the cooling concentrated hydrolyzed liquor was taken at the first sign of $(\text{NH}_4)_2\text{SO}_4$ crystal formation. The sample was placed on a glass slide and observed under an optical microscope. Figures 15 and 16 show the photomicrographs of the $(\text{NH}_4)_2\text{SO}_4$ crystals at the early stage of crystallization. The final product has shown to be quite large in size. The sieve analysis indicated the mass average size to be $\sim 420\ \mu\text{m}$ (Figure 13). The photomicrograph of the sieved crystals (mass average size $\sim 420\ \mu\text{m}$) is shown in Figure 17.

5. OPTIMIZATION OF DESIGN VARIABLES BY COMPUTER SIMULATION

Computer simulations were run to optimize crystal growth and nucleation rate design variables. All data in this section was obtained solely through theoretical computer simulation; currently, no experimental data exist to confirm these results. In the following discussion, an understanding of MSMPR and DDO crystallizer operation by the reader is assumed. The crystal growth and nucleation rate equations are:

$$G = k_G s^a$$

$$B^\circ = k_N G^i M_T^j,$$

respectively (White and Randolph, 1989). Where,

G = growth rate

k_G = growth rate constant

s = supersaturation

a = exponent linking growth rate to supersaturation

B° = nucleation rate

k_N = nucleation rate constant

i = exponent linking nucleation rate to growth rate

M_T = suspension density

j = exponent linking nucleation rate to suspension density, (White and Randolph, 1989).

The computer program used is entitled DDO.FOR, (Randolph and Sutradhar, 1992). Its purpose is to estimate ratios of the MSMPR (Mixed Suspension Mixed Product Removal) reactor output parameters to the DDO (Double Draw Off) reactor output parameters. Imputing values to

the computer of the MSMPR per pass yield, a (exponent above), i and j (exponents above), the DDO ratio, and a dimensionless cut-off size will result in output consisting of the DDO per pass yield, and ratios (DDO to MSMPR) of growth rates (G/G_o), slurry densities (M_T/M_{To}), and mass mean sizes ($L_{4,3}/L_{4,3o}$). Note that the MSMPR values are denoted by the subscript "o".

The current system input parameters were calculated or estimated from previous experiments. The variables throughout the simulations were i and j, the exponents relating the crystal nucleation rate to the growth rate and the suspension density, respectively. An adjustable parameter was X_f , the dimensionless cut-off size:

$$X_f = L_f / (G_o \tau).$$

Where,

L_f = crystal fines cut-off size

G_o = MSMPR growth rate

τ = reactor residence time, (Randolph and Sutradhar, 1992).

Using crystal fines cut-off sizes of 30, 45, 60, and 100 μm for DDO operation, plots were obtained for the mass mean size vs. X_f . Output data was also obtained for the growth rates, slurry densities, and DDO per pass yield. In the simulations, i was allowed to vary between 1 and 2, where j was allowed to vary from 0.5 to 1. For the following discussion, please refer to Figures 18 through 21. In all four figures, as i is increased the mass mean size ratio also increases. However, as j increases, the mass mean size ratio decreases. A large effect is also shown from the dimensionless cut-off size, X_f . As X_f is increased, the mass mean size increases. Hence, as bigger crystals are removed from the reactor, the remaining crystals are of a larger size population. The average crystal size remaining will be increased, thus the resulting mass mean size ratio is

increased. An optimum for increasing the mass mean size ratio is found at $i = 2$, $j = 0.5$, and $X_f = 1.11$ (100 μm). However, the parameters estimated from previous experiments show that the approximate fines cut-off size is 30-50 μm . For $X_f = 0.33$ (30 μm), the optimum is observed to be $L_{4,3}/L_{4,30} = 2.99$ at $i = 2$ and $j = 0.5$. For $X_f = 0.5$ (45 μm), the optimum is observed to be $L_{4,3}/L_{4,30} = 3.27$ at $i = 2$ and $j = 0.5$. These simulation results show the mass mean size for DDO operation is estimated to increase by a factor of three over MSMPR operation at the optimum i and j values. At these same parameter values, $i = 2$ and $j = 0.5$, the growth rate ratio, G/Go , is shown to be 0.25, which is its maximum value for these simulations. This means the DDO crystal growth rate is only 0.25 times the crystal growth rate during MSMPR operation. Although, at these i and j values, the per pass yield is not at its maximum, its value is 0.88, which is approximately 95% of its maximum value of 0.93. The slurry density ratio shows similar behavior. Although it is not at its maximum value of 24.05, the slurry density ratio has a value of 22.87, which is again 95% of its maximum.

The data for the per pass yield and the slurry density ratio are less sensitive to changes in i and j as are the growth and mass mean size ratios, which can both vary as much as 40%, depending on the (i,j) pair chosen.

An advantage of DDO operation is the large increase of slurry density, which even at the lower factor of 22.87, shows a large increase over the MSMPR slurry density. This large increase in slurry density comes from the overall increase in crystal size and residence time during the DDO operation (i.e. the DDO operation removes the small crystal sizes from the crystallizer and leaves the larger sized crystals in the reactor for continued growth). The drop in growth rate during DDO operation to 0.25 its MSMPR value is also linked to the increase in both residence

time and crystal size.

Another advantage of DDO operation is the increase in the mass mean size, which theoretically can be increased by a factor of three. As the smaller crystal size population is removed, the mass mean size within the reactor will increase. As i is increased, the effect of growth rate on nucleation rate is emphasized. For this case, the DDO growth rate is less than 1 $\mu\text{m}/\text{min}$, and the larger emphasis effect will cause the nucleation rate to decrease. Since the nucleation rate is lowered, fewer crystals will nucleate, leaving more reactant to be consumed by the growing larger crystals. Similarly, as j is decreased, this removes the influence of the suspension density from the nucleation rate (i.e. here the suspension density is larger than unity). The nucleation rate is again lowered, and the same effect results.

In conclusion, these simulations show decreasing the nucleation rate will increase the average mass mean crystal size in solution during DDO operation. The parameters that have been adjusted to decrease the nucleation rate were the exponents i and j . Different crystal removal cut-off sizes were also used. Another method to increase the average crystal mass mean size is to increase the cut-off size. However, if the cut-off size is increased too much, the average mass mean crystal size will begin to drop (White and Randolph, 1989). For the experimental set up, the crystal cut-off size could be increased to 100+ μm . Currently, the crystal cut-off size is 30-45 μm .

References

Divers, E. and Haga, T. "Imidosulphonates", *J. Chem. Soc.* 61, 943, 1892.

Randolph, A. D., Mukhopadhyay, S. and Unrau, E. "Production of Ammonium Sulfate Fertilizer from FGD Waste Liquors", DOE Quarterly Technical Report, October-December 1994.

Randolph, A. D. and Sutradhar, B. C. "Instructions for the Use of Programs DDO.FOR, FD.FOR & MDDO.FOR", Dept. of Chem. Eng., University of Arizona, 1992.

Seidell, A. "Solubilities of Inorganic and Organic Compounds", D. Van Nostrand Company, Inc., NY, 1940

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

Table 1. Element Analysis for the crystals obtained by re-liming the Dravo waste scrubber liquor.

Element	Wt%
Ca	15.84
Na	6.81
Mg	0.12
Fe	0.18
N	4.18
S	18.69

Table 2. Comparison of Molar Ratios for the Theoretical and present Experimental salt.

Description	Molar Ratios			
	Ca/N	Ca/S	N/S	Na/N
Theoretical				
Single salt, $\text{Ca}_3\text{N}_2(\text{SO}_3)_4 \cdot 10\text{H}_2\text{O}$	1.5	0.75	0.5	0.0
Double salt, $\text{CaNaN}(\text{SO}_3)_2 \cdot 3\text{H}_2\text{O}$	1.0	0.50	0.5	1.0
Experimental	1.0	0.61	0.60	1.0

Table 3. Element Analysis of the final crystalline product obtained by evaporative crystallization of hydrolyzed liquor.

Element	Amount Present in Product Crystal
Ca	4300 ppm
Mg	540 ppm
Fe	0.03 ppm
N	18.46 %
SO ₄ ²⁻	64.52 %

University of Arizona 94-4208-1
Calcium Amine Disulfonate Crystals
Mag= 5.50 K X Carbon Coated
10µ

DRAYO LIME
COMPANY

Figure 1. Scanning electron photomicrograph of the calcium salt of N-S compounds.

Operator: leica
Client: none
Job: Job number 8
Label: CaAmineDisulfCryst 94-4208.1 (14 Nov 94 11:23:09)

Figure 2. Surface element analysis for SEM photograph 1.

Client : University of Arizona

CaAmineDisulfCryst 94-4208.1 (Monday, November 14, 1994 10:58)

Sample Carbon Coated

Figure 3. X-ray mapping of the elements present on the surface of N-S containing compounds.

**DRAVO LIME
COMPANY**

Figure 4. Calibration curve for the estimation of NH_4^+ ion concentration in the hydrolyzed liquor.

Figure 5. Plot of the high temperature/pressure acid hydrolysis at 0.5 M H_2SO_4 .

Figure 6. Plot of the high temperature/pressure acid hydrolysis at 1.0 M H_2SO_4 .

Figure 7. Plot of the high temperature/pressure acid hydrolysis at 2.0 M H_2SO_4 .

Figure 8. Comparison of the acid hydrolysis at 95°C and 115°C in 1 M H₂SO₄.

Figure 9. Process Flow Diagram for the production of $(\text{NH}_4)_2\text{SO}_4$.

Figure 10. Solubility of $(\text{NH}_4)_2\text{SO}_4$ in an aqueous sulfuric acid solution.

Figure 11. Photomicrograph of gypsum crystals obtained from the hydrolyzed liquor.

Figure 12. Crystallization of $(\text{NH}_4)_2\text{SO}_4$.

Figure 13. Cumulative Weight Fraction vs. Size of $(\text{NH}_4)_2\text{SO}_4$ crystals obtained by evaporative crystallization.

Figure 14. Population Density vs. Size of $(\text{NH}_4)_2\text{SO}_4$ crystals obtained in batch crystallization.

Figure 15. Photomicrograph of $(\text{NH}_4)_2\text{SO}_4$ crystals at initiation of crystallization; magnification = 40X.

Figure 16. Photomicrograph of $(\text{NH}_4)_2\text{SO}_4$ crystals at initiation of crystallization; magnification = 100X.

Figure 17. Photomicrograph of sieved $(\text{NH}_4)_2\text{SO}_4$ crystals; size = 420 μm , magnification = 40X.

Mass Mean Size vs. X_f

$$X_f = L_f / (G_o \cdot \tau), j=0.5$$

Figure 18.

Mass Mean Size vs. X_f

$$X_f = L_f / (G_o \cdot \tau), j=0.7$$

Figure 19.

Mass Mean Size vs. X_f

$$X_f = L_f / (G_o \cdot \tau), j=0.8$$

Figure 20.

Mass Mean Size vs. X_f

$$X_f = L_f / (G_o \cdot \tau), j=1.0$$

Figure 21.