RI 9297

REPORT OF INVESTIGATIONS/1990

Recovery of Sulfur From Phosphogypsum: Conversion of Calcium Sulfide to Sulfur

By David A. Rice, Olice C. Carter, Jr., Alexander May, Margaret M. Ragin, and Robert G. Swanton

1910 ★ 80 ★ 1990
YEARS

BUREAU OF MINES

March 3, 1849

UNITED STATES DEPARTMENT OF THE INTERIOR

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This report is based upon research conducted under an agreement between the University of Alabama and the Bureau of Mines.

Library of Congress Cataloging in Publication Data:

Recovery of sulfur from phosphogypsum : conversion of calcium sulfide to sulfur / by David A. Rice ... [et al.].

p. cm. - (Report of investigations; 9297)

Includes bibliographical references.

Supt. of Docs. no.: I 28.23:9297.

1. Sulphur. 2. Phosphogypsum. 3. Calcium sulphide–Metallurgy. I. Rice, David A. (David Arthur) II. Series: Report of investigation (United States. Bureau of Mines); 9297.

TN23.U43 [TN890] 622 s–dc20 [661'.1] 89-600337
CIP

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mL	milliliter
g	gram	mL/min	milliliter per minute
g/mL	gram per milliliter	mm	millimeter
h	hour	μm Hg	micrometer of mercury
in	inch	mm Hg	millimeter of mercury
L	liter	pct	percent
m^2	square meter	ppm	part per million
m^2/g	square meter per gram	psi	pound per square inch
meq	millequivalent	wt pct	weight percent
min	minute		

RECOVERY OF SULFUR FROM PHOSPHOGYPSUM: CONVERSION OF CALCIUM SULFIDE TO SULFUR

By David A. Rice,[1] Olice C. Carter, Jr.,[2]
Alexander May,[3] Margaret M. Ragin,[4] and Robert G. Swanton[5]

ABSTRACT

As part of a cooperative effort between the Bureau of Mines and the Florida Institute of Phosphate Research (FIPR), with input from the phosphate industry, the conversion of phosphogypsum to sulfur is being investigated. The proposed process incorporates the thermal reduction of phosphogypsum to calcium sulfide (CaS) and a hydrometallurgical treatment to convert calcium sulfide to sulfur (S°). The research described herein is focused on the latter half of the process. It was demonstrated that calcium sulfide could be converted to ammonium bisulfide (NH_4SH), and that ammonium bisulfide could be oxidized by air in the presence of a catalyst, to elemental sulfur, which was adsorbed on the catalyst. Two methods for recovering sulfur from the catalyst were developed: (1) thermal treatment to volatilize sulfur, and (2) leaching the sulfur from the catalyst with liquid anhydrous ammonia. Over 90 pct of the sulfur adsorbed on activated carbon (the catalyst) was recovered by both methods. Based upon the encouraging laboratory investigations, a hydrometallurgical scheme was proposed for the overall conversion of calcium sulfide to elemental sulfur.

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INTRODUCTION

As part of its mission to ensure that the Nation has an adequate supply of minerals at acceptable economic, environmental, and social costs, the Bureau of Mines is developing a process to convert phosphogypsum to elemental sulfur. This investigation was cofunded by the Bureau and FIPR, Bartow, FL.

The voluntary cooperation of the following Florida phosphate companies in offering valuable advice and suggestions on the research efforts is gratefully acknowledged: Gardinier, Inc.; Agrico Chemcial Co.; Farmland Industries Inc.; Royster Co.; W. R. Grace & Co.; Occidental Chemical Corp.; Conserve; International Minerals & Chemical Corp.; USS Agri-Chemicals Inc.; and C. F. Industries Inc.

Forecasts of sulfur supply between 1990 and 2000 predict a depletion in primary sulfur reserves and an increase in sulfur demands and prices on a worldwide scale (*1*).[6] The fertilizer industry in the United States annually consumes about 65 pct of the Nation's sulfur (*2*). This sulfur is used to make sulfuric acid, which is mixed with phosphate rock to make phosphoric acid, the major ingredient used to make phosphate fertilizers. A byproduct of phosphoric acid production is the calcium sulfate dihydrate, phosphogypsum. The sulfur, although consumed, is not lost, but is converted to phosphogypsum, from which it is potentially available. By the year 2000, the estimated quantity of stockpiled phosphogypsum in Florida will be about 1 billion tons (*3*). The available sulfur from this stockpile would help meet the increased demand for sulfur in the United States.

The Bureau conducted the phosphogypsum research in two phases: (1) thermal catalytic reduction of phosphogypsum to calcium sulfide, which will be published later by the Bureau, and (2) development of a method to convert calcium sulfide to sulfur. The research described herein is focused on the latter phase.

INITIAL CONSIDERATIONS

Theoretically, the direct oxidation of dry calcium sulfide to elemental sulfur by air is not possible. Thermodynamic evaluation of literature data on the dry calcium-oxygen-sulfur system showed that, at equilibrium, calcium sulfate ($CaSO_4$) is formed at all reasonable conditions at which elemental sulfur is stable, and that at high temperatures, calcium oxide (CaO) and sulfur dioxide (SO_2) are the stable products (*4*). However, laboratory experience and literature references (*5-6*) indicate that sulfide can be oxidized to elemental sulfur in aqueous systems. Therefore, a hydrometallurgical process was indicated. The Elcor process (*7*) involved treating calcium sulfide with water (H_2O) and carbon dioxide (CO_2), resulting in hydrogen sulfide (H_2S) and calcium carbonate ($CaCO_3$), as shown in reaction A. The Bureau investigated (*8*) a method for converting calcium sulfide to sulfur, which involved converting calcium sulfide, which is only slightly water soluble, to the very soluble sodium bisulfide (NaSH), by ion exchange, and then releasing hydrogen sulfide by treating the sodium bisulfide with water and carbon dioxide in a reaction analogous to reaction A. The hydrogen sulfide was then converted to sulfur by the Claus process (*9-10*).

$$CaS + H_2O + CO_2 \rightarrow H_2S + CaCO_3. \qquad (A)$$

However, applying the Claus process to the larger tonnages of stockpiled phosphogypsum would create many additional problems, and experts in the phosphate industry advised against this approach. Therefore, direct oxidation of aqueous sulfide by air was considered. Tests were performed on direct oxidation of aqueous slurries of pure calcium sulfide by air and/or oxygen with and without catalysts. The sulfur recoveries were low when the direct oxidation techniques were used. Rosenwald, Hamblin, Urban, and Zimmerman (*11*) claimed that ammonium bisulfide (NH_4SH)[7] could be oxidized to sulfur with high yields.

A hydrometallurgical scheme was then developed to convert calcium sulfide to ammonium bisulfide and then the method of Rosenwald, Hamblin, Urban, and Zimmerman was applied to oxidize the ammonium bisulfide to sulfur.

OVERALL POTENTIAL PROCESS

The hydrometallurgical scheme, combined with the catalytic thermal reduction of phosphogypsum, results in an overall potential process for converting phosphogypsum to sulfur. The reactions involved are shown by reaction B, the thermal reduction of phosphogypsum, and by reactions C and D, the hydrometallurgical process. Carbon dioxide, from reaction B, is used in the formation of calcium sulfide (reaction C), and the ammonium hydroxide (NH_4OH) (reaction D), is recycled to reaction C.

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2. \qquad (B)$$

$$CaS + NH_4OH + CO_2 \rightarrow NH_4SH + CaCO_3. \qquad (C)$$

$$NH_4SH + 1/2O_2\,(\text{air}) \underset{(\text{carbon})}{\rightarrow} NH_4OH + S^\circ. \qquad (D)$$

There are four major steps in the scheme: (1) conversion of calcium sulfide to ammonium bisulfide, (2) oxidation of ammonium bisulfide to sulfur, (3) absorption of sulfur on carbon, and (4) removal of sulfur from carbon.

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[6] Italic numbers in parentheses refer to items in the list of references at the end of this report.

[7] NH_4SH is named ammonium bisulfide or ammonium hydrosulfide. In this report, reference to sulfide, or ammonium sulfide in solution refers to NH_4SH (unless specifically stated otherwise) since this is the predominate species of sulfide present at pH values less than 13.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance and advice of David P. Borris, Executive Director, FIPR; and Mike Lloyd, Research Director, Processing, FIPR.

The authors also gratefully acknowledge Thomas A. Phillips, Bureau of Mines, Washington, DC, for consultation, engineering input, and assistance in helping prepare the flowsheet shown in the "Results and Discussion" section.

MATERIALS USED

The following materials were used in experiments performed that produced data for this report:

Calcium Sulfide.–Two types were used. The first type was calcium sulfide made by thermal reduction of phosphogypsum using magnetite as a catalyst. This material was used as is, without purification. The second type was a Fisher[8] commercial-grade "purified" powder analyzed as 90.22 pct CaS.

Mullite Beads.–Each bead was approximately 2 mm in diameter. The beads were used to promote the flow of ammonium bisulfide solutions and air through packed columns and served as a surface to support the activated carbon.

Activated Carbons.–Several types were used: (1) Baker acid-washed carbon, laboratory grade, and (2) Calgon Corp. commercial-grade activated carbons: Filtrasorb 400 (F-400); Filtrasorb 300 (F-300); a very high purity, high-surface area carbon (APA); and a chemically pure grade carbon (CPG). F-400 and F-300 were manufactured to remove organic pollutants from water. CPG was produced by high-temperature steam activation and an acid wash. The properties of these carbons are given in table 1.

Sulfur-Loaded Carbon (SLC).–SLC was prepared using F-400 activated carbon and ammonium bisulfide by techniques similar to those previously described by May and Sweeney (*12*). In brief, the carbon was placed in laboratory columns and loaded with sulfur by concurrently flowing ammonium bisulfide solution and air downward through the carbon granules. The ammonium bisulfide solution was recycled through the column until the carbon was loaded with sulfur. The SLC samples were dried at 105° C and stored in sealed plastic bottles prior to use. Samples, designated SLC-1 and SLC-2, were prepared using the above procedure and used in some of the experiments in this report. When analyzed, they were approximately 30 and 40 pct S, respectively.

Ammonium Bisulfide.–Solutions of ammonium bisulfide were prepared from calcium sulfide. Fisher ammonium sulfide solution, assays as $(NH_4)_2S$, was 22 pct. Concentrated solutions of ammonium bisulfide were made by reacting ammonium hydroxide with hydrogen sulfide.

Anhydrous Ammonia (NH_3).–Liquid anhydrous ammonia was prepared by condensing Linde commercial-grade ammonia using a stainless steel condensing coil, which was immersed in a dry ice-acetone bath. The liquefied ammonia was prepared immediately before use and kept in a covered beaker.

Hydrogen Sulfide Gas.–Commercial-grade hydrogen sulfide gas was used for preparation of ammonium bisulfide.

Other Reagents.–Chemically pure reagent-grade chemicals and de-ionized water were used.

Table 1.–Typical properties of commercial-grade activated carbons

	F-400	F-300	APA	CPG
Surface area[1] . . . . m^2/g . .	950-1,050	950-1,050	1,520	1,000-1,000
Minimum iodine number	900	1,000	1,225	900
Mesh size	-12, +40	-12, +40	-12, +40	-12, +40
Ash, water soluble . . . . pct . .	0.5	0.5	0.07	0.5
Density, packed, dry . . . . g/mL . .	0.49	0.52	0.40	0.52
Maximum total S . . . . pct . .	[2]0.8	ND	ND	ND
Acid washed	No	No	Yes	Yes

ND Not determined.

[1] N_2 BET adsorption equation method.

[2] Analysis of specific C used in tests by the Bureau.

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[8] Reference to specific products does not imply endorsement by the Bureau of Mines.

ANALYTICAL METHODS

Analysis of calcium sulfide for total sulfur was performed using the Association of Official Analytical Chemists (AOAC) method 3.108 (*13*). In this method, all sulfur species are oxidized to sulfate by fusion of the sample with sodium peroxide (Na_2O_2) and sodium carbonate (Na_2CO_3), and the resulting sulfate was determined by adding barium chloride ($BaCl_2 \cdot 2H_2O$) and weighing the precipitated barium sulfate ($BaSO_4$). Total sulfur on carbon catalysts was determined using a LECO sulfur determinator (*14*).

Analyses of SLC's for elemental sulfur were performed by extracting the sulfur with carbon disulfide (CS_2).

Analyses of ammonium bisulfide solutions were as follows: Total sulfur was determined by oxidation of sulfide and other sulfur species by sodium peroxide to sulfate, and determination of sulfate was by precipitation with barium chloride and weighing the precipitated barium sulfate. However, since strong sulfide solutions react explosively with sodium peroxide, these solutions were first added to zinc chloride ($ZnCl_2$) solution (AOAC reagent 6.123) (*13*) to precipitate zinc sulfide (ZnS), which then could be oxidized smoothly. Sulfur species in solution were determined by iodometric methods (*15*). Sulfate was determined by precipitation with barium chloride and weighing the precipitated barium sulfate. Hydrogen sulfide was determined by absorption in zinc chloride followed by iodometric methods. Polysulfides were detected qualitatively by their color. Ammonia in water was determined by acid titration. Analyses for trace elements were performed by inductively coupled plasma spectrographic analysis (*16*).

EXPERIMENTAL METHODS

CONVERSION OF CALCIUM SULFIDE TO AMMONIUM BISULFIDE

A new approach for conversion of calcium sulfide to ammonium bisulfide was investigated. Conversion of calcium sulfide to ammonium bisulfide was accomplished by treating calcium sulfide with solutions of ammonium carbonate, or ammonium bicarbonate (NH_4HCO_3), or ammonium hydroxide and carbon dioxide; the latter shown in reaction C. The reaction of carbonate, bicarbonate, and carbon dioxide plus ammonium hydroxide with calcium sulfide all produced ammonium bisulfide. The carbonate contains an excess amount of ammonium ion over that needed by ammonium bisulfide and would not be suitable for use in the process scheme. Ammonium hydroxide and carbon dioxide, in stoichiometric quantities, are the reagents that would be used in the process scheme as indicated by reactions B, C, and D. Since ammonium hydroxide and carbon dioxide are equivalent to ammonium bicarbonate, the latter was used for routine laboratory preparation of ammonium bisulfide (reaction E).

$$CaS + NH_4HCO_3 \rightarrow CaCO_3 + NH_4SH. \qquad (E)$$

Ammonium bisulfide is an unstable compound and exists only in aqueous solutions (*10*), and even in solution, it has a great tendency to evolve hydrogen sulfide (reaction F). Closed reaction vessels are needed to prevent loss of hydrogen sulfide.

$$NH_4SH + H_2O \rightarrow NH_4OH + H_2S. \qquad (F)$$

Loss of hydrogen sulfide may also occur through the reaction of calcium sulfide with water (reaction G) and may occur simultaneously with the reactions in reaction C or reaction E.

$$CaS + H_2O \rightarrow CaO + H_2S. \qquad (G)$$

Reactions C and D indicate that a vacuum should be produced as gaseous carbon dioxide is converted to solid calcium carbonate and oxygen is consumed to oxidize sulfide to sulfur, while reaction G indicates that pressure should be produced as gaseous hydrogen sulfide is evolved. The reaction between calcium sulfide and ammonium bicarbonate (reaction E) should not produce a pressure or a vacuum since no gaseous reactant or product is present. Operations, both in the laboratory and in any potential process, must safely contain any pressures or vacuums produced, so this aspect of the production of ammonium bisulfide was investigated.

Stoichiometric quantities of calcium sulfide and ammonium bicarbonate were placed in a heat-resistant glass bottle, water was added to completely fill the bottle and to exclude air, the bottle was tightly sealed, and the contents were stirred by a magnetic stirrer for 1 h. The calcium carbonate was filtered off, and the solutions were stored in plastic bottles or used immediately to oxidize the ammonium bisulfide to sulfur. Commercial-grade calcium sulfide was used in the initial preparations of ammonium bisulfide to prove the method (reactions C and E), while calcium sulfide, which had been made from phosphogypsum by the thermal process, was used to confirm the application of the method. Difficulties were encountered in making concentrated solutions of ammonium bisulfide from calcium sulfide in the laboratory because of the large quantities of calcium carbonate forming and the necessity of countercurrent washing of the filtered calcium carbonate.

CONVERSION OF AMMONIUM BISULFIDE TO SULFUR

Tests Using Laboratory-Grade Carbon

Early tests on the conversion of ammonium bisulfide to sulfur used fixed-volume reactors consisting of 1-, 2-, and 3-L heat-resistant glass, round-bottom flasks and ordinary laboratory glass distillation apparatus. About 0.3 g of carbon catalyst and the ammonium bisulfide solutions to be oxidized to sulfur were added to the fixed-volume reactors. Later tests used glass columns, 7/8 in ID by 12 in length, containing a packed bed of 100 g of mullite beads with 1.0 g of carbon on their surface. Filter flasks, bubblers, and variable-speed peristaltic pumps were used.

Early tests on oxidizing ammonium bisulfide were done in fixed-volume reactors, to control the oxygen-to-sulfur ratios, which were maintained near 1.0, and to prevent the loss of hydrogen sulfide. A known volume of ammonium bisulfide solution was transferred to the 1-, 2-, or 3-L heat-resistant glass round-bottom flasks, carbon catalyst was added, the reactor was sealed, and the contents were stirred several hours. The carbon was removed by filtering and the ammonium polysulfide [$(NH_4(S_4)SH)$] solution was decomposed into sulfur by distilling about 20 pct of the volume of the solutions. These tests showed that the ammonium bisulfide could be oxidized to ammonium hydroxide and ammonium polysulfide (reaction H) and that the resulting polysulfide solutions could then be distilled to form sulfur (reaction I).

$$5NH_4SH + 2O_2\ (\text{air}) \xrightarrow[(\text{carbon})]{} 4NH_4OH + NH_4(S_4)SH. \qquad (H)$$

$$NH_4(S_4)SH \xrightarrow[(\text{distill})]{} NH_3 + H_2S + 4S. \qquad (I)$$

The ammonia, water, and hydrogen sulfide would recombine in the distillate to form ammonium bisulfide (reaction J), which could be recycled into the process.

$$NH_3 + H_2S \xrightarrow[(H_2O)]{} NH_4SH. \qquad (J)$$

Ammonium polysulfide is the predominate polysulfide formed (*5, 11*) on oxidation of aqueous sulfides.

By having a fixed volume of air and oxygen-to-sulfur ratios near 1.0, the ammonium bisulfide solutions were restricted to small volumes and low concentrations. A technique was later developed whereby the conversion of ammonium bisulfide to elemental sulfur was carried out using a carbon catalyst in a packed bed. The distillation step was eliminated and elemental sulfur was formed directly on the carbon catalyst. The ammonium bisulfide solutions were recycled through the carbon bed, while air was drawn in the same direction through the carbon. Oxygen-to-sulfur ratios were adjusted by the concentrations of the ammonium bisulfide solutions and the pumping rates of the solutions and the air. The solutions turned from a pale yellow to a dark red color, then became transparently clear. Pumping was continued until the solutions were transparent and sulfur was formed in situ on the carbon.

Tests on Commercial-Grade Activated Carbons

Laboratory column testing was carried out to evaluate four grades of commercial-grade coal-derived granular activated carbons for use in oxidizing ammonium bisulfide to sulfur. These carbons were F-400, F-300, APA, and CPG. Four identical test units were set up for comparing the carbons on a side-by-side basis. Each unit, illustrated in figure 1, consisted of a 7/8-in-diam glass column containing 50 mL of granular activated carbon. Predetermined concentrations of ammonium bisulfide solutions were recycled through each column using four peristaltic pump heads operating on one drive. Air was passed concurrently with the ammonium bisulfide through the column at predetermined flow rates.

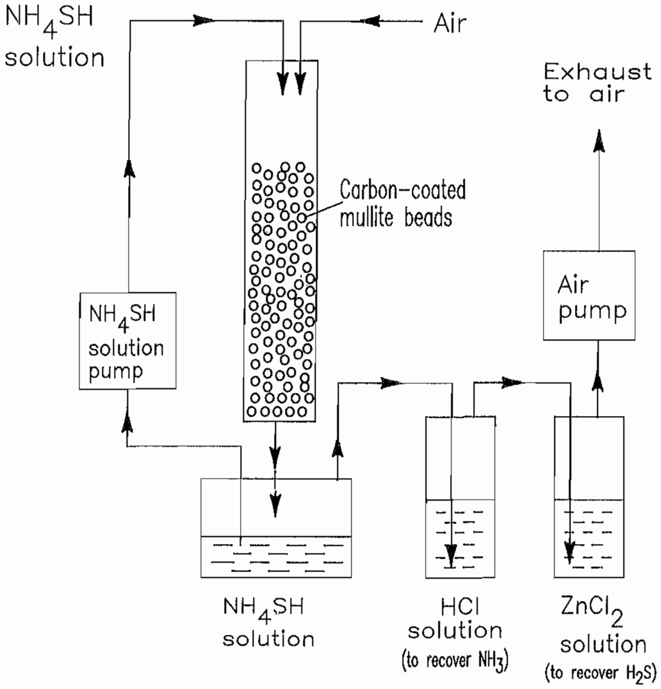

Figure 1.–Laboratory test apparatus for converting ammonium bisulfide to sulfur.

The duration of each test was 6 h. Five four-carbon test series were completed. At the completion of each test, the spent bisulfide solution was analyzed for total sulfur. The SLC was rinsed with distilled water, dried, and analyzed for total sulfur. The distribution of the initially available sulfur in the ammonium bisulfide solution to the loaded carbon and to the spent ammonium bisulfide liquor products was calculated. Total sulfur on the loaded carbon was determined by the LECO sulfur determinator method. Elemental sulfur was determined by extracting the sulfur with carbon disulfide. The amount of sulfur reporting as the offgas was calculated by difference.

REMOVAL OF SULFUR FROM CARBON

Laboratory studies were carried out using the procedures described in this section to evaluate the potential of (1) thermal treatment to sublime or distill sulfur from the carbon and (2) chemical leaching using liquid anhydrous ammonia to solubilize the sulfur.

Thermal Methods

The thermal removal of sulfur from SLC was investigated using both vacuum distillation and a nitrogen (N_2) carrier gas to assist sulfur vapor transport.

Vacuum distillation tests were conducted using a laboratory oven-vacuum distillation apparatus. Two to three grams of SLC-1 was heated to predetermined temperatures (200° to 450° C) under 72- to 125-μm Hg vacuum in a quartz reaction chamber connected to a condensing tube, cold trap, and a two-stage laboratory vacuum pump. At the conclusion of each test, the carbon and sulfur condensate were removed and weighed.

Nitrogen carrier gas tests were carried out in a stainless steel pipe reactor of 59.8-mL capacity, using 22.5 g (30 mL) of SLC-1 for each test. Prior to heating, the loaded reactor was purged with 10 equivalent volumes of nitrogen. The reactor was then brought to temperature, and preheated nitrogen gas was passed through the reactor at predetermined flow rates. The volatilized sulfur was collected in a straight-pipe condenser. At the end of the test, the condensed sulfur product was weighed and the sulfur yield was calculated.

Sulfur Extraction With Liquid Anhydrous Ammonia

A novel method for extraction of sulfur from SLC by leaching with liquid anhydrous ammonia was investigated. The suitability of the leached carbon for recycling to the loading step after sulfur extraction was also examined.

The extraction of sulfur from carbon using liquid anhydrous ammonia was investigated using the stainless steel continuous flowthrough system shown in figure 2. The design of this apparatus provides for the use of an inert atmosphere. Each leaching test used 105 g of dry SLC, analyzing 41 pct S. All components of the system were purged with helium prior to introduction of liquid anhydrous ammonia. The leaching test was initiated by metering the liquid anhydrous ammonia into the bottom of the temperature-controlled reactor. The liquid anhydrous ammonia solution containing the dissolved sulfur exited the top of the reactor and passed through a chilling coil. Timed aliquots (300 to 500 mL) of the sulfur-ammonia solution were collected in tared beakers. The initial aliquots of effluent from the reactor were dark purple, which is indicative of dissolved sulfur in ammonia. The flow of ammonia was continued until the sulfur-ammonia solution became nearly clear. The beakers were immediately weighed after filling and then allowed to evaporate, leaving a sulfur product. Cumulative sulfur recoveries were calculated based upon the amount of extracted sulfur present in each of the timed aliquots and on the original amount of sulfur in the SLC sample.

Carbon Recyclability

Locked-cycle testing to investigate the feasibility of reloading an activated carbon after removal of its sulfur load by ammonia leaching consisted of two parts: (1) loading of sulfur onto the activated carbon by oxidation of ammonium bisulfide and (2) leaching of sulfur using liquid anhydrous ammonia in the continuous flowthrough system.

Loading of the carbon was carried out in a glass column. For the first cycle, a 100-g charge of F-400 carbon was loaded with sulfur. Air required for oxidation was passed downward through the carbon bed at a rate of 1,460 mL/min. Ammonium bisulfide solution, having an initial concentration of 19 pct S, was recirculated with downward flow, at a rate of 4.0 mL/min. The time for each loading step was 4.0 h. After loading, the carbon was rinsed with distilled water, removed from the column, dried at 105° C, and weighed. This carbon was the feed to the ammonia-leaching step.

Leaching of the SLC was carried out using the continuous-flow leaching apparatus and the technique described above. The temperature was held constant at 15° C for all tests. After each leaching test, the sulfur-laden ammonia (2.0 L) was allowed to evaporate under ambient conditions. The sulfur residue remaining in each beaker was weighed and was reported as the sulfur product. The leached carbon was removed from the reactor, weighed, and retained for the next loading cycle.

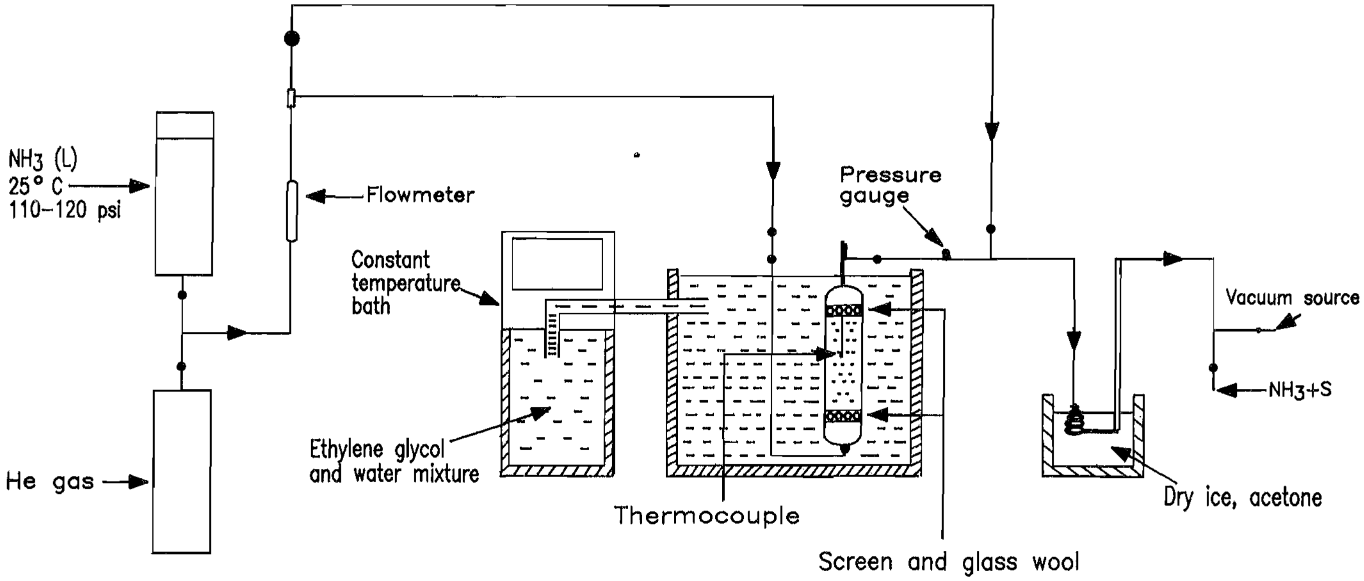

Figure 2.–Continuous flowthrough system for ammonia leaching.

RESULTS AND DISCUSSION

PREPARATION OF AMMONIUM BISULFIDE FROM CALCIUM SULFIDE

Preliminary laboratory testing was carried out to verify that ammonium bisulfide could be prepared from commercial-grade chemicals. For this work, 27.7114 g of 90.22 pct CaS plus 27.40 pct NH_4HCO_3 and 150 mL of water were placed in a reaction vessel, which was then sealed and stirred overnight. The mole ratio of ammonium bicarbonate to calcium sulfide was 1.002. The calcium carbonate formed in the reaction was filtered off and washed with deionized water, and the filtrate and wash water were combined and diluted to 500 mL. The nominal concentration of the resultant ammonium bisulfide solution was 2.213 pct or 2.222 g S per liter, with a density of 1.0042 g/mL. Hydrogen sulfide, which was evolved during the first 10 min of the experiment, was absorbed in zinc chloride solution, and both solutions were subsequently analyzed. The ammonium bisulfide and zinc chloride solutions contained 1.925 g total sulfur and 0.194 g of sulfur, respectively. Additional data are shown in table 2.

Ammonium bisulfide solutions prepared in the manner described in the previous paragraph were found to contain $S^{=}$ as the predominant species, with minimal amounts of oxidized sulfur species being formed, as indicated by the chemical analysis shown in table 3.

Verification of the reaction shown by reactions C and D was confirmed by adding carbon dioxide to a slurry of 5.00 g CaS in an aqueous solution of 0.931 normal ammonium hydroxide. An initial carbon dioxide pressure of 2 psi soon dropped to a vacuum of 3 psi. On continuing the addition of carbon dioxide, the pH of the solution dropped from about 11 to 7.5. The calcium carbonate was filtered, and the filtrate was oxidized to sulfur by the fixed-volume reactor-distillation method. The sulfur recovery was 44 pct of that in the original calcium sulfide.

Verification of the reaction shown by reaction E was confirmed numerous times by routinely making ammonium bisulfide solutions from calcium sulfide plus ammonium bicarbonate. Sulfur recoveries were near 90 pct in the solutions plus about 9 pct H_2S, based on the amount of sulfur initially in the calcium sulfide. Yields of ammonium bisulfide solutions, based on the amount of calcium carbonate formed compared with the amount potentially available from calcium sulfide, were 98 to 100 pct. This indicated that the reaction shown by reaction E was essentially quantitative.

Table 2.–Chemical analysis of reaction solutions prepared from commercial-grade chemicals

	S, pct
Total S in NH_4SH	86.7
H_2S	8.7
Balance	4.6
Total	100.0

Table 3.–Sulfur species in ammonium bisulfide solution

	S, pct
$S^{=}$	95.7
$S_2O_3^{=}$	3.9
$SO_4^{=}$	.4
$SO_3^{=}$	.0
Total	100.0

Calcium carbonate produced by reaction E was thoroughly washed with water. Two slurries of this calcium carbonate were made; one of 20.4 wt pct $CaCO_3$ and the other of 9.0 wt pct $CaCO_3$. After 3 h settling, no further change was observed and the percentages of solids in the settled material were 39.9 and 30.9 pct from the initial 20.4 and 9.0 pct slurries, respectively. Both slurries were vacuum filtered using a funnel. The calcium carbonate filter cakes contained 50.7 and 52.6 pct H_2O, respectively. These tests, plus attempts to make concentrated solutions of ammonium bisulfide, indicated that single-batch preparation of ammonium bisulfide was limited to about 20 pct $CaCO_3$ or about 10 pct NH_4SH because of the quantity of solids in the slurries. Higher concentrations of ammonium bisulfide were made but not in single-batch operations.

Reactions C, E, F, and G were investigated by the following experiment. Equimolar amounts of dry calcium sulfide and dry ammonium bicarbonate were added to a dry filter flask equipped with a manifold to direct any gas to a zinc chloride solution or to water in two separate 250-mL cylinders. Water was added to the flask containing the calcium sulfide and ammonium bicarbonate through a water seal to prevent any loss of gas on adding the water, and the contents were stirred with a magnetic stirrer. During the first few minutes, hydrogen sulfide was evolved and trapped by the zinc chloride solution. After 10 min, the pressure equilibrated, as shown by the solution levels in manifold tubes in zinc chloride solution and in the water. All openings to the zinc chloride, water, and reagent flask were closed, and the solution was stirred overnight. On opening the tube to the cylinder of water the next morning, all the water was sucked out of the cylinder into the reaction flask, indicating a vacuum had been produced. The evolution of hydrogen sulfide may have been due to reaction F, or due to reaction G, which could have occurred before the solid ammonium bicarbonate dissolved in the water. The existence of the vacuum probably occurred because the oxygen in the air in the sealed flask was consumed as shown by reaction C.

The exact polysulfide form, as shown in reactions H and I, was not characterized. However, polysulfides were easily detected by their bright yellow color. On distillation, the solutions became clear, the pH dropped from 9.2 to 6.9, 20 pct of the sulfur in the solutions was recovered as hydrogen sulfide, and equimolar quantities of ammonia and hydrogen sulfide were formed. Reproducibility of the experimental data was poor but was consistent enough to confirm the reactions indicated by reactions H and I.

PREPARATION OF AMMONIUM BISULFIDE FROM CALCIUM SULFIDE MADE FROM PHOSPHOGYPSUM

A sample of calcium sulfide, prepared by thermal reduction of phosphogypsum, was placed in a sealed glass bottle and stirred for 2 h with a 17 pct excess of ammonium bicarbonate solution. The resultant solution was filtered from the precipitates of calcium carbonate, silicon dioxide (SiO_2), carbon, and iron compounds. The yield from this reaction was 99 pct of the calcium carbonate potentially available from the calcium sulfide, based on the weight of the precipitate, less the silicon dioxide, carbon, and iron in the form of iron oxides. The sulfur recovery as ammonium bisulfide was 70 pct of the amount potentially available from the calcium sulfide. Table 4 shows the quantitative analysis of calcium sulfide prepared from phosphogypsum.

Table 4.–Quantitative analysis of calcium sulfide prepared from phosphogypsum

	Pct
Analysis of CaS:	
Ca	33.0
C	17.0
Fe	7.9
$SO_4^=$	3.7
SiO_2	14.5
Total S	28.8
Possible composition:	
CaS	56.6
C	17.0
Fe_3O_4	10.9
$CaSO_4$	5.2
SiO_2	14.5

NOTE.–X-ray diffraction analysis: CaS, C, Fe_3O_4, and $CaSO_4$.

Results of the inductively coupled plasma spectrographic analyses of ammonium bisulfide solutions made from (1) calcium sulfide prepared from phosphogypsum, (2) commercial calcium sulfide, and (3) Fisher commercial-grade ammonium bisulfide are given in table 5. The ammonium bisulfide prepared from calcium sulfide from phosphogypsum had 1.8 ppm C in solution compared with 214,000 ppm C available from the calcium sulfide, most of which was removed by precipitation of calcium carbonate. This table also shows that most metallic ions, such as aluminum and iron, are removed in the preparation of the ammonium bisulfide solutions.

CONVERSION OF AMMONIUM BISULFIDE TO SULFUR

Tests Using Laboratory-Grade Carbon

An aliquot of 50 mL of the ammonium bisulfide solution, made from commercial-grade calcium sulfide, was placed in the apparatus shown in figure 1 and cycled over the carbon-coated mullite beads for 6 h. The solution flow rate was 1.77 mL/min and the air flow rate was 64 mL/min, giving an initial oxygen-to-sulfur ratio of 1.04. The carbon-coated beads were washed with water and dried, and their sulfur content was determined by extracting with carbon disulfide. The washings were combined with the remaining solution and analyzed for sulfur species. The exhaust air was passed through hydrochloric acid (HCl) to absorb ammonia and through a zinc chloride solution to absorb hydrogen sulfide. Analyses of these various components are given in table 6 as a percentage of total sulfur or total ammonia in the original solution.

Table 5.–Analyses of ammonium bisulfide solutions, parts per million

(All samples were NH_4SH diluted to 17.1 pct S)

	Solution from CaS from phosphogypsum	Solution from commercial-grade CaS	Solution from commercial-grade NH_4SH
ELEMENTS WITH DETECTABLE CONCENTRATION LIMITS			
B	1.01	0.57	<0.05
Ca	1.78	1.48	.63
Na	36.10	<.50	<.50
P	47.90	37.60	20.40
Sb	7.51	6.70	5.94
Si	34.40	19.00	10.10
ELEMENTS WITH CONCENTRATION LESS THAN THE DETECTION LIMIT GIVEN			
Ag	<0.10	<0.10	<0.10
Al	<.10	<.10	<.10
As	<.10	<.10	<.10
Au	<.05	<.05	<.05
Ba	<.10	<.10	<.10
Cd	<.20	<.20	<.20
Cr	<.30	<.30	<.30
Cu	<.20	<.20	<.20
Fe	<.20	<.20	<.20
Hg	<.05	<.05	<.05
K	<1.00	<1.00	<1.00
Mg	<.50	<.50	<.50
Mn	<.10	<.10	<.10
Mo	<.50	<.50	<.50
Nb	<.10	<.10	<.10
Ni	<.50	<.50	<.50
Pb	<.50	<.50	<.50
Pt	<.50	<.50	<.50
Se	<.50	<.50	<.50
Sn	<1.00	<1.00	<1.00
Ti	<.10	<.10	<.10
V	<.20	<.20	<.20
Zn	<.50	<.50	<.50

Table 6.–Sulfur and ammonia distribution in products

	Pct
S:	
$S^=$	0.70
$S_2O_3^=$	31.30
$SO_4^=$	.56
SO_3	0
H_2S	[1]6.48
S on carbon	45.97
Total S	85.01
Balance	14.99
NH_3:	
Evolved in air	[2]12.85
In solution	85.74
Total NH_3	98.59

[1] 3.87 meq.

[2] 3.91 meq.

Comparing these results with the original solution analysis shows that the sulfide has been reduced from 95.7 to 0.70 pct, while the thiosulfate increased from 3.9 to 31.30 pct. The unaccounted difference of 14.99 pct of the sulfur may be tetrathionate, which is colorless, and would not have been detected in the sulfur species analyses employed. The low sulfur recovery of 45.97 pct indicated that improvements were needed, which is addressed below.

Some of the results using the packed column with mullite beads are given in table 7. The percentages of each sulfur species are the amounts of sulfur in each species after oxidation of ammonium bisulfide, compared with the total amount of sulfur in the original ammonium bisulfide solutions. Tests 1 through 12 were designed to detect the effects of ammonium bisulfide concentration and oxygen-to-sulfur ratios on the yield of sulfur. Three concentrations were used, and at least three oxygen-to-sulfur ratios were used for each concentration: one ratio near the optimum of 0.8 to 1.0, and the other two ratios below and above the optimum. One gram of carbon catalyst was used in each test, and 0.42 to 2.33 g of elemental sulfur was recovered from the carbon. These results show that, in general, the higher ammonium bisulfide solution concentrations produce higher sulfur yields and lower amounts of thiosulfate and sulfate. The quantities of hydrogen sulfide were not greatly different for the different concentrations. The effects of the oxygen-to-sulfur ratios were somewhat erratic. At ammonium bisulfide concentrations of 6.3 and 20.6 pct, the best sulfur yields occurred when the oxygen-to-sulfur ratio was 1.0, but this was not the case when the ammonium bisulfide was 8.6 pct.

Table 7.–Sulfur loading on carbon-coated mullite beads

Test	Initial NH_4SH sol conc, pct	Test duration, h	O-S ratio	Final sol conc, pct $S^=$	Final sol conc, pct $S_2O_3^=$	Final sol conc, pct $SO_4^=$	Final sol conc, pct H_2S	S^o loading, pct	Total S species, pct
1	6.3	4.0	0.5	1.0	29.2	0.9	3.9	42.8	78.4
2	6.3	4.0	1.0	.7	24.2	1.1	4.5	63.5	94.0
3	6.3	4.0	2.0	0	21.3	1.0	9.8	60.5	92.6
Av ...	6.3	4.0	1.2	.6	24.9	1.0	6.0	55.6	88.3
4	8.6	2.3	.4	.2	24.8	1.9	2.7	62.8	92.3
5	8.6	4.0	.8	.3	26.9	1.0	8.7	48.8	85.6
6	8.6	1.0	1.0	0	23.1	1.2	1.0	57.0	82.3
7	8.6	1.5	1.4	.4	24.4	.9	5.5	60.1	91.4
Av ...	8.6	2.2	.9	.2	24.8	1.3	4.5	57.2	87.9
8	20.6	2.5	.2	.1	14.1	.6	6.4	60.2	81.4
9	20.6	4.0	1.6	.1	14.3	.4	7.6	70.8	93.1
10	20.6	1.3	1.0	.1	16.9	.9	6.7	73.8	98.4
11	20.6	1.4	1.0	.1	12.9	.8	6.3	74.1	94.1
12	20.6	1.8	1.0	0	8.3	.3	5.7	69.2	83.5
Av ...	20.6	2.0	1.0	.1	13.3	.6	6.5	69.6	90.1
13[1]	2.8	.7	1.5	0	16.9	.9	6.0	65.1	93.6
14[1]	6.0	1.0	1.0	0	11.1	6.6	14.1	56.1	97.9
Av ...	4.0	1.3	1.3	0	14.0	11.2	10.0	60.6	95.7
15[2]	20.6	6.0	1.6	.1	16.8	.4	ND	15.0	ND

ND Not determined.

[1] NH_4SH made from CaS from phosphogypsum.

[2] No carbon catalyst.

Tests 13 and 14 were run using ammonium bisulfide made from phosphogypsum, while the other tests used ammonium bisulfide solutions made from commercial-grade calcium sulfide. The high-sulfate concentrations in these tests were traced to high sulfate in the original calcium sulfide made from the phosphogypsum and were not due to oxidation of ammonium bisulfide. Sulfate does not enter into the oxidation reaction of ammonium bisulfide, and hydrogen sulfide is potentially recoverable in the process. The yields of sulfur from the calcium sulfide made from phosphogypsum, corrected for sulfate and hydrogen sulfide, are equivalent to the best yields of sulfur made from commercial-grade calcium sulfide. As shown in table 5, little or no contamination of ammonium bisulfide occurs in the process of its preparation, and the present results indicate that impurities in phosphogypsum would have no detrimental effect on the sulfur process.

Test 15 was run without a carbon catalyst. The low sulfur yield of 15 pct demonstrates the necessity of the catalyst.

Tests on Commercial-Grade Activated Carbons

Laboratory studies were carried out under a variety of operating conditions using four commercial-grade bituminous coal-derived activated carbons. The properties of these carbons are given in table 1. The results of the loading tests are given in table 8. In all tests, the total amount of sulfur available from the ammonium bisulfide solution was held constant at 21 g, and the carbon volume was held constant at 50 mL.

In terms of grams of S^o per 100 g of carbon, APA carbon consistently exhibited the highest sulfur loading in each of the five test series, with the highest loading being 81 g of S^o per 100 g of carbon in series 2. This very high purity acid-washed carbon had the lowest density and the highest reported surface area, 1,525 m^2/g. However, in terms of grams of S^o loaded per square meter of available surface area, F-400 carbon consistently loaded more sulfur. Thus, for example, in series 2, about 0.65 g of sulfur was loaded per 1,000 m^2 of F-400 carbon, compared with 0.53 g of sulfur per 1,000 m^2 of APA carbon. The other test series give similar comparisons. Based on these results, it appears that acid washing does not, by itself, improve the adsorption density of sulfur, other factors being equal.

Comparing F-300 carbon with F-400 carbon, which has the same surface area of 950 to 1,050 m^2/g, F-400 carbon exhibits higher loading, both in terms of grams of sulfur adsorbed per 100 g of carbon and in terms of grams of sulfur per 1,000 m^2 of available surface area. The F-400 carbon has a mesh size of plus 12 minus 40 and is somewhat finer than the plus 8- minus 30-mesh F-300 carbon, consequently having more external surface area available for absorption of sulfur. These results would also be consistent with a loading mechanism controlled by diffusion. In either case, the results strongly suggest that the finest size carbon, consistent with materials handling and transport, should be considered for use. While no evidence of bed plugging has yet been observed, this is likely to occur as higher sulfur loadings are achieved through optimization of the system.

Table 8.–Results of loading tests on commercial-grade activated carbons

Test series and carbon type	Sulfur loading on carbon, g sulfur				Sulfur distribution, pct		
	carbon wt, g	wt, g	per 100 g carbon	per 1,000 m^2	Sulfur on carbon	Spent solution	Offgas
1:							
F-300	26.20	11.20	43	0.43	52	3	45
F-400	24.48	11.15	46	.46	52	2	46
APA	20.00	12.05	60	.40	56	3	41
CPG	26.15	11.85	45	.43	55	4	41
2:							
F-300	25.88	14.29	55	.55	67	11	22
F-400	24.45	15.94	65	.65	75	8	17
APA	19.63	15.92	81	.53	75	8	17
CPG	25.61	15.01	59	.56	70	9	21
3:							
F-300	26.35	14.39	55	.55	69	8	23
F-400	24.82	15.19	61	.61	73	7	20
APA	20.20	15.07	75	.49	72	7	21
CPG	26.00	14.09	54	.52	73	8	19
4:							
F-300	26.00	11.73	45	.45	55	37	8
F-400	24.80	12.62	51	.51	59	33	8
APA	20.01	15.56	78	.51	73	21	6
CPG	26.17	15.32	59	.56	66	26	8
5:							
F-300	26.20	9.78	38	.38	46	45	9
F-400	24.82	11.63	47	.47	54	38	8
APA	20.06	13.21	66	.43	62	31	7
CPG	26.08	11.33	43	.41	53	41	6

The ultimate selection of a carbon for a sulfur recovery process will, of course, be economically dictated. It appears, however, that since a higher sulfur loading can be achieved with a lower grade carbon, on an available surface area basis, the use of a higher grade carbon with incremental cost for the additional processing would probably not be warranted.

Referring to the sulfur distributions (table 8), it can be seen that the amount of sulfur available in the ammonium bisulfide solution, which was recovered from the carbon, ranged from 52 to 75 pct. All of these recoveries would probably be unacceptably low for a commercial process. However, no attempt was made to optimize recovery through control of the loading parameters, such as solution concentration, solution flow rate, air flow rate, and process design, e.g., countercurrent stage loading.

It is quite evident that there are sharp differences in the amount of sulfur being lost to the offgas (test series 1 through 3) and the spent solution (test series 4 and 5). Thus, in test series 1 through 3, 19 to 46 pct of the available sulfur is lost to the offgas as hydrogen sulfide, and in series 4 and 5, about the same amounts are lost to the spent solution. While the reasons for these differences remain to be determined, in either case the sulfur may be potentially recoverable through stage loading of the carbon columns. In the latter case, overoxidation of the ammonium bisulfide solution to thiosulfates or sulfates must be minimized.

REMOVAL OF SULFUR FROM CARBON

Thermal Methods

Work by May, Rice, and Carter (*17*) at temperatures and pressures ranging from 120° to 140° C and 10 to 30 µm Hg, respectively, showed that while pure flowers of sulfur could be easily sublimed in the absence of carbon, it was extremely difficult to do so in the presence of carbon. It was concluded that the sulfur vapor had a high affinity for the carbon surface functional groups and that low-temperature vacuum distillation would probably not be a potential candidate for sulfur recovery. Consequently, tests were run at elevated temperatures under vacuum and also with the use of an inert carrier gas.

The results of laboratory batch testing using vacuum distillation to vaporize sulfur from SLC are shown in figure 3. Only 35 pct of the sulfur could be vaporized at 250° C with a 2-h heating time. Above 250° C, sulfur vaporization increased sharply to a maximal recovery in excess of 90 pct at 350° C at the 2-h heating time. The two tests run at the 4-h heating time showed that only 20 pct of the sulfur can be vaporized at 200° C, whereas 97 pct of the sulfur is recoverable at 450° C. The latter data point also confirms that essentially all of the sulfur on the carbon is in a form that is potentially recoverable by thermal treatment. Additional experiments were run to determine if N_2 could be used as a carrier gas to assist in transporting the sulfur vapor from the heated zone of the reactor. Tests were conducted to determine the effects of heating time and temperature and nitrogen gas flow rate on sulfur recovery. The optimal temperature for distilling sulfur from SLC-1 at constant treatment time of 135 min and a nitrogen flow rate of 450 mL/min was determined to be approximately 525° C (shown in figure 4).

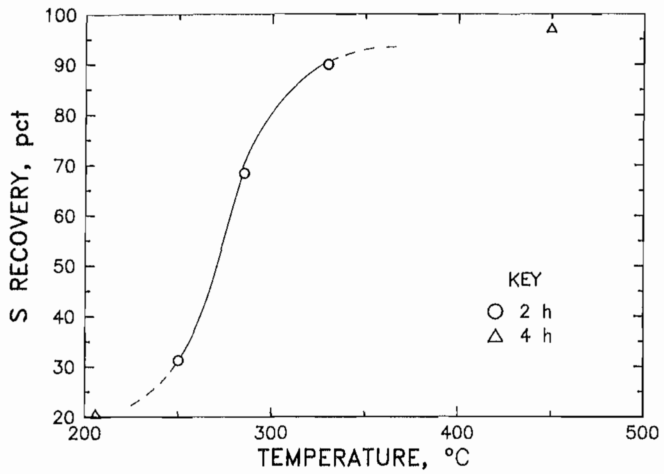

Figure 3.–Recovery of sulfur from SLC-1 as function of temperature using vacuum distillation. Heating times of 2 and 4 h were used.

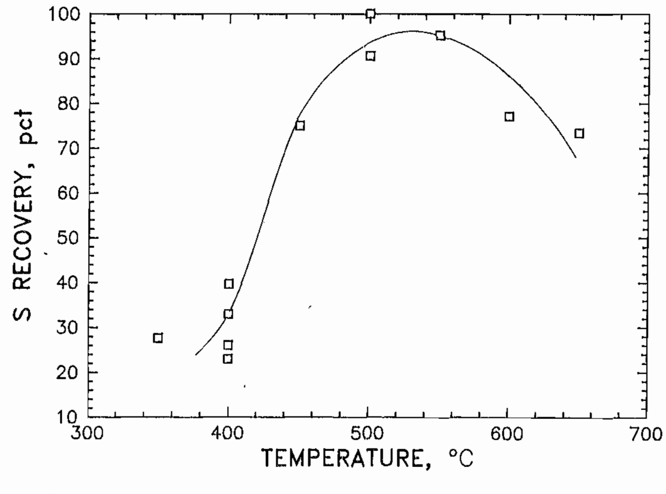

Figure 4.–Recovery of sulfur from SLC-1 as function of temperature.

Figure 5 shows the effects of heating time on sulfur recovery from SLC-2 (stored several months) for various nitrogen flow rates, at 525° C. In all tests, with sufficient time, maximal recovery was about 80 pct. Sulfur recovery from carbon is also seen to increase markedly with increasing nitrogen flow rate. For example, at the lowest flow rate of 40 mL/min and a 50-min heating time, recovery is only 42 pct, whereas at the highest flow rate, 450 mL/min, 80 pct recovery is achieved at the same heating time of 1 h.

Figure 6, developed from the data in figure 5, shows the relationship of sulfur recovery to the total volume of nitrogen used in each test at 525° C. From this plot it is quite evident that a total volume of about 10 L of nitrogen gas (25° C, 760 mm Hg) was required to achieve a maximal recovery of 80 pct under the rather wide range of experimental conditions used. Since the 10-L minimum nitrogen volume is far in excess of the volume of the pipe reactor (59.8 mL), the mechanism of sulfur displacement from the carbon is believed to be diffusion controlled.

The maximum sulfur recovery obtained with SLC-2 in the nitrogen carrier gas test series (figs. 5-6) was 80 pct, as compared with over 90 pct recovery obtained with SLC-1 in the vacuum distillation and carrier gas test series shown in figures 3 and 4, respectively. It is not known if the differences in ultimate recovery are due to the different techniques employed, i.e., nitrogen carrier gas versus vacuum, or to differences in the preparation and storage time of the specific samples used for each series. These aspects will have to be addressed in future studies, since either possibility could affect the sulfur extraction in an actual process.

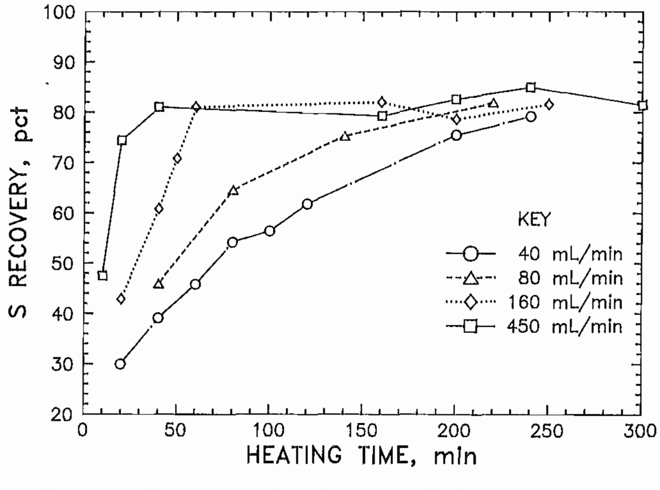

Figure 5.–Recovery of sulfur from SLC-2 as function of heating time.

Sulfur Extraction With Liquid Anhydrous Ammonia

Based upon practical and environmental considerations, May, Rice, and Carter (*17*) selected liquid anhydrous ammonia as a potential candidate for leaching sulfur from carbon. The results of early batch tests showed that, in fact, the sulfur could be dissolved from the carbon to produce a sulfur-laden ammonia liquor, which upon evaporation of the ammonia yielded an elemental sulfur product. About 70 to 75 pct of the sulfur was recovered from a 10.0-g SLC sample, analyzing 7.8 pct S, with a leaching time of 20 min. A patent has been granted on this aspect of the investigation (*18*).

The technical feasibility of improving sulfur recoveries beyond 70 to 75 pct was investigated using a continuous flowthrough system (fig. 2). This apparatus permitted the use of an inert atmosphere, which was used since Ruff and Hecht (*19*) indicated that atmospheric oxygen as well as moisture may oxidize sulfur in sulfur-ammonia solutions.

Four continuous leaching tests were conducted in which dry, freshly prepared SLC-2 was leached in the "inert" helium atmosphere using liquid anhydrous ammonia at predetermined temperatures. The results of the tests are summarized in figure 7, which presents cumulative sulfur recovery as a function of leaching time. From these data it is quite evident that the extraction of sulfur increases substantially with increasing temperature.

The leaching temperatures mentioned below have been rounded for reporting purposes but are exact temperatures on figure 7. At a temperature of +15° C, over 90 pct of the sulfur was extracted in about 20 min of leaching. At the lowest temperature, -29° C, less than 10 pct of the sulfur was extracted for the same time period. The two tests, at 0° C, gave yields of about 80 and 65 pct for the same 20-min leach time. The differences in cumulative recoveries between these two tests are believed to be due to temperature variations experienced during testing. The temperatures inside the reactor were difficult to control because of the heat of reaction of ammonia with the SLC. The poor sulfur extraction obtained at -29° C is in agreement with the observations of Ruff and Hecht (*19*) that the temperature must be greater than -11.5° C for rhombic sulfur to initially dissolve in ammonia. Since the ammonia leaching was successful, the development of a new flowsheet (fig. 8) for the recovery of sulfur from phosphogypsum was designed. The ammonia used in the formation of ammonium bisulfide and that used to leach the SLC are both recycled in the process. These ammonia cycles are two entirely independent systems. No effort has been made to optimize leaching efficiency with regard to ammonia requirements, although it is visualized that any practical process would almost certainly use some form of countercurrent leaching technique.

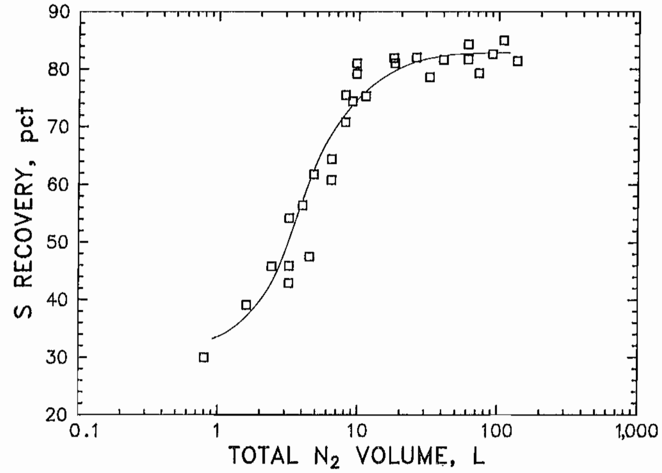

Figure 6.–Recovery of sulfur from SLC-2 as function of total nitrogen volume at constant temperature.

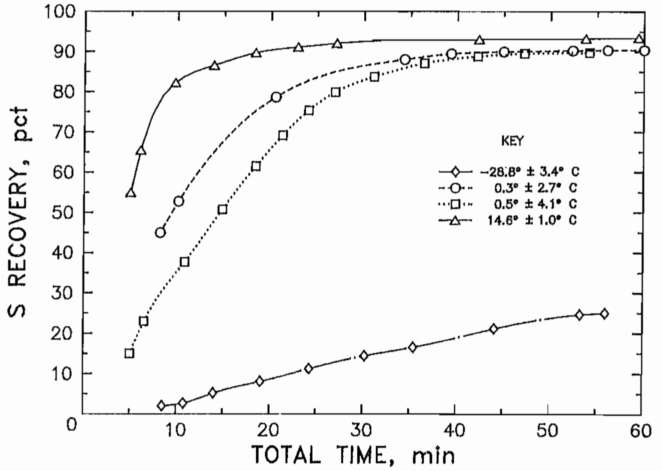

Figure 7.–Cumulative recovery of sulfur from SLC-2 as function of total leaching time using liquid anhydrous ammonia.

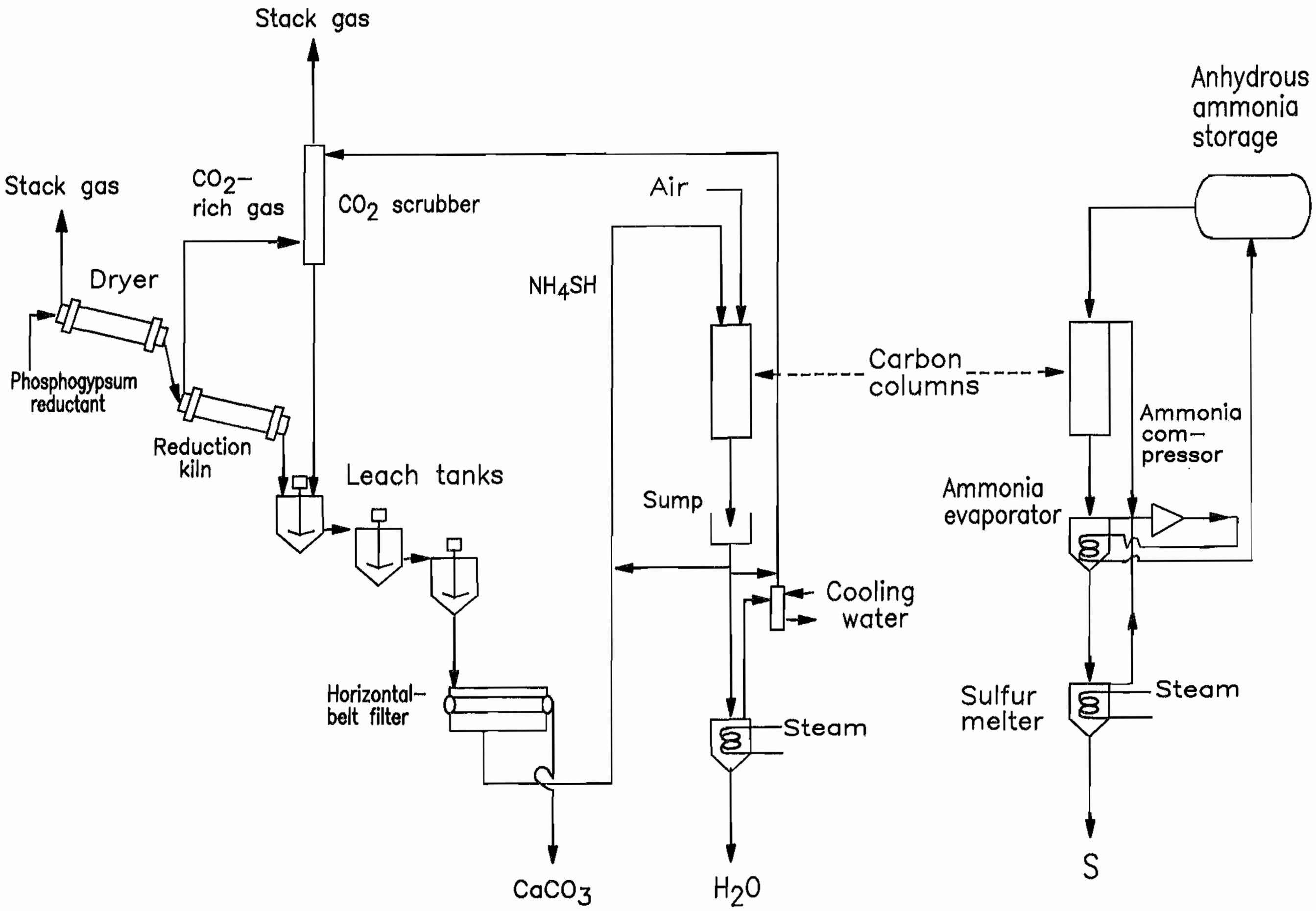

Figure 8.–Flowsheet for recovery of sulfur from phosphogypsum, incorporating ammonia leaching.

Carbon Recyclability

Locked-cycle testing was carried out to investigate the technical feasibility of reloading an activated carbon after removal of its sulfur load by ammonia leaching. The cycle consists of two parts: (1) loading of sulfur onto the activated carbon by oxidation of ammonium bisulfide and (2) leaching of sulfur using liquid anhydrous ammonia in the continuous flowthrough system. Ten full cycles were completed. In this phase of the program, no extended effort has been made to optimize the loading or leaching steps of the cycle. The specific purpose of the present test series was expressly to determine if the carbon would remain active or whether it would catastrophically degrade after leaching with ammonia.

The results of the 10 locked-cycle loading and leaching tests are presented in figure 9. These data graphically show that the carbon has good potential for recycling after stripping its sulfur load using liquid anhydrous ammonia.

The leached carbon weight remains constant throughout the 10 test cycles. The actual weights of the final sulfur products produced closely correspond to the weight differences between the SLC and the leached carbon.

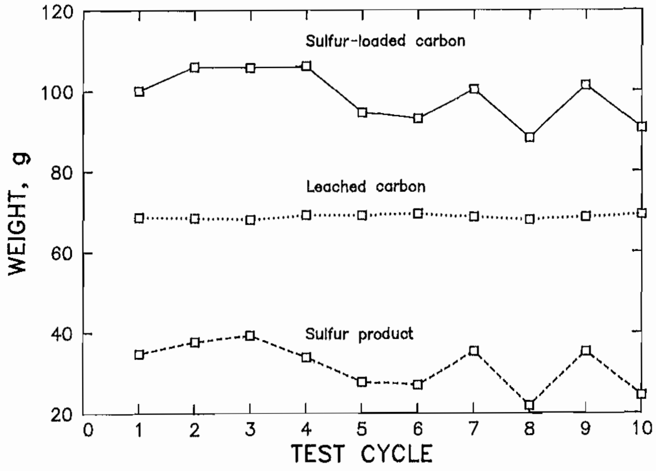

Figure 9.–Carbon recycle testing: material weight as function of test cycle number.

Thus, the sulfur being loaded onto the carbon, as indicated by weight gain during loading, reports as a final sulfur product. It is apparent that essentially all of the sulfur on the carbon is being recovered during leaching in each cycle (or that a steady state is quickly reached). These data indicate that insoluble species are not building up on the carbon and that the carbon is not otherwise physically degrading. The recovery trend over the 10 cycles shows that catastrophic degradation of the carbon does not occur. In fact, the "bouncing back" of recoveries in the seventh and ninth cycles to almost as high a level as in the first cycle indicates that the carbon remains quite active. It should be noted that the individual data points in figure 9 have been connected by straight lines since the peaks and dips in weight recoveries are believed to be real and are due to subtle variations in testing techniques from cycle to cycle, as opposed to statistical variation.

CONCLUSIONS

The conclusions from this investigation are as follows:

1. Calcium sulfide can be converted to ammonium bisulfide.
2. Ammonium bisulfide can be oxidized to elemental sulfur using a carbon catalyst.
3. Sulfur produced by oxidation of ammonium bisulfide absorbs onto the catalyst and must be removed in order to produce a final sulfur product.
4. Sulfur may be removed from the carbon by a novel leaching technique using liquid anhydrous ammonia.
5. Phosphogypsum was converted by thermal reduction to calcium sulfide; the calcium sulfide was hydrometallurgically converted to ammonium bisulfide; the ammonium bisulfide was catalytically oxidized to sulfur; and the sulfur was recovered by extracting with liquid anhydrous ammonia.
6. Essentially all of the sulfur absorbed on activated carbon, produced by oxidation of ammonium bisulfide, is potentially recoverable as an elemental sulfur product.
7. Leaching of carbon using liquid anhydrous ammonia can recover essentially 100 pct of the sulfur on the activated carbon, as demonstrated by locked-cycle testing.
8. The carbon can be recycled and reloaded with sulfur following ammonia leaching for sulfur recovery. The carbon remains active after leaching, can be reloaded to approximately its original level, and physical degradation appears to be minimal.
9. Distillation of sulfur from carbon, which has been loaded with sulfur by oxidation of ammonium bisulfide, is also technically feasible using either a vacuum or an inert carrier gas such as nitrogen.

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