Regeneration of FGD Waste Liquors: Production of Ammonium and Potassium Sulfate Mixed Fertilizer

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by

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Progress Summary
October 1993 - December 1993

In the 2nd quarterly report, we discussed the lime/limestone process which precipitates N-S compounds by adding lime/limestone in a narrow pH range, and which can be an alternative to the K_2SO_4 process. In this report, we focused on investigations of the lime/limestone process.

First, we established a overall flow diagram for the lime/limestone process. Based on the diagram, we performed preliminary experimental investigations to outline practical process conditions. Our major investigations concerned about effects of pH on precipitation of the N-S compounds and precipitation characteristics of N-S compounds in a continuous crystallization system. We also performed an experimental investigation to study crystallization characteristic of the ammonium sulfate in the hydrolysis liquor. In studying effects of pH, we performed batch precipitation of the N-S compounds in a broad range of pH and investigated the effects of pH on the amount of required lime, the amount of the precipitate, and the fraction of N-S compounds precipitated. The result revealed the optimum range for precipitation of N-S compounds to be pH = 7.6 - 8.6. In studying continuous crystallization characteristics of the N-S compounds, a bench scale 4-liter continuous crystallization system was built to compare a typical Mixed-Suspension-Mixed-Product-Removal (MSMPR) crystallizer and Double-Draw-Off (DDO) crystallizer. In a preliminary test, the DDO was shown to be superior by increasing the average size of the precipitated crystals of N-S compounds from 97 μm to 142 μm and thus enhancing the filterability.

In order to obtain information for a practical design of the lime/limestone process, we also set up a material balance for a 300 MWe power plant facility. A preliminary calculation showed that a process on the scale could produce approximately 56 tons ammonium sulfate fertilizer per day.

The experimental results obtained up to now have demonstrated a practical feasibility of the lime/limestone process. However, all investigations required for developing the regeneration process are not complete. Therefore, detailed investigations need to continue next year with emphasis on this lime/limestone process for further investigation of the lime/limestone as an alternative process to the K_2SO_4 process.

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1. Introduction

The ultimate goal of this project is to develop a simple process for regeneration of waste FGD scrubbing liquors. The research performed so far was focused on experimental investigations of the K_2SO_4 process. In the K_2SO_4 process, N-S compounds accumulated in waste scrubbing liquor are precipitated as potassium salts by a metathetical reaction with added K_2SO_4. The precipitated potassium salts are then converted by hydrolysis in a sulfuric acid environment to ammonium and potassium sulfates which are salable as mixed fertilizer. In the investigation of the K_2SO_4 process, it was notable that more than 60 % of the added potassium remained in the scrubbing liquor after precipitation of N-S compounds as potassium salts. This observation indicates that loss of the dissolved potassium in recycling the mother liquor to the main scrubbing unit, probably as entrainment on the gypsum precipitates, would be a serious detriment to the economy of the regeneration process. For essential improvement of the K_2SO_4 process, we consider a different route of the regeneration process which uses additives other than K_2SO_4. In a preliminary test, we observed that addition of lime/limestone to scrubbing liquor in a narrow pH range could precipitate N-S compounds in the scrubbing liquor. An element analysis also showed that the precipitated crystals are probably a mixture of $CaSO_4$ and CaADS (Calcium Amine Disulfonate) [ADS is a major species of N-S compounds in waste scrubbing liquor]. This lime/limestone process is a new process which can serve as an alternative to the K_2SO_4 process because one does not need to purchase/introduce a new chemical additive to precipitate N-S compounds in the Fe^{II}-EDTA wet scrubbing processes. In this report, we focused on investigations of the lime/limestone process.

The lime/limestone process to be studied is presented in Fig.1. The downstream of the scrubber (stream-1; pH < ~ 6.5, flow rate = Q_t) is split into two streams: one is a major stream and the other is a bleed (stream-5) which is approximately 10 % of the whole flow of the scrubber. This bleed is taken to neutralize the filtrate stream (stream-8, pH ~ 8
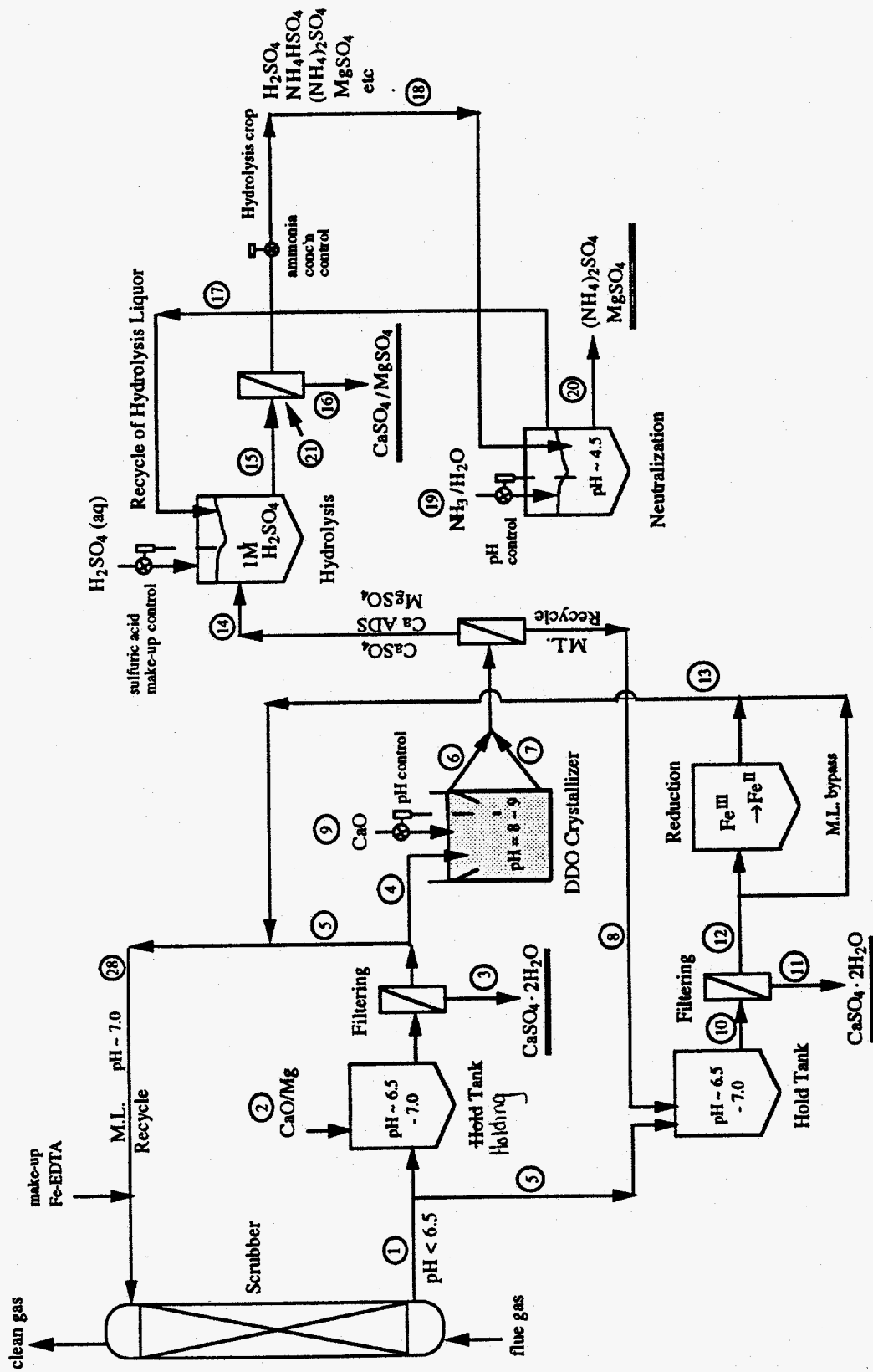
Fig.1 Process flow diagram for the lime/limestone process. Ammonia is used for neutralization of the crystal crop product after hydrolysis.

- 9) which comes out after separation of the precipitated N-S compounds. The major split stream is fed to the holding tank where lime is added to neutralize the liquor and precipitate gypsum product. The crystal crop in the holding tank is then filtered to separate the gypsum product. The filtrate is split into two streams: a bleed (stream-4) of approximately 10 % of the whole flow of the scrubber goes into a DDO (Double Draw-Off) crystallizer for precipitation of N-S compounds in the liquor while the major stream (stream-5) is recycled back to the scrubber. In the DDO crystallizer, the bleed stream (stream-4) is contacted with lime until the pH is adjusted to approximately 8 - 9. Here, a precipitate forms which is most likely magnesium and calcium sulfate and CaADS. The precipitated crystals are filtered to remove most of the scrubbing liquor. The filtered crystals are fed to the hydrolyzer. The filtrate (flow rate ~ 0.1 Q_t) is recycled to the holding tank where it is almost neutralized by mixing with the bleed stream (stream-5). The liquor in the hold tank is then filtered to remove gypsum product. After passing the filter, some portion of liquor is passed through the reduction unit and then recycled to the scrubber, while the other portion of the liquor is directly recycled as a bypass of the reduction unit. In the hydrolyzer, the precipitated crystal crop of CaADS is hydrolyzed in approximately 1 molar sulfuric acid at ~ 100 °C to ammonium sulfate and gypsum. A portion of the hydrolysis crop is withdrawn to remove the magnesium and calcium sulfate crystals which were either formed by hydrolysis of CaADS or were originally fed to the hydrolyzer along with the CaADS precipitate. If the ammonium ions formed by hydrolysis are sufficiently concentrated in the hydrolysis liquor, the filtered hydrolysis liquor is fed to a neutralization unit via the ammonium concentration control valve. Here, due to the acid condition of the hydrolysis, this hydrolysis liquor is considered to be close to a 1 molar sulfuric acid solution which dissolves ammonium bisulfate and sulfate and magnesium sulfate and bisulfate. In the neutralizer, the hydrolysis liquor is neutralized with ammonia (thus, the neutralizer operates as a reactive crystallizer). From the neutralizer, a crystal crop is taken out and filtered to yield a mixture of ammonium and magnesium sulfate (small portion)

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crystals, which can be marketed as a fertilizer. The filtrate is then recycled to the hydrolyzer.

The lime/limestone process described in Fig.1 is drawn based on our preliminary observations and therefore has aspects that requires further study, which are summarized in our proposal submitted for extension of this project to next year. In this study, we proceed with preliminary experimental investigations of the lime/limestone process: major investigations made here concern the effects of pH on precipitation of the N-S compounds and precipitation characteristics of N-S compounds in a continuous crystallization system. We also performed an experimental investigation to study crystallization characteristic of the ammonium sulfate in the hydrolysis liquor. In order to obtain information for a practical design of the lime/limestone process, a preliminary material balance is also provided for a 300 MWe power plant facility.

2. Experimental Studies

2.1 Effects of pH on precipitation of N-S compounds

For the lime/limestone process described in Fig.1, precipitation characteristics of N-S compounds by addition of lime was studied via a series of batch experiments. Of various precipitation characteristics of N-S compounds, pH dependence is of our prime concern. Thus we performed precipitation of the N-S compounds in a broad range of pH and investigated effects of pH on the amount of required lime, the amount of the precipitate, and the precipitated fraction of N-S compounds.

2.1.1 Experimental Procedure

Batch precipitation of N-S compounds was performed in a bench scale. 100 ml of Dravo waste scrubbing liquor was taken into a 200 ml beaker. A known amount of reagent

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grade CaO was added to the liquor. Then the liquor was allowed to stand at room temperature for 3 hrs with magnetic stirring and the pH of the liquor was measured. After that, the crystal crop formed are filtered, slightly washed with D.I. water, dried, and weighed. Next, hydrolyzable nitrogen content in the precipitates was determined by the following procedure. 1 gram of the precipitate was introduced into 50 ml of 1 M H_2SO_4 solution. The crystal crop was then completely hydrolyzed at 100 °C for 24 hrs. After completion of the hydrolysis, the ammonium concentration of the hydrolysis liquor was measured using an Orion ammonium ion selective electrode (Orion Model 95-12). The measured ammonium concentration was converted to the amount of CaADS equivalent contained in the precipitates by

$$\text{CaADS equiv. (g)} = \text{measured } NH_4^+ \text{ conc'n (M/l)} \times \text{vol. of hydrolysis liquor (ml)} \times \frac{215}{1000}.$$

2.1.2 Results and Discussion

The pH of the original waste scrubbing liquor provided by Dravo Lime Co. was approximately 6.5 - 7.0. By adding pure CaO, the pH of the liquor was varied from 7.6 to 9.2. Fig.2 shows the amount of pure CaO required to increase the pH of the liquor. Addition of CaO monotonically increased pH of the liquor upto pH ~ 9.0. Addition of approximately 1 g CaO/100 ml M.L. increased the pH of the liquor to 8.5. Fig.3 shows dependence of the amount of precipitated crystals on the pH of the liquor. As the pH of the liquor increased, the amount of precipitated crystals increased. As indicated in the figure, the trend of the increase appeared to be divided into two regions: below and above pH ~ 8.6 (here, we suspected if the two regions showed up because the liquor pH was taken as abscissa. To confirm this, Fig.3 is replotted as the amount of precipitated crystals vs. the amount of added CaO and presented in Fig.4. In Fig.4, we again observe the existence of the two regions). Below pH ~ 8.6, the amount of precipitates increased relatively slowly as pH of the liquor increased. The color of the precipitates was white around pH ~ 7.6 and
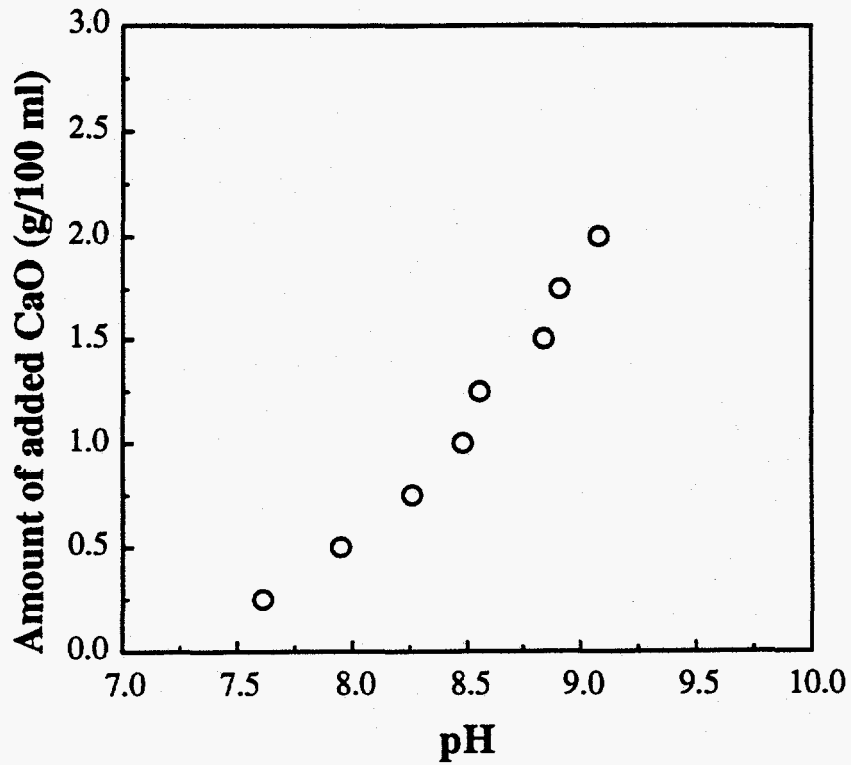
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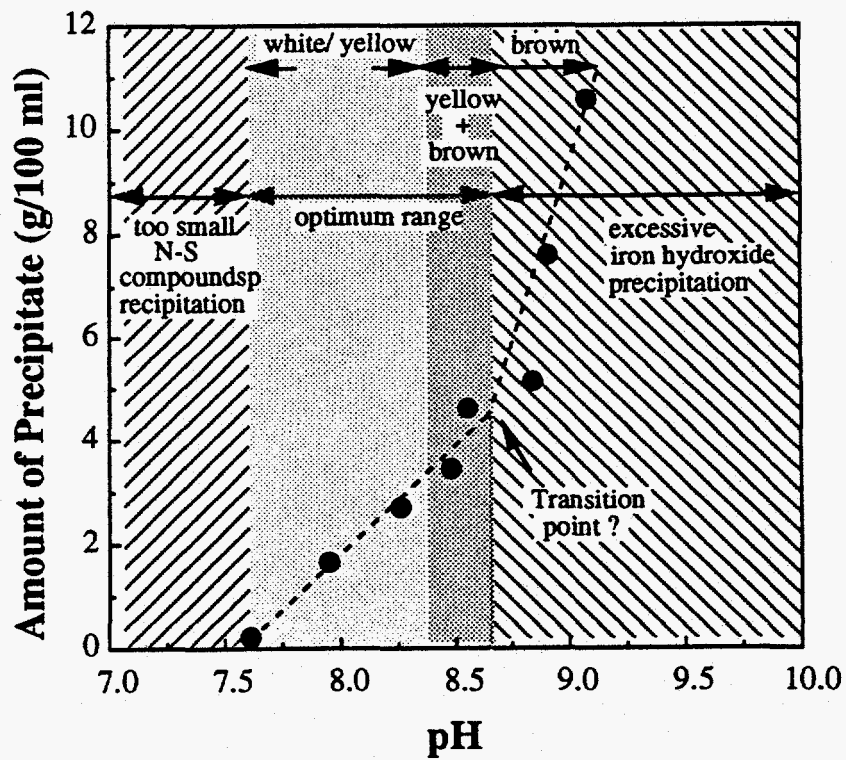**Fig.2** Effect of CaO addition on the liquor pH.

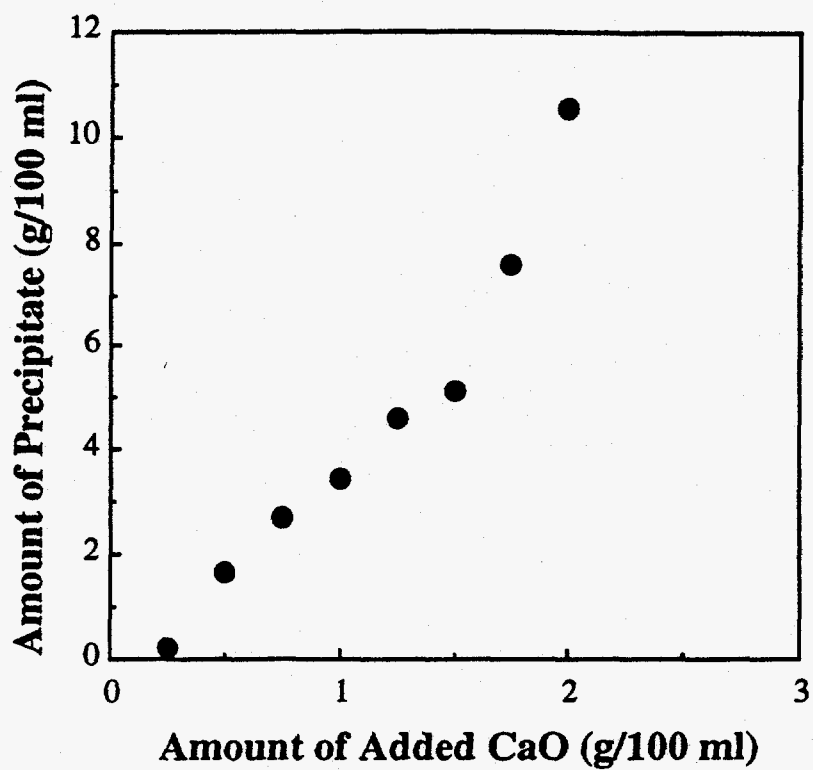**Fig.3** Amount of the precipitates vs. pH.

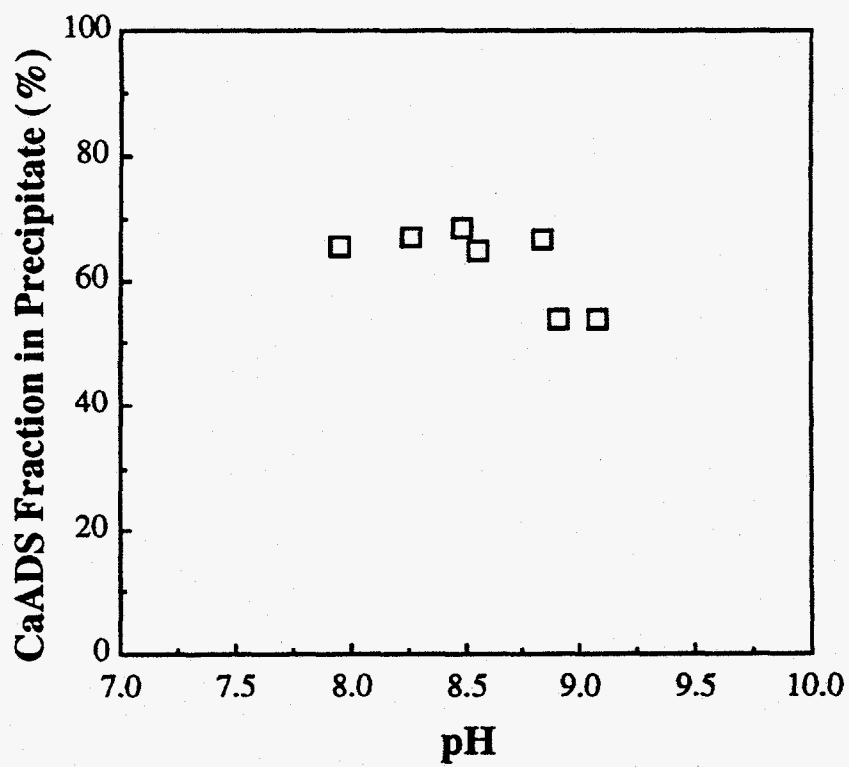Fig.4 Amount of the precipitate vs. amount of the added CaO.

Fig.5 CaADS fraction in the precipitate vs. pH.

gradually took on a yellowish brown color as the pH increased to around 8.6. The precipitates were, therefore, considered to be mainly composed of $CaSO_4$ and CaADS below pH ~ 8.6. Above pH ~ 8.6, increment in the amount of the precipitated crystals with pH was far greater than that below pH ~ 8.6. In addition, the precipitates took on more brownish color with the increase of pH because precipitation of iron hydroxides became significant. In order not to precipitate too much iron hydroxides, it seems that an optimum liquor pH would be below pH = 8.6. Below pH ~ 7.6, however, the amount of precipitated crystals was too small to expect an appreciable removal of N-S compounds. Therefore, an optimum pH for precipitation of N-S compounds ranges 7.6 < pH < 8.6. Fig.5 shows fraction of N-S compounds (as a CaADS equivalent in terms of nitrogen content) in the precipitated crystals. For the crystals precipitated in pH range ~ 7.6 - 8.8, approximately 65 wt % of the precipitated crystals were observed to be equivalent to CaADS. As pH of the liquor is increased about 9, the CaADS content in the precipitate slightly decreased. The observed large value of CaADS content in the precipitate seems to indicate that a significant amount of the N-S compounds in the liquor was actually precipitated to form crystals which were not washable as easily as entrainments. Fig.6 shows what fraction of the N-S compounds in the scrubbing liquor was removed after precipitation by lime addition. The waste scrubbing liquor provided by Dravo lime Co. had approximately ~ 0.312 M/liter N-S compounds (this was measured by hydrolyzing the liquor under 1 M sulfuric acid environment and then measuring ammonium ion formed after the hydrolysis). This concentration of N-S compounds corresponds ~ 50,000 ppm in terms of ADS (this is greater by an order of magnitude than the value provided by Dravo. However, a communication with Dravo indicated that their value may be incorrect). As the pH of the liquor was increased, the fraction of N-S compounds removed from the liquor increased. Approximately 40 % of the removal fraction could be reached around pH ~ 8.5. The higher removal fraction may be reached above pH ~ 8.5, but it would be accompanied by an increased precipitation of iron hydroxides. Fig.7 presents how much ammonium
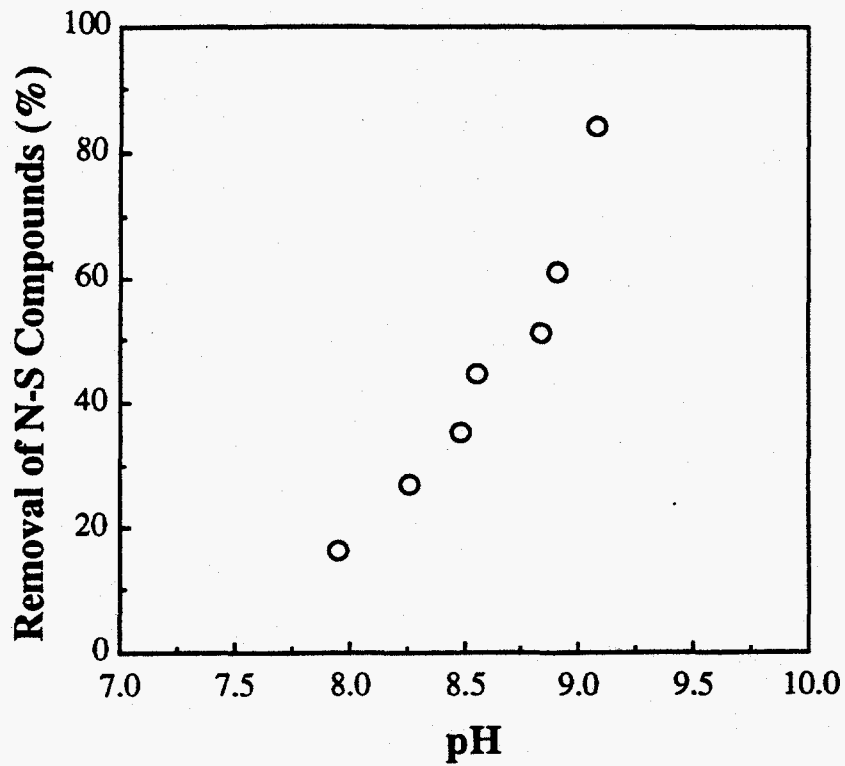
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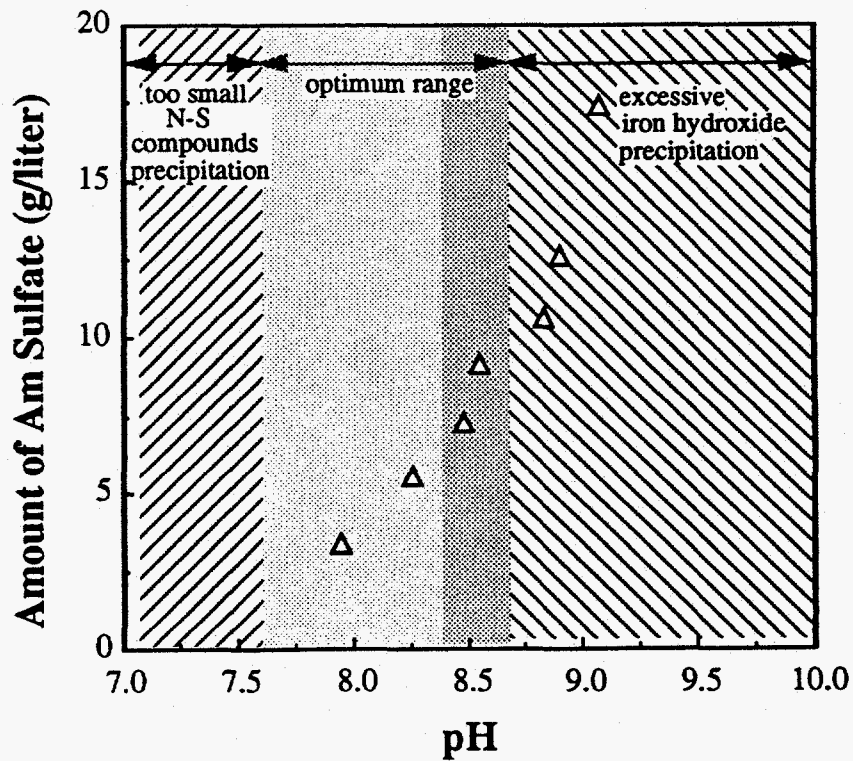**Fig.6** Removed fraction of N-S compounds vs. pH.

Fig.7 Amount of the ammonium sulfate producible vs. pH

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sulfate is producible after hydrolysis. As the pH of the liquor is increased, the amount of ammonium sulfate producible increases because more N-S compounds precipitated with the pH of the liquor. Since an extreme pH for precipitating N-S compounds (i.e., pH < 7.6 or pH > 8.6) raises problems such as too small amount of precipitates or too much precipitation of iron hydroxides, an optimum is recommended between pH = 7.6 and 8.6. Around pH ~ 8.5, approximately 7 g ammonium sulfate per liter of scrubbing liquor can be produced.

2.2 Continuous Crystallization of N-S compounds

In continuous precipitation of N-S compounds, a process condition of prime concern is crystallizer operation which leads to increasing the size of the precipitates and thus enhancing their processibility. For this investigation, we set up a 4-liter bench scale continuous crystallizer and compared characteristics of a MSMPR (Mixed Suspension Mixed Product Removal) and a DDO (Double Draw Off) crystallizer. The MSMPR crystallizer is similar to a typical CSTR (constant stirred tank reactor). The DDO crystallizer employs the principle of size dependent residence time in order to improve the mean particle size of the product crystals. In DDO configuration, an overflow stream, which removes fine crystals at a classification cut size, is drawn at a rate faster than the mixed under flow. This faster removal of fines allows the remaining particles to grows larger and thus, if the cut size is small enough, the overall mean size is larger than that of the MSMPR. The DDO crystallizer is particularly suitable for application in low natural slurry density systems and its efficacy has been demonstrated in the precipitation of gypsum in wet FGD processes (Chang & Brna, 1984; Randolph *et al*, 1984, 1990). Among the major advantages of the DDO configuration are the large particle size, high suspension density and low vessel fouling. Detailed concept and theory on DDO operation is available in literature (Randolph & Larsdon, 1988; White & Randolph, 1989).

2.2.1 Experimental Set Up

Fig.8 shows the experimental set up used for continuous crystallization performance tests. A 4-liter plexiglas crystallizer is incorporated into the set up. Scrubbing liquor is stored in a 50 gal M.L. feed tank and fed to the crystallizer by the M.L. feed pump. To control pH in the crystallizer, a pH electrode is immersed in the crystallizer. The pH electrode is electrically connected to a pH controller, which is set up to turn on and off the lime slurry feed pump to maintain the pH of the crystallizer at a set point. Lime slurry is stored in a 5 gal lime slurry feed tank. Overflow of the DDO crystallization configuration is drawn off via an inverted cone tube (I.D. = 3.5 cm, length = 40 cm). In a laboratory bench scale DDO crystallizer operation, the underflow is usually so small that particles in the crystallizer are hardly taken out. To avoid this, the underflow is set to periodically discharge the crystal crop. For periodical discharge of the underflow, a liquid level probe & controller is incorporated into the crystallizer. The liquid level control unit is adjusted so that the underflow stream is discharged approximately every 30 minutes. In testing MSMPR crystallization performance, the crystallizer set up described above is operated without the inverted cone tube for the overflow in the DDO. For each test, a steady state was obtained by operating the crystallizer for at least 12 hrs. Then a crystal crop is sampled from the product stream of the crystallizer, filtered, and dried. The dry crystals obtained are sieved for size analysis using a sonic sifter (Allen-Bradley, Model L3p).

2.2.2 Results and Discussion

For comparison of MSMPR and DDO crystallization operations, we performed continuous precipitation of N-S compounds under a fixed precipitation condition (mean residence time of the crystallizer, $\tau = 1$ hr; pH = 8.4). In the DDO crystallization, a DDO ratio of $R = (Q_o + Q_u)/Q_u = 10$, was used [Q_o and Q_u are the flow rate of the overflow and underflow, respectively].

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Fig. 8 Experimental set up for continuous crystallization tests.

1. M.L. feed tank
2. lime slurry feed tank
3. stirrer
4. pH controller
5. lime slurry feed pump
6. M.L. feed pump
7. pH electrode
8. liquid level probe
9. invert cone tube
10. 4-liter crystallizer
11. baffle & baffle tube
12. liquid level controller
13. overflow pump
14. underflow pump
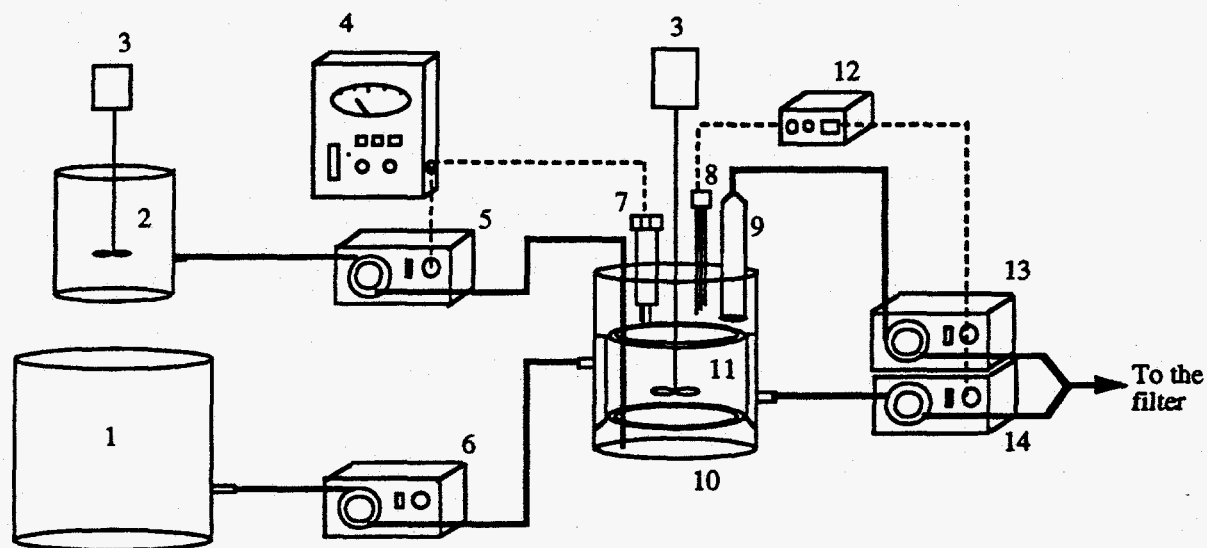
------- electrical control line
——— liquid flow line

Fig.9 is a cumulative weight fraction vs. particle size plot for N-S compounds precipitated by the addition of lime slurry in the MSMPR and DDO crystallization configurations. In the MSMPR crystallization, a significant portion of the precipitated crystals (more than 70 wt % of the precipitated crystals) were distributed in the particle size less than 100 μm. Contrary to the MSMPR, the DDO crystallization configuration made more than 80 wt % of the precipitated crystals distributed in the particle size greater than 100 μm. Weight average size of the crystals obtained from the two continuous crystallization configurations was calculated as 97 μm for the MSMPR and 142 μm for the DDO. As demonstrated in the precipitation of gypsum in wet FGD processes (Chang & Brna, 1984; Randolph *et al*, 1984, 1990), this result indicates that DDO crystallization is suitable for increasing the particle size in precipitation of N-S compounds.

For morphological study of the N-S compounds precipitated by lime addition micrographs of the crystals obtained by the DDO crystallization were obtained. Figs.10(a), (b), and (c) are photomicrographs of the precipitated crystals in 250 μm, 120 μm, and 74 μm range, respectively. For the 250 μm crystals shown in Fig.10(a), most crystals formed agglomerates such that it was difficult to identify certain morphologies of individual crystals. For the 120 μm crystals shown in Fig.10(b), at least three different crystal shapes can be observed. A further scanning of this crystal sample revealed that parallelogram crystals were most predominant among the observable shapes. For the 74 μm crystals shown in Fig.10(c), morphologies of individual crystals were similar to those observed in the 120 μm range but contained opaque crystals more. For the three different sizes of crystals, the content of CaADS equivalent was obtained from the ammonium ion concentration measured after complete hydrolysis of the crystals. For the crystals precipitated in the 250 μm, 120 μm, and 74 μm ranges, the content of CaADS equivalent was obtained as 64, 66, and 57 wt %, respectively. The observed lower fraction of CaADS for the 74 μm range crystals seems to result because the crystals in this size range contain
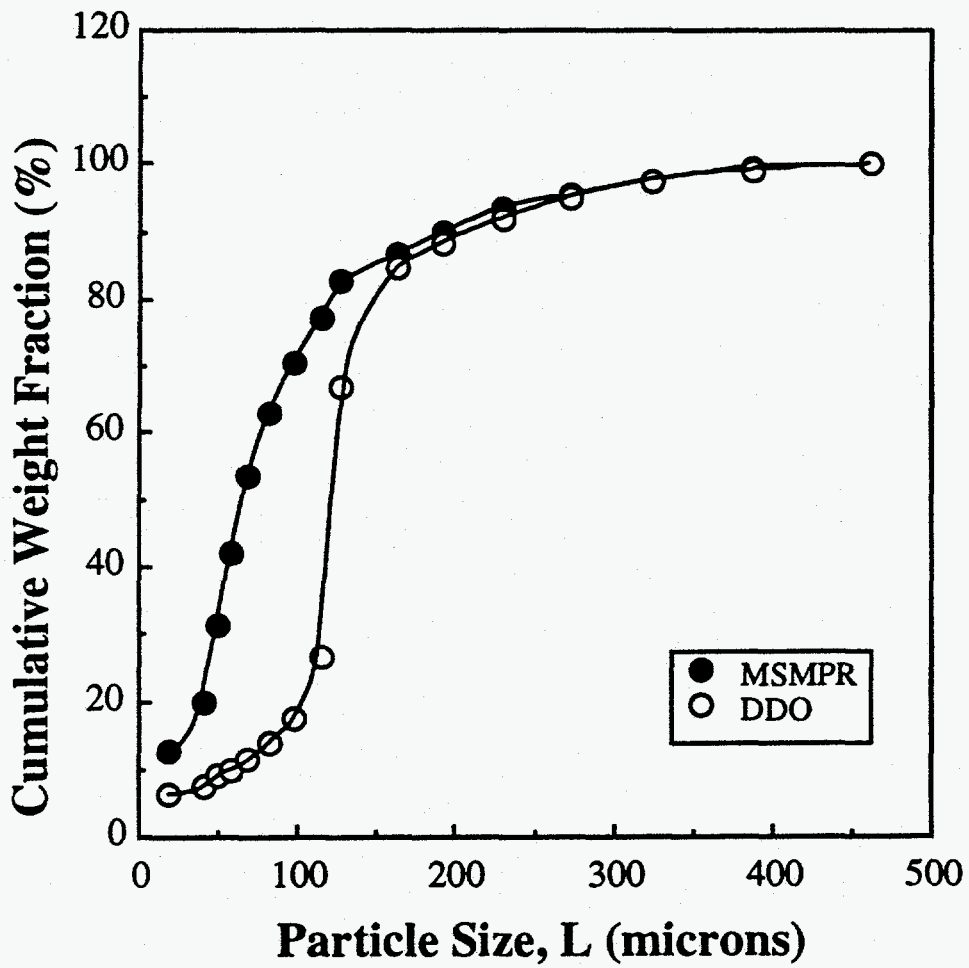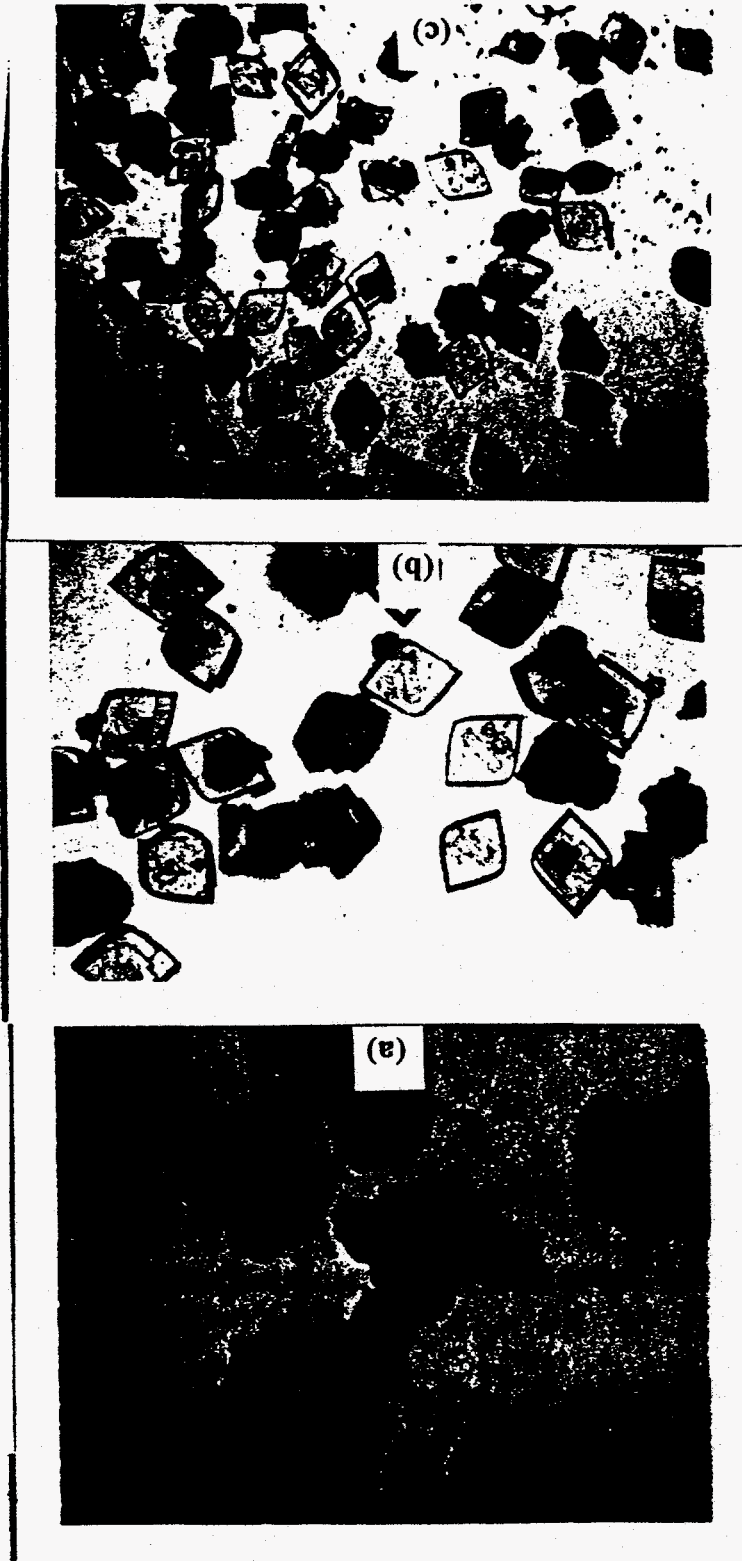
Fig. 9 Cumulative weight fraction vs. particle size.

Fig.10 Photomicrographs of the crystals obtained after a continuous crystallization. The crystals were obtained in (a) 250 μm, (b) 120 μm, (c) 74 μm sieve.

more of the black opaque particles, which are considered as non-hydrolyzable iron hydroxides. From the observation of significantly large content (approximately 2/3 of the crystals by weight) of CaADS equivalent in the precipitated crystals, the parallelogram crystals might be CaADS.

2.3 Crystallization of Ammonium Sulfate in Hydrolysis Liquor

In the regeneration process described in Fig.1, precipitated N-S compounds are converted to ammonium sulfate in the hydrolyzer. If the precipitated N-S compounds are continuously fed to the hydrolyzer, eventually the hydrolysis liquor would be saturated and ammonium sulfate would crystallize out. Here, we study the crystallization characteristics of ammonium sulfate in hydrolysis liquor. A reason for this study is to see the effect of EDTA on crystallization of ammonium sulfate because EDTA, which is expected to be contained in the hydrolysis liquor as an entrainment of the N-S compounds, may play a role as a crystallization inhibitor.

2.3.1 Experimental Procedure

Due to the limited quantity of N-S compounds that could prepared from the Dravo scrubbing liquor, it was difficult to saturate a hydrolysis liquor with ammonium sulfate by hydrolysis of N-S compounds. Therefore, in actual tests, we used a simulated hydrolysis liquor prepared by the following procedure. First, 9 gallons of scrubbing liquor was filtered to remove gypsum crystals. The mother liquor was then saturated at room temperature with ammonium sulfate by adding 7 kilograms of $(NH_4)_2SO_4$. After standing a day, the saturated liquor was filtered to remove undissolved solids. This filtration step was taken to remove most of magnesium sulfate originally contained in the scrubbing liquor. Then, 3 kilograms of sulfuric acid is added to the liquor (this makes the acid concentration

of the liquor similar to the acid concentration of an actual hydrolysis liquor, i.e., 1 M sulfuric acid solution). Next, 2.5 kilograms of ammonium sulfate were added and the temperature of the liquor was elevated to 60 °C to dissolve the ammonium sulfate. Then the liquor was ready for crystallization test.

A schematic of the set up used for ammonium sulfate crystallization is presented in Fig.11. The simulated hydrolysis liquor prepared by the procedure described above is stored at 60 °C in a 5 gal tank. The liquor was fed to a DDO crystallizer which operates at 23 °C as a cooling crystallizer. The mean residence time was 1 hr and the DDO ratio of the crystallizer was 10. The inverted cone tube use for the overflow was made of a glass tube (I.D. = 3.5 cm, length = 40 cm). At the end of the DDO crystallization, crystal slurry is sampled from the underflow product and analyzed in terms of the chemical composition and the size of the crystals.
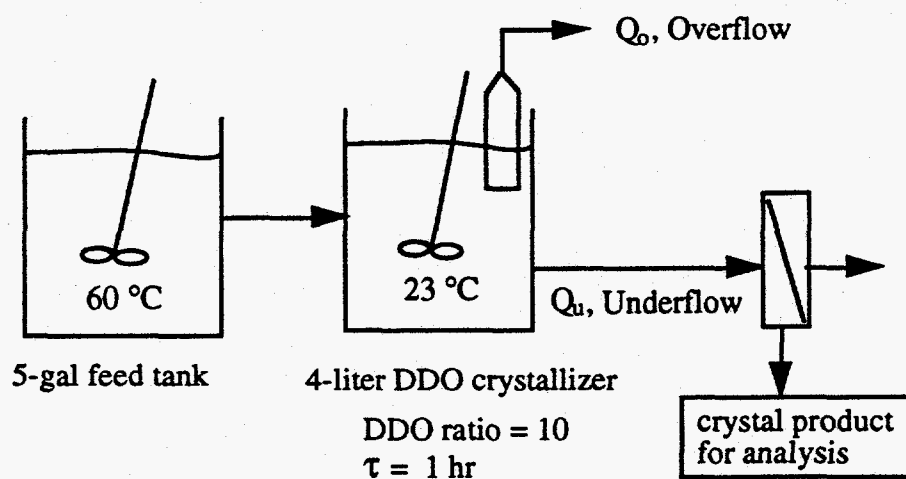

Fig.11 Schematic of the set up used for ammonium sulfate crystallization.

2.3.1 Results and Discussion

Fig.12 shows photomicrographs of the crystals obtained by the DDO crystallization. As shown in the micrographs, a unique shape was obtained in different size of the crystals. To examine the chemical composition of the crystals, an element analysis was performed, the results of which are presented in Table 1.

Table 1 Element analysis for the crystals obtained after the DDO cooling crystallization of the simulated hydrolysis liquor.

	Compounds	M.W.	Elements (wt %)				N/S ratio
			N	Mg	Ca	S	
Exp.	DDO crystallization		7.33	5.5	0.3	15.86	0.462
	batch crystallization		7.42	-	-	16.52	0.449
Theo.	$(NH_4)_2SO_4$	132	21.2	-		24.2	0.875
	NH_4HSO_4	115	12.2	-	-	27.8	0.438
	$(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$	361	7.8	6.7	-	17.7	0.438

The crystals obtained by the DDO operation contained 7.4 wt % nitrogen and 15.86 wt % sulfur. The chemical composition can be compared with ammonium sulfate since it seems most probable compound. When compared with theoretical composition of ammonium sulfate, we see that these values do not correspond to ammonium sulfate. Another possibility is Boussingltite, $(NH_4)_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. The nitrogen and sulfur content of the crystals obtained looked close to those of Boussingltite. However, the magnesium content was too small for Boussingltite. A direct comparison of the chemical composition with ammonium bisulfate was also unsatisfactory. To reexamine the result of the element analysis, the element analysis was repeated for the crystals obtained from a batch crystallization. However, the batch and DDO crystallization results were almost the same. Since the crystal substance was not clarified by a direct comparison, we conjectured
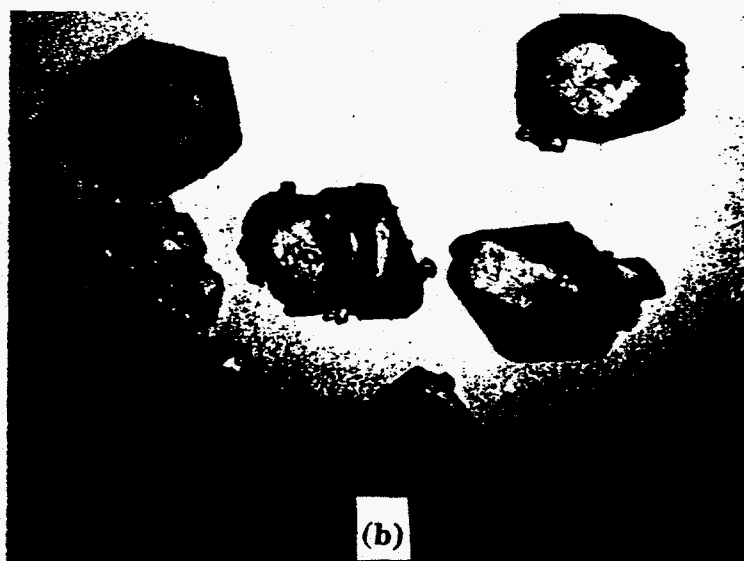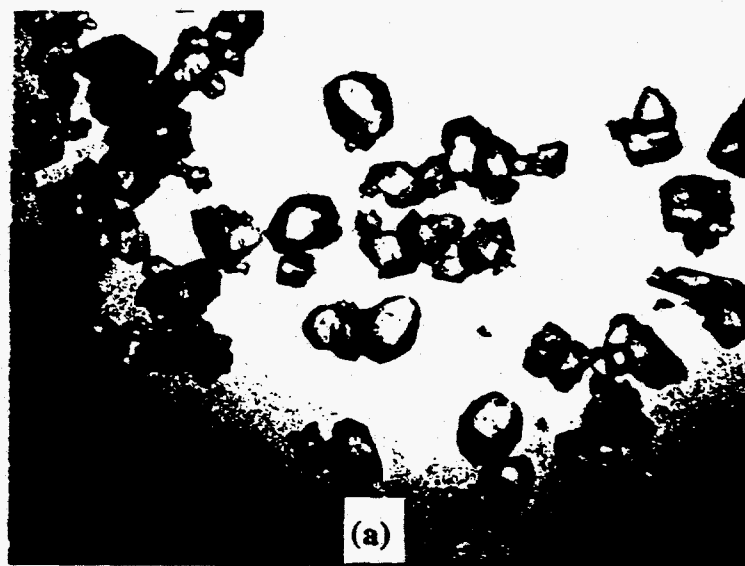
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Fig.12 Photomicrographs of the crystals obtained after a continuous crystallization of the simulated hydrolysis liquor. The crystals were obtained in (a) 210 μm and (b) 500 μm sieve.

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the obtained crystals could be a complicated compound mixture. Thus we compared the nitrogen to sulfur content ratio for an indirect comparison. The comparison of N/S content ratio revealed that the crystals were close to ammonium bisulfate. From this observation, we considered the crystals to be ammonium bisulfate. The observed nitrogen and sulfur content of the crystals, which are small compared to ammonium bisulfate, seemed to result from the content of the compounds such as crystal water. Further literature investigation of the solubility curve in a [$(NH_4)_2SO_4 + H_2SO_4 + H_2O$] system showed that under the strong acid environment we used, ammonium sulfate with sulfuric acid or ammonium bisulfate easily forms a sold crystal phase.

Fig. 13 shows a plot of cumulative weight fraction vs. particle size for the crystals obtained from the DDO operation. In the plot, we see a significant amount of the crystals had grown to a large size. The weight average size of these crystals was also as large as 424 μm. The observed large average crystal size implies the efficiency of the DDO crystallization.
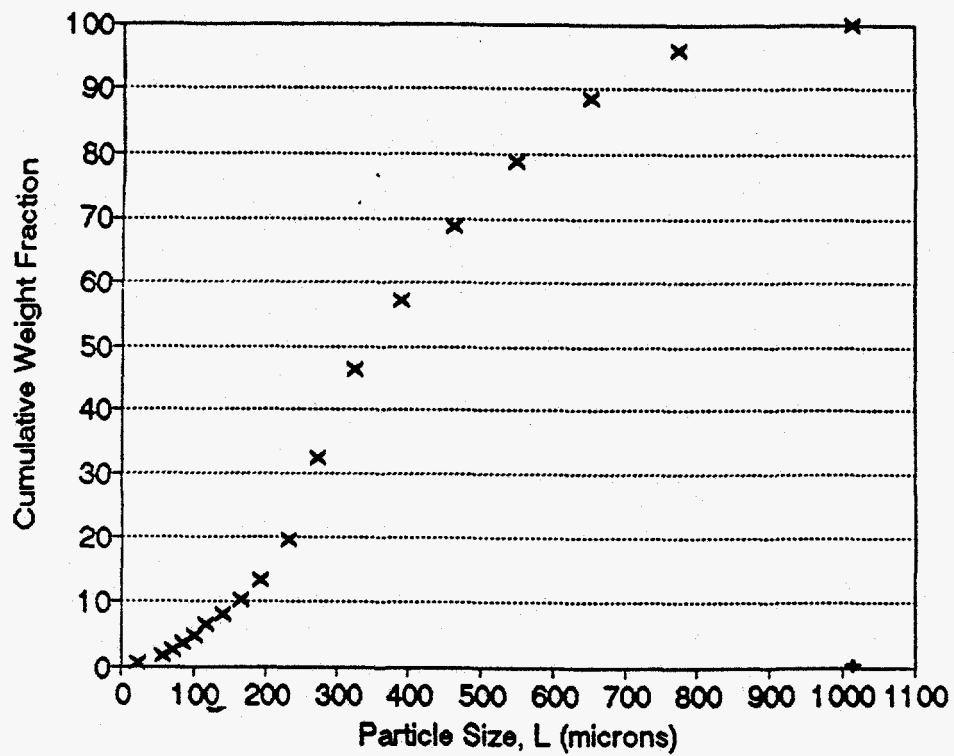
Fig.13 Cumulative weight fraction vs. particle size for the crystals obtained from the DDO cooling crystallization of the simulated hydrolysis liquor.

3. Preliminary Process Design

In order to obtain an estimation for the process streams of the lime/limestone process presented in Fig.1, a preliminary material balance was established for a basis of 300 MWe power plant facility. To simplify the calculation, the bleed for precipitation of N-S compounds, i.e., stream-4, was taken as 840 GPM for 300 MWe facility. Other basic assumptions and conditions are summarized in Table 2.

Table 2 Basis for the preliminary material balance

Bleed flow. : 840 GPM (correspond to 300 MW power plant) (stream-4)	

Composition	$MgSO_4$	= 10,000 ppm
	$CaSO_4$ =	1,000 ppm
	Na_2SO_4 =	1,000 ppm
	Fe-EDTA =	3,000 ppm
	N-S compounds = 0.312 M/liter	
SP. Gravity	1.11	

Assumptions
1. N-S compounds are precipitated at pH ~ 8.3.
2. The neutralizer is operated at 2.5 wt% sulfuric acid environment.

• Material Balance around the precipitation crystallizer (DDO-1)

We consider a material balance around the crystallizer (DDO-1) for precipitation of N-S compounds. The bleed of the scrubbing liquor from the scrubber and the lime feed stream was fed into the precipitation crystallizer to precipitate N-S compounds and the precipitated crystal crop was continuously taken out as over- and under- flow of the DDO crystallizer. The flow streams around this crystallizer are schematically presented in Fig.14. A material balance around the crystallizer is obtained as follows:

1). Total mass input rate by the bleed scrubbing liquor was calculated as follows.

Total Mass Input = (volume flow rate) x (s.p. gravity of the bleed liquor)
= 840 gal/min x 3.79 liter/gal x 1.11 g/ml x 1000 ml/liter x 1 lb/453.6 g x 60 min/hr
= 467434 lb/hr

2). The flow rate of the constituents of the input stream is calculated with the concentration data given in Table 2. For example, CaADS input rate is calculated by

CaADS in the input stream of the DDO-1
= (volume flow rate) x (CaADS concentration)
= 840 gal/min x 3.79 liter/gal x 0.312 mole CaADS/liter x 215 g/1M CaADS x 1 lb/453.6 g x 60 min/hr
= **28248 lb/hr**

3). To determine the lime addition rate, the crystallizer was assumed to operate at pH ~ 8.3. From the batch experiment result presented in Fig.2, the required amount of lime was estimated 0.75 g CaO/100 ml. Thus we obtain

lime addition rate = 0.75 g /100 ml x 191016 liters/hr x 1000 ml/liter x 1 lb/453.6 g
= **3158 lb/hr**
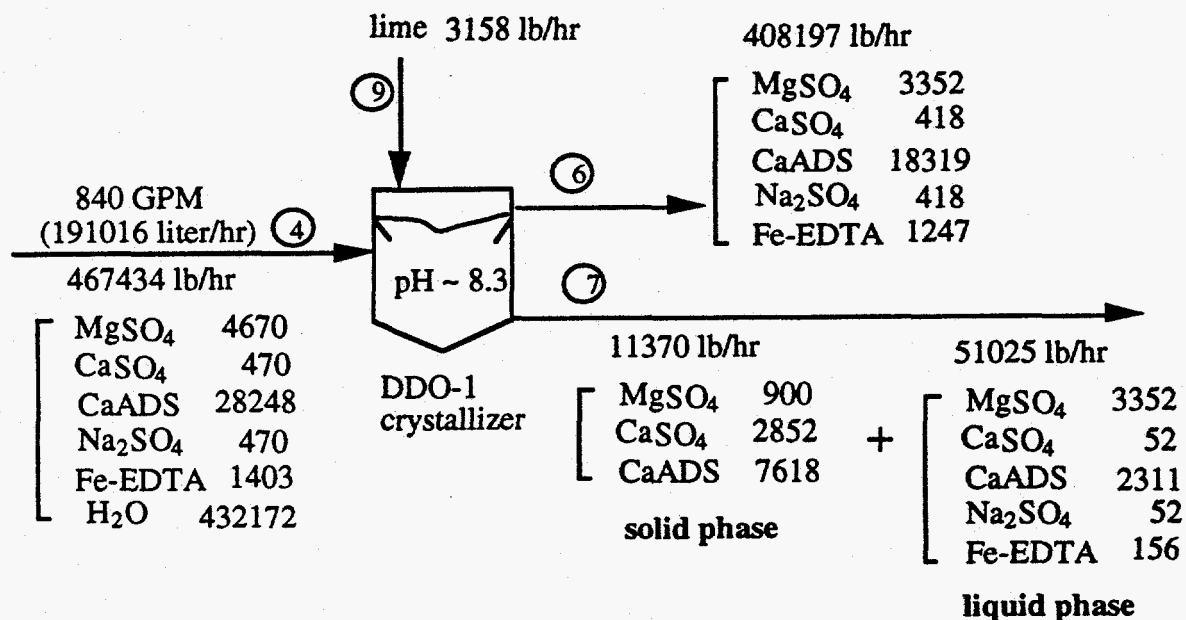
Fig.14 Material balance around the precipitation crystallizer (DDO-1).

4). Using the batch experiment result presented in Fig.3, the total amount of precipitated crystal crop after the DDO-1 crystallizer was calculated. From the batch experiment result, it was assumed that 2.7 g crystals/100 ml M.L. were precipitated at pH ~ 8.3 and that 67% of the precipitated crystals is equivalent to CaADS. Then,

a) Total Amount of crystals precipitated after the DDO-1.
= (input M.L. to DDO-1) x 2.7 g/100 ml
= 191016 liter/hr x 2.7 g/100 ml x 1000 ml/liter x 1lb/453.6 g
= **11370 lb/hr**

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b) Amount of CaADS precipitated after the DDO-1.
$$= \text{(Total amount of crystals precipitated)} \times 0.67$$
$$= 11370 \text{ lb/hr} \times 0.67$$
$$= 7618 \text{ lb/hr}$$

For calcium balance, we assumed that a part of the added lime was used to make CaADS while the rest of the added lime was converted to $CaSO_4$, and then estimated the amount of $CaSO_4$ in the precipitated crystals.

c) $CaSO_4$ in the precipitated crystal crop
- (lime for making $CaSO_4$) = (lime added) - (lime consumed to make CaADS)
$$= 3158 - (7618 \times 56 / 215)$$
$$= 1174 \text{ lb/hr}$$

- production of $CaSO_4$ = (lime for making $CaSO_4$) x (M.W. of $CaSO_4$) / (M.W. of CaO)
$$= 1174 \text{ lb/hr} \times 136/56$$
$$= 2852 \text{ lb/hr}$$

The crystal crop precipitated after the DDO-1 crystallizer was assumed to be composed of CaADS, $CaSO_4$, and $MgSO_4$, and then the amount of $MgSO_4$ in the precipitated crystals was estimated as:

d) ($MgSO_4$ precipitated) = (total crystals precipitated) - (CaADS precipitated) - ($CaSO_4$ precipitated)
$$= 11370 - 7618 - 2852$$
$$= 900 \text{ lb/hr}$$

5). For a DDO operation of the crystallizer, the over- and under- flow rates were estimated by assuming DDO ratio = 9 (thus, the liquid phase in the DDO-1 crystallizer was assumed to be distributed as 8:1 ratio for the overflow and underflow).

(liquid phase flow rate) = (input of M.L. to DDO-1) + (input of lime) - (total crystals precipitated)
$$= 467434 + 3158 - 11370$$
$$= 459222 \text{ lb/hr}$$

$$\begin{bmatrix} MgSO_4 & : 4670 - 900 = 3770 \\ CaADS & : 24248 - 7618 = 20630 \\ CaSO_4 & : 470 \\ Na_2SO_4 & : 470 \\ Fe\text{-}EDTA & : 1403 \end{bmatrix}$$

- Distribute the liquid phase as 8:1 ratio for the overflow and underflow.

(overflow) = 408197 lb/hr

$$\begin{bmatrix} MgSO_4 & : 3352 \\ CaADS & : 18319 \\ CaSO_4 & : 418 \\ Na_2SO_4 & : 418 \\ Fe\text{-}EDTA & : 1247 \end{bmatrix}$$

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$$\text{(underflow in liquid phase)} = 51025 \text{ lb/hr} \quad \begin{bmatrix} MgSO_4 & : 3352 \\ CaADS & : 2311 \\ CaSO_4 & : 52 \\ Na_2SO_4 & : 52 \\ Fe\text{-}EDTA & : 156 \end{bmatrix}$$

In the above described material balance around the DDO-1 crystallizer, a sulfate balance may not match. This mismatch is finally reflected in the water balance. This happened because some part of the added lime was assumed to be converted to $CaSO_4$ but the amount of SO_4 ions precipitated as the $CaSO_4$ was not taken into account. However, this discrepancy is so small compared to the major species of concern that the result would not deviate much from the numbers given in the enclosed flow sheet.

• Material Balance around the hydrolyzer (DDO-2)

The flow streams around this hydrolyzer are schematically presented in Fig.15. The solid crystal product precipitated in the DDO-1 crystallizer is fed to the hydrolyzer (DDO-2) along with the make-up sulfuric acid solution and the liquor stream recycled from the neutralizer. The feed rate of the solid crystal product was determined in the DDO-1 crystallizer. In this DDO-2 crystallizer, N-S compounds in the solid crystal product feed are converted by hydrolysis to ammonium sulfate. For the case of CaADS, the stoichiometry of the hydrolysis reaction can be written by

$$Ca[NH(SO_3)_2] + 2H_2O \rightarrow CaSO_4 + \tfrac{1}{2}H_2SO_4 + \tfrac{1}{2}(NH_4)_2SO_4$$
$$\text{CaADS}$$
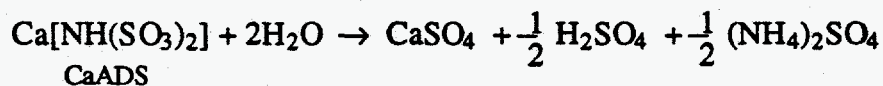
This hydrolysis stoichiometry shows the consumption of H_2O and production of H_2SO_4 along with $(NH_4)_2SO_4$, which should be considered in the material balance of the hydrolyzer. Under the acid condition of the hydrolysis liquor, the ammonium sulfate formed may be combined with H_2SO_4 and actually exist as ammonium bisulfate form. However, the form of the product would not affect the overall material balance. The liquor stream recycled from the neutralizer was assumed to be composed of H_2SO_4, $(NH_4)_2SO_4$,

and H_2O. The neutralizer was assumed to crystallize $(NH_4)_2SO_4$ in 2.5 wt % H_2SO_4 around room temperature and then the liquor stream was recycled from the neutralizer saturated with approximately 44 wt % $(NH_4)_2SO_4$. For the hydrolysis of potassium salts of N-S compounds, we observed that sulfuric acid concentration in the hydrolyzer could be adjusted from 0.5 M to 2 M H_2SO_4 (approximately 5 - 20 wt %) without affecting the hydrolysis characteristics of the N-S compounds. Assuming these hydrolysis characteristics also apply for CaADS, the flow rate of the recycle stream from the neutralizer was determined to yield the sulfuric acid concentration in the hydrolysis crop product at the acid range. In the material balance provided in Fig.15, the recycle stream from the neutralizer was determined so that the hydrolyzer was operated under 7.1 wt % of H_2SO_4.

As shown in the overall process diagram in Fig.1, the hydrolysis liquor coming from the hydrolyzer was fed to the neutralizer after $CaSO_4/MgSO_4$ was removed. In the neutralizer, the portion of sulfuric acid produced by the hydrolysis of N-S compounds was neutralized with
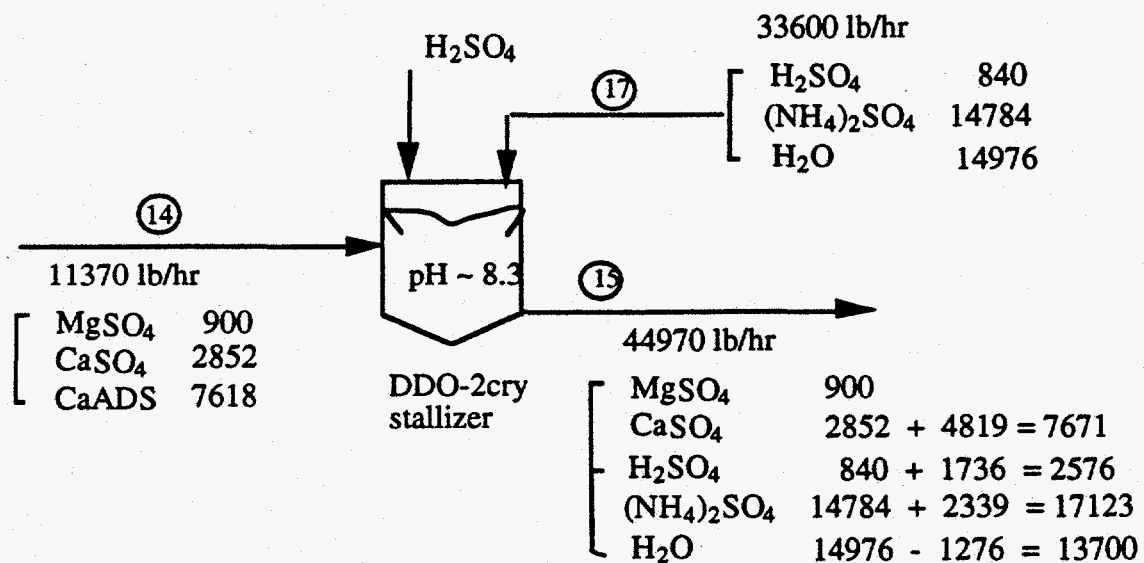
Fig.15 Material balance around the hydrolyzer (DDO-2)

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ammonia to yield $(NH_4)_2SO_4$. Therefore, the net production of $(NH_4)_2SO_4$ becomes twice that of $(NH_4)_2SO_4$ produced in the hydrolyzer (because, from the stoichiometry of the hydrolysis, equimolar amount of $(NH_4)_2SO_4$ and H_2SO_4 are produced from CaADS). Table 3 provides a summary of material balances for the lime/limestone process in Fig.1. In Table 3 it is noted that the net production of $(NH_4)_2SO_4$ for 300 MWe facility is estimated as 4678 lbs/hr (56 tons/day).

Table 3 Estimated flow rates for the streams in the regeneration process in Fig.1.
unit : (lbs/hr)

Stream		Total flow rate	MgSO$_4$	CaADS	CaSO$_4$	Na$_2$SO$_4$	Fe-EDTA	H$_2$O
4	bleed liquor	467434	4670	28248	470	470	1403	432172
9	lime addition	3158						
6	O'Flow M.L.	408197		18319	418	418	1247	balance
7	U'Flow Slurry	478804	4252	9929	2904	52	156	balance
8	M.L. Recycle	459222	3770	20630	470	470	1403	balance
14	M.L. w/xtals	11370	900	7618	2852			-
	Filter Wash							

Stream		Total flow rate	MgSO$_4$	NH$_3$	CaSO$_4$	H$_2$SO$_4$	(NH$_4$)$_2$SO$_4$	H$_2$O
	H$_2$SO$_4$							
17	DDO-2 M.L. R (% in M.L)	33600				840 (2.5)	14784 (44)	14976 (53.5)
15	Slurry out DDO-2	44970	900		7671	2576	17123	13700
16	filter cake	8571	900		7671			
18	M.L. DDO-2 (% in M.L)	36399				2576 (7.1)	17123 (47.0)	13700 (45.9)
19	NH$_3$ Reactant	1888		612				1276
	Rxn AmSO$_4$ & Water	2339				(- 1736)	2339	
17	M.L. Recycle (% in M.L)	33600				840 (2.5)	14784 (44)	14976 (53.5)
20	Production of AmAmSO$_4$	4678 (56 ton/day)					4678	

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