FINAL DETERMINATION

105 0055

Agrico Chemical Company
South Pierce Chemical Works
Polk County

Prilled Sulfur Pellet Handling and Melting Facility

State Permit Number
AC 53-55780

Florida Department of Environmental Regulation
Bureau of Air Quality Management

Central Air Permitting

April 20, 1984

TWIN TOWERS OFFICE BUILDING
2600 BLAIR STONE ROAD
TALLAHASSEE, FLORIDA 32301-8241

BOB GRAHAM
GOVERNOR

VICTORIA J. TSCHINKEL
SECRETARY

April 26, 1984

CERTIFIED MAIL-RETURN RECEIPT REQUESTED

Mr. L. C. Lahman, Plant Manager
Agrico Chemical Company
South Pierce Chemical Works
Post Office Box 1969
Bartow, Florida 33830

Dear Mr. Lahman:

Enclosed is Permit Number AC 53-55780, dated April 26, 1984, to
Agrico Chemical Company, issued pursuant to Section 403, Florida
Statutes.

Acceptance of this permit constitutes notice and agreement that
the department will periodically review this permit for
compliance, including site inspections where applicable, and may
initiate enforcement actions for violation of the conditions and
requirements thereof.

Sincerely,

C. H. Fancy, P.E.
Deputy Bureau Chief
Bureau of Air Quality
Management

CHF/pa

Enclosure

cc: William S. Hornbeck, P.E., Agrico Chemical Company
     H. W. Long, Agrico Chemical Company
     Dan Williams, DER Southwest District

Response to Public Comment

(AC 53-55780)

Agrico Chemical Company
Sulfur Pellet Handling and Melting Facility
Polk County

The company's construction permit application for installation of a sulfur pellet handling and melting facility in Polk County, Florida has been reviewed by FDER. Public notice of the Department's proposed action and hearing was published in the Lakeland Ledger on February 16, 1984. An additional opportunity for public comment and notice of cancellation of Public Hearing was published in the Lakeland Ledger on March 23, 1984. Copies of the preliminary determination and application were available for public inspection at DER's Southwest District Offices in Tampa and the Bureau of Air Quality Management in Tallahassee.

There were no comments from the public as a result of the public notice period.

The final action of the Department will be to issue the permit as noticed in the public review process.

AFFIDAVIT OF PUBLICATION

THE LEDGER

Lakeland, Polk County, Florida

Case No ....

STATE OF FLORIDA)
COUNTY OF POLK)

Before the undersigned authority personally appeared Walter Garris, who on oath says that he is Controller of The Ledger, a daily newspaper published at Lakeland in Polk County, Florida; that the attached copy of advertisement, being a....................

...Notice...

....

in the matter of ....

....Proposed. Agency. Action. and. Hearing.................

....

in the ....

....

Court, was published in said newspaper in the issues of..........

....February. 16;. 1984...............................

....

Affiant further says that said The Ledger is a newspaper published at Lakeland, in said Polk County, Florida, and that the said newspaper has heretofore been continuously published in said Polk County, Florida, daily, and has been entered as second class matter at the postoffice in Lakeland, in said Polk County, Florida, for a period of one year next preceding the first publication of the attached copy of advertisement; and affiant further says that he has neither paid nor promised any person, firm or corporation any discount, rebate, commission or refund for the purpose of securing this advertisement for publication in the said newspaper.

Signed ...Walter Garris...
Controller

Sworn to and subscribed before me this ......17th........

day of ......February...................... A.D. 19..84

AFFIDAVIT OF PUBLICATION

THE LEDGER

Lakeland, Polk County, Florida

Case No ....

STATE OF FLORIDA)
COUNTY OF POLK)

Before the undersigned authority personally appeared Walter Garris, who on oath says that he is Controller of The Ledger, a daily newspaper published at Lakeland in Polk County, Florida; that the attached copy of advertisement, being a....................

Notice
....

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in the matter of ....

DEC Notice
....

....

in the ....

....

Court, was published in said newspaper in the issues of ....

....March 23, 1984...

....

Affiant further says that said The Ledger is a newspaper published at Lakeland, in said Polk County, Florida, and that the said newspaper has heretofore been continuously published in said Polk County, Florida, daily, and has been entered as second class matter at the postoffice in Lakeland, in said Polk County, Florida, for a period of one year next preceding the first publication of the attached copy of advertisement; and affiant further says that he has neither paid nor promised any person, firm or corporation any discount, rebate, commission or refund for the purpose of securing this advertisement for publication in the said newspaper

Signed ....
Controller

Sworn to and subscribed before me this ....27th.........

day of ....March.................... A.D. 19....84

STATE OF FLORIDA

DEPARTMENT OF ENVIRONMENTAL REGULATION

TWIN TOWERS OFFICE BUILDING
2600 BLAIR STONE ROAD
TALLAHASSEE, FLORIDA 32301-8241

BOB GRAHAM
GOVERNOR

VICTORIA J. TSCHINKEL
SECRETARY

PERMITTEE:

Agrico Chemical Company
P. O. Box 1969
State Road 630
Bartow, Florida 33830

Permit Number: AC 53-55780
Date of Issue:
Expiration Date: October 30, 1985*
County: Polk
Latitude/Longitude: 27° 45' 45" N
                        81° 56' 28" W
Project: Wet Prilled Sulfur Pellet
Handling and Melting
Facility

     This permit is issued under the provisions of Chapter(s) 403 , Florida Statutes, and Florida Administrative Code Rule(s) 17-2 and 17-4 . The above named permittee is hereby authorized to perform the work or operate the facility shown on the application and approved drawing(s), plans, and other documents attached hereto or on file with the department and made a part hereof and specifically described as follows:

For the construction of an underground receiving and unloading pit located in a partially enclosed receiving shed, construction of a conveyor from the receiving pit to a 150 ton storage hopper which will distribute by means of a screw conveyor, wet prilled sulfur pellets to three 900 ton melters.

The source is located within the existing facility of the South Pierce Chemical Complex south of Lakeland, Florida, in Polk County. The universal transverse mercator (UTM) coordinates of the source are Zone 17:407.6 km East and 3071.3 km North.

List of Attachments:

1. Application AC 53-55780 - Received Southwest District, 5-10-82.
2. Incompleteness letter to L. C. Lahaman from DER, 6-9-82.
3. Additional information received, 9-22-82.
4. Extension of time request to C. H. Fancy from Agrico 11-22-82.
5. Letter to Steve Smallwood from H. Long, Agrico, submitting test data, 2/8/83.
6. Emission Factor Determination for Prilled Sulfur by Dale Lundgren, 2-28-83.
7. Letter from Steve Smallwood to Dale Lundgren to request clarification of emission data, 3-17-83.
8. August 5, 1983 letter from Ed de la Parte to Steve Smallwood responding to request for information submitted March 17, 1983 to Dale Lundgren.
9. Letter from Agrico's H. Long to Ed Huck 9/22/83 submitting answers on technical clarification of issues.

* 18 months after the validity of the permit is established

Protecting Florida and Your Quality of Life

PERMITTEE: Agrico Chemical   I. D. Number:
         Company   Permit Number: AC 53-55780
                                    Date of Issue:
                                    Expiration Date: October 30, 1985

GENERAL CONDITIONS:

1. The terms, conditions, requirements, limitations, and
restrictions set forth herein are "Permit Conditions" and as
such are binding upon the permittee and enforceable pursuant to
the authority of Sections 403.161, 403.727, or 403.859 through
403.861, Florida Statutes. The permittee is hereby placed on
notice that the department will review this permit periodically
and may initiate enforcement action for any violation of the
"Permit Conditions" by the permittee, its agents, employees,
servants or representatives.

2. This permit is valid only for the specific processes and
operations applied for and indicated in the approved drawings
or exhibits. Any unauthorized deviation from the approved
drawings, exhibits, specifications, or conditions of this
permit may constitute grounds for revocation and enforcement
action by the department.

3. As provided in Subsections 403.087(6) and 403.722(5),
Florida Statutes, the issuance of this permit does not convey
any vested rights or any exclusive privileges. Nor does it
authorize any injury to public or private property or any
invasion of personal rights, nor any infringement of federal,
state or local laws or regulations. This permit does not
constitute a waiver of or approval of any other department
permit that may be required for other aspects of the total
project which are not addressed in the permit.

4. This permit conveys no title to land or water, does not
constitute state recognition or acknowledgement of title,
and does not constitute authority for the use of submerged
lands unless herein provided and the necessary title or
leasehold interests have been obtained from the state. Only
the Trustees of the Internal Improvement Trust Fund may express
state opinion as to title.

5. This permit does not relieve the permittee from liability
for harm or injury to human health or welfare, animal, plant or
aquatic life or property and penalties therefor caused by the
construction or operation of this permitted source, nor does it
allow the permittee to cause pollution in contravention of
Florida Statutes and department rules, unless specifically
authorized by an order from the department.

PERMITTEE: Agrico Chemical   I. D. Number:
          Company   Permit Number: AC 53-55780
                                    Date of Issue:
                                    Expiration Date: October 30, 1985

GENERAL CONDITIONS:

6. The permittee shall at all times properly operate and
maintain the facility and systems of treatment and control (and
related appurtenances) that are installed or used by the
permittee to achieve compliance with the conditions of this
permit, as required by department rules. This provision
includes the operation of backup or auxiliary facilities or
similar systems when necessary to achieve compliance with the
conditions of the permit and when required by department
rules.

7. The permittee, by accepting this permit, specifically
agrees to allow authorized department personnel, upon
presentation of credentials or other documents as may be
required by law, access to the premises, at reasonable times,
where the permitted activity is located or conducted for the
purpose of:

   a. Having access to and copying any records that must be
       kept under the conditions of the permit;

   b. Inspecting the facility, equipment, practices, or
       operations regulated or required under this permit;
       and

   c. Sampling or monitoring any substances or parameters at
       any location reasonably necessary to assure compliance
       with this permit or department rules.

   Reasonable time may depend on the nature of the concern
being investigated.

8. If, for any reason, the permittee does not comply with or
will be unable to comply with any condition or limitation
specified in this permit, the permittee shall immediately
notify and provide the department with the following
information:

   a. a description of and cause of non-compliance; and

   b. the period of noncompliance, including exact dates and
       times; or, if not corrected, the anticipated time the
       noncompliance is expected to continue, and steps being
       taken to reduce, eliminate, and prevent recurrence of
       the noncompliance.

PERMITTEE: Agrico Chemical   I. D. Number:
          Company   Permit Number: AC 53-55780
                                     Date of Issue:
                                     Expiration Date: October 30, 1985

GENERAL CONDITIONS:

     The permittee shall be responsible for any and all damages
which may result and may be subject to enforcement action by
the department for penalties or revocation of this permit.

9.   In accepting this permit, the permittee understands and
agrees that all records, notes, monitoring data and other
information relating to the construction or operation of this
permitted source, which are submitted to the department, may be
used by the department as evidence in any enforcement case
arising under the Florida Statutes or department rules, except
where such use is proscribed by Sections 403.73 and 403.111,
Florida Statutes.

10. The permittee agrees to comply with changes in department
rules and Florida Statutes after a reasonable time for
compliance, provided however, the permittee does not waive any
other rights granted by Florida Statutes or department rules.

11. This permit is transferable only upon department approval
in accordance with Florida Administrative Code Rules 17-4.12
and 17-30.30, as applicable. The permittee shall be liable for
any non-compliance of the permitted activity until the transfer
is approved by the department.

12. This permit is required to be kept at the work site of the
permitted activity during the entire period of construction or
operation.

13. This permit also constitutes:

     ( ) Determination of Best Available Control Technology (BACT)
     ( ) Determination of Prevention of Significant Deterioration
         (PSD)
     ( ) Compliance with New Source Performance Standards.

14. The permittee shall comply with the following monitoring and
record keeping requirements:

     a. Upon request, the permittee shall furnish all records
         and plans required under department rules. The reten-
         tion period for all records will be extended
         automatically, unless otherwise stipulated by the
         department, during the course of any unresolved
         enforcement action.

PERMITTEE: Agrico Chemical   I. D. Number:
          Company   Permit Number: AC 53-56780
                                     Date of Issue:
                                     Expiration Date: October 30, 1985

GENERAL CONDITIONS:

   b. The permittee shall retain at the facility or other
       location designated by this permit records of all
       monitoring information (including all calibration and
       maintenance records and all original strip chart
       recordings for continuous monitoring instrumentation),
       copies of all reports required by this permit, and
       records of all data used to complete the application
       for this permit. The time period of retention shall
       be at least three years from the date of the sample,
       measurement, report or application unless otherwise
       specified by department rule.

   c. Records of monitoring information shall include:

       - the date, exact place, and time of sampling or
         measurements;
       - the person responsible for performing the sampling
         or measurements;
       - the date(s) analyses were performed;
       - the person responsible for performing the analyses;
       - the analytical techniques or methods used; and
       - the results of such analyses.

15. When requested by the department, the permittee shall
within a reasonable time furnish any information required by
law which is needed to determine compliance with the permit.
If the permittee becomes aware that relevant facts were not
submitted or were incorrect in the permit application or in any
report to the department, such facts or information shall be
submitted or corrected promptly.

   SPECIFIC CONDITIONS:
Note: All capacities are based on long tons and all emissions are
based on short tons.

   1. The only type of solid formed sulfur handled or melted
at the South Pierce Chemical Works facility shall be in prill
(pellet) form and shall be Fletcher process wet-formed prill
pellets, such as those manufactured by Coastal and PVC, or a
tested, verified, and department approved equivalent.

   2. The maximum hours of operation of this facility shall be
8,760 per year. The maximum production shall not exceed 75 tons
per hour, 1,800 tons per day, or 600,000 tons per year.

PERMITTEE: Agrico Chemical
             Company

I. D. Number:
Permit/Number: AC 53-55780
Date of Issue:
Expiration Date: Oct. 30, 1985

SPECIFIC CONDITIONS:

3. The maximum total emissions of sulfur particulate shall not exceed 2.8 pounds in any hour from the handling and melting facility.

4. The maximum total emissions of sulfur particulate shall not exceed 12 tons per year from the handling and melting facility.

5. The maximum total emissions of hydrogen sulfide (H_2S) shall not exceed 1 pound in any one hour or 5 tons per year from the handling and melting facility.

6. Sulfur prill received at South Pierce shall not be unloaded if the moisture content is less than three (3) percent. The moisture content will be monitored and if necessary adjusted by the addition of moisture as specified in Attachment 9.

7. A wet scrubber device servicing the drop point from the conveyor from the unloading pits to the 150 ton dump hopper will be properly installed and maintained as specified in facility diagrams and sketches in Attachment 9. The particulate emission from the scrubber exhaust shall not exceed 1 pound per hour as determined by DER Method 5. The angle of incline on the conveyor belt shall not exceed 15°.

8. A wet scrubber device servicing the 150 ton dump hopper and the manifold feed to the three 900 ton melters will be properly installed and maintained as specified in facility diagram and sketches in Attachment 9.

    A. The particulate emission from the scrubber exhaust shall not exceed .2 pounds per hour as determined by DER Method 5.

    B. The hydrogen sulfide emission from the scrubber exhaust shall not exceed .75 pounds per hour as determined by EPA Method 16.

9. The final disposition of the spent caustic soda solution from the hydrogen sulfide scrubber to which the melters are vented shall be handled and processed in accordance with the conditions specified in Attachment 9. This condition is necessary to prevent emission of hydrogen sulfide gas from the receiving waters. Additional treatment may be required to meet wastewater discharge requirements of the department.

PERMITTEE: Agrico Chemical   I. D. Number:
          Company   Permit/Number: AC 53-55780
                              Date of Issue:
                              Expiration Date: October 30, 1985

SPECIFIC CONDITIONS:

10. On site storage of sulfur pellets in open storage piles is not allowed.

11. In order to minimize any wind entrainment of sulfur particulate during the unloading operation, Agrico will install a wind anemometer that will sound an alarm when the five minute average wind speed exceeds 18 miles per hour. Sulfur pellet unloading operations will be terminated until the wind has subsided to below 18 miles per hour, five minute average.

12. This facility will be constructed in the physical location described on the plot plan submitted to the Department of Environmental Regulation. This shall be in accordance with the property ownership map of the South Pierce Chemical Works area and an aerial map made in 1983 submitted depicting the area surrounding the construction of this source.

13. Clean up and housekeeping procedures: During operation the area superintendent or the superintendent's designate will survey the entire area for fugitive sulfur on a daily basis. If a significant spill occurs, such as a break in a conveyor belt, the sulfur shall be reclaimed from the spill area as soon as possible, that day. The area beneath the conveyor will be paved to facilitate easy recovery of the sulfur without introducing contamination.

14. The permittee shall establish and all equipment operators shall attend a training program, designed by Agrico and approved by the department, on equipment operating practices to assure the minimization of unconfined particulate matter.

15. There shall be no visible emissions resulting from the remelting of the wet prilled sulfur pellets in excess of 10% opacity (6 minute average) at any point in the plume that is more than 2 meters downwind of the point at which the wet prilled sulfur pellets are melted.

16. Within 30 days after issuance of the construction permit, a sulfur particulate and hydrogen sulfide source emissions monitoring plan, and a sulfur particulate perimeter deposition monitoring plan that describes the sampling locations, the sample

PERMITTEE: Agrico Chemical
Company

I. D. Number:
Permit/Number: AC 53-55780
Date of Issue:
Expiration Date: October 30, 1985

SPECIFIC CONDITIONS:

collecting and analysis procedures, and quality assurance measures
to be employed shall be submitted to the Bureau of Air Quality
Management by the permittee.

A. After approval by the department, the deposition monitoring
network shall be established expeditiously and operated
continuously. A data report shall be submitted to the
Southwest District and the Bureau of Air Quality Management
within 30 days of the end of each calendar quarter. After 12
months of data have been collected and validated, the
department will reevaluate the deposition monitoring network
results in detail, and make any changes to the approved
monitoring plan that are warranted.

B. The source emissions monitoring plan shall include:

(1) Records of the tonnage processed, type and supplier of
the pellets, and moisture as received and added.

(2) A method to sample the particulate emissions from the
railcar/truck unloading operation.

(3) Physical sampling and Lundgren test of sampled
pellets.

(a) About 10 lb of pellets for each 300 tons of
pellets processed.

(b) Each 400 lb of sample collected to be riffled
down to 20 lb of composite sample.

(c) Three 5 lb samples of composite sample to be
tested in Lundgren test chamber at approximately
1, 2 and 3% moisture.

(d) One 5 lb sample to be retained for 2 years for
QA check by DER.

(e) Results to be reported to DER quarterly (with
report on results of deposition monitoring).

(f) This plan will be reconsidered after fully
evaluating one full year of valid data.

PERMITTEE: Agrico Chemical
              Company

I. D. Number:
Permit Number: AC 53-55780
Date of Issue:
Expiration Date: October 30, 1985

SPECIFIC CONDITIONS:

17. Compliance with the process limitations of this permit shall be demonstrated by recordkeeping of: Daily hours of operation for sulfur handling and melting; any spillage recovery, the amounts of sulfur associated with each activity; the times of such spillage and recovery; and other related information necessary to properly interpret the recorded data. Data shall be maintained on file by permittee for a minimum of two years subject to inspection and review as required by DER. Annual reports shall be filed with the DER Southwest District office prior to March 1 of each following year.

18. The initial compliance testing for these sources shall consist of the following:

A. An onsite inspection by department personnel verifying that construction of the facility is in accordance with permit conditions.

B. Certification by the permittee that the employee training program as required has been instituted.

C. The witnessing by department personnel of a satisfactory demonstration of sulfur pellet handling and remelting.

D. The Department of Environmental Regulation shall conduct visible emissions testing by DER Method 9 during facility operations at 90 to 100% of the maximum designed processing rate to determine whether the conditions in specific condition No. 14 should be modified.

E. Scrubbers exhaust tests as required by Specific Conditions 7 and 8. After the initial testing, Agrico will perform annual compliance tests using the same procedure.

19. After satisfactory completion of the initial compliance test and prior to 90 days before the expiration of this permit, a complete application for an operating permit shall be submitted to the DER Southwest District office. The permittee may continue to operate in compliance with all terms of this construction permit until its expiration date or the issuance of an operating permit as authorized by Florida Administrative Code Rule 17-2.210(1).

PERMITTEE: Agrico Chemical   I. D. Number:
            Company   Permit Number: AC 53-55780
                                           Date of Issue:
                                           Expiration Date: October 30, 1985

SPECIFIC CONDITIONS:

20. All conditions of this permit that do not relate solely to
the construction of the source shall be made a part of any
subsequently issued operating permit.

21. Agrico is aware of a pending inquiry by the department into
development of a rule concerning sulfur transportation, handling and
storage and acknowledges that the rule ultimately adopted could, if
made applicable to this category of sources, require substantial
modification of the facility which is the subject of this permit.
Agrico agrees to comply with any such rule within the time period
established within the rule, or, if not so specified, on a
reasonable time schedule developed between the permittee and the
department. Agrico, by accepting this condition, does not waive its
rights to participate in rulemaking proceedings nor to appeal or
otherwise challenge the validity (as opposed to the applicability)
of the adopted rule.

Issued this 26 day of _April_ 1984

**STATE OF FLORIDA DEPARTMENT OF
ENVIRONMENTAL REGULATION**

Victoria J. Pschinkel

ATTACHMENT   1

Agrico *777*
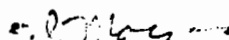ONE OF THE WILLIAMS COMPANIES

May 7, 1982

Mr. Dan Williams
Florida Department of Environmental Regulation
7601 Highway 301, North
Tampa, Florida 33610

Dear Dan,

Enclosed please find 4 copies of an application permit
to construct a prilled sulfur unloading facility at South Pierce.
Also, included is a copy of a letter sent to Steve Smallwood
discussing P.S.D. review.

If you have any questions or require additional information,
please feel free to contact me.

Sincerely,

Ed Mayer,
Environmental Engineer

D.E.R.

MAY 10 1982

SOUTHWEST DISTRICT
TAMPA

Agrico
ONE OF THE WILLIAMS COMPANIES

May 3, 1982

Mr. Steve Smallwood
Bureau of Air Quality Management
Florida Department of Environmental Regulation
Twin Towers Office Building
2600 Blair Stone Road
Tallahassee, Florida 32301

Dear Mr. Smallwood,

Pursuant to 40 CFR 52.21 and 52.520, Agrico Chemical Company hereby requests a determination that PSD review is not required prior to construction of prilled sulfur handling facilities at the South Pierce Chemical Complex in Polk County, Florida.

Agrico is planning to construct facilities for unloading and moving 600,000 long tons per year of prilled sulfur. The entire amount of sulfur will be used in the manufacture of sulfuric acid at the existing and permitted acid plants. The prilled sulfur will contain approximately 2% moisture. At this moisture content, fine particles are very effectively held to the prill. Thus, the moisture content prevents aerosolization, or release, of particulates to the ambient air.

PSD review is required only for "major modifications" (40 CFR 52.21 (i)). If the proposed change will not result in a significant net emissions increase of any pollutant subject to regulations under the Clean Air Act, the change is not "major" (52.21 (b) (2)), and no review is required.

"Significant net emissions increase" means any increase in the sum of proposed emissions increases and "Contemporaneous" emissions changes which is above stated "de minimis" levels (40 CFR 52.21 (b) (3), (23)). Agrico's proposed changes will not result in a "significant net emissions increase". The following chart summarizes the effect of the proposed changes and compares them to the "de minimis" levels.

	(TPY)	
	Particulates	H2S
Proposed emissions increase	4.56	8.4
Unreviewed "contemporaneous" emission changes	0	0
TOTAL	4.56	8.4
"De Minimis" levels (40 CFR 52.21 (b) (23))	25	10

The attachment to this letter more fully explains the derivation of the above numbers.

Based upon this information, Agrico requests a determination that its proposed addition is not a "major modification", and therefore, no PSD review is required prior to construction. If you have any questions, or if you need any further data, do not hesitate to call.

Sincerely,

Ed Mayer,
Environmental Engineer

EEM/lgm

EMISSIONS CALCULATIONS

I. PARTICULATE EMISSIONS

A. Estimated Emissions Increase

On February 28, 1979, Dr. Dale A. Lundgren, of the University of Florida, issued a report entitled "Determination of Emission Factors for Fugitive Emission Sources". The paper summarized research conducted to determine the emission rate of dust in the movement of prilled sulfur. The results of the research indicated that for prilled sulfur with 2% moisture, an emission rate of .0068 lb. of particulate per ton of material could be expected in a transfer-convey operation. At South Pierce, the sulfur will be unloaded from trucks and/or railcars and transferred into a silo.

Prill will arrive at the South Pierce Chemical Works by truck or railcar and will be transferred to a storage silo. The system will handle a maximum of 600,000 long tons per year and 1800 long tons in a 24 hour period.

On a yearly basis the following emissions are expected:

Assume: .0068 Lb/Ton Emission Factor
2 Transfer Locations

$$600,000 \frac{L\ Tons}{Yr.} \times .0068 \frac{Lb}{Ton} \times 2\ dumps \times 1.12 \frac{Ton}{L\ Ton} \times \frac{1\ Ton}{2000\ Lb} = 4.56 \frac{Ton}{Yr.}$$

TOTAL ESTIMATED EMISSIONS = 4.56 Ton/Yr. (Particulates)

B. Contemporaneous Emission Changes

On January 21, 1981, South Pierce was granted a PSD permit for addition of certain facilities. Since that time there has been no change in particulate emissions. Therefore, there are no "contemporaneous" emissions increases or decreases.

II. HYDROGEN SULFIDES

A. Estimated Emission Increase

Technical data obtained from Dr. Mike D. Raymont of the Sulfur Development Institute of Canada indicated that 25-50 PPM of H_2S could normally be released during melting of the prilled sulfur. Occasionally some sulfur could release as much as 250 PPM, however, this would be rare.

II. HYDROGEN SULFIDES (Continued)

The H2S scrubber will be designed to control the worst case situation of a release of 250 PPM H2S.

On a yearly basis the following emissions are expected:

Assume: 250 PPM H2S input
The scrubber as designed by Barnard & Burk
of Baton Rouge, LA is 95% efficient.

$$\text{███████████} \times .00025 \frac{\text{L Ton H2S}}{\text{L Ton}} \times .05 \times 1.12 \frac{\text{Ton}}{\text{L Ton}} = 8.4 \text{ Ton/Yr. H2S}$$

TOTAL ESTIMATED EMISSIONS = 8.4 Ton/Yr. (H2S)

B.   Contemporaneous Emissions Changes

On January 21, 1981, South Pierce was granted a PSD permit for addition of certain facilities. Since that time, there have been no changes in H2S emissions. Therefore, there are no "contemporaneous" emissions increases or decreases.

AC 53-55 780

DER

STATE OF FLORIDA
DEPARTMENT OF ENVIRONMENTAL REGULATION

APPLICATION TO OPERATE/CONSTRUCT AIR POLLUTION SOURCES

D.E.R.

MAY 10 1982

SOUTHWEST DISTRICT
TAMPA

SOURCE TYPE: __Prilled Sulfur__ [X] New[1] [ ] Existing[1]

APPLICATION TYPE: [X] Construction [ ] Operation [ ] Modification

COMPANY NAME: __Agrico Chemical Company__ COUNTY: __Polk__

Identify the specific emission point source(s) addressed in this application (i.e. Lime Kiln No. 4 with Venturi Scrubber; Peeking Unit No. 2, Gas Fired) __H2S Scrubber__

SOURCE LOCATION: Street __State Road 630__ City __Polk County__

UTM: East __407.6 Km E__ North __3071.3 Km N__

Latitude __27__ ° __45__ ' __45__ "N Longitude __81__ ° __56__ ' __28__ "W

APPLICANT NAME AND TITLE: __Agrico Chemical Company__

APPLICANT ADDRESS: __P. O. Box 1969, S.P.C.W, Bartow, Florida 33830__

SECTION I: STATEMENTS BY APPLICANT AND ENGINEER

A. APPLICANT

I am the undersigned owner or authorized representative* of __Agrico Chemical Company__

I certify that the statements made in this application for a __Construction__ permit are true, correct and complete to the best of my knowledge and belief. Further, I agree to maintain and operate the pollution control source and pollution control facilities in such a manner as to comply with the provision of Chapter 403, Florida Statutes, and all the rules and regulations of the department and revisions thereof. I also understand that a permit, if granted by the department, will be non-transferable and I will promptly notify the department upon sale or legal transfer of the permitted establishment.

*Attach letter of authorization

Signed: _L. C. Lahman_

L. C. Lahman, Plant Manager
Name and Title (Please Type)

Date: _5/6/82_ Telephone No. _813-428-1423_

B. PROFESSIONAL ENGINEER REGISTERED IN FLORIDA (where required by Chapter 471, F.S.)

This is to certify that the engineering features of this pollution control project have been designed/examined by me and found to be in conformity with modern engineering principles applicable to the treatment and disposal of pollutants characterized in the permit application. There is reasonable assurance, in my professional judgment, that the pollution control facilities, when properly maintained and operated, will discharge an effluent that complies with all applicable statutes of the State of Florida and the rules and regulations of the department. It is also agreed that the undersigned will furnish, if authorized by the owner, the applicant a set of instructions for the proper maintenance and operation of the pollution control facilities and, if applicable, pollution sources.

Signed: _William S. Hornbeck_

William S. Hornbeck
Name (Please Type)

Agrico Chemical Co.
Company Name (Please Type)

P. O. Box 1969, Bartow, Fla. 33830
Mailing Address (Please Type)

(Affix Seal)

Florida Registration No. _20095_ Date: _5/6/82_ Telephone No. _813-428-1423_

[1]See Section 17-2.02(15) and (22), Florida Administrative Code. (F.A.C.)

DER FORM 17-1.122(16) Page 1 of 10

SECTION II: GENERAL PROJECT INFORMATION

A. Describe the nature and extent of the project. Refer to pollution control equipment, and expected improvements in source performance as a result of installation. State whether the project will result in full compliance. Attach additional sheet if necessary.

Receiving and melting of prilled sulfur (See Appendix A for Further description)

B. Schedule of project covered in this application (Construction Permit Application Only)

Start of Construction ___August, 1982___ Completion of Construction ___August, 1984___

C. Costs of pollution control system(s): (Note: Show breakdown of estimated costs only for individual components/units of the project serving pollution control purposes. Information on actual costs shall be furnished with the application for operation permit.)

Covers and shed for unloading - $20,000

H_2S Scrubber - $20,000

D. Indicate any previous DER permits, orders and notices associated with the emission point, including permit issuance and expiration dates.

None

E. Is this application associated with or part of a Development of Regional Impact (DRI) pursuant to Chapter 380, Florida Statutes, and Chapter 22F-2, Florida Administrative Code? _____ Yes __X__ No

F. Normal equipment operating time: hrs/day __24__ ; days/wk __7__ ; wks/yr __52__ ; if power plant, hrs/yr _____ ;

if seasonal, describe: _____

G. If this is a new source or major modification, answer the following questions. (Yes or No)

1. Is this source in a non-attainment area for a particular pollutant?   No

   a. If yes, has "offset" been applied?

   b. If yes, has "Lowest Achievable Emission Rate" been applied?

   c. If yes, list non-attainment pollutants.

2. Does best available control technology (BACT) apply to this source? If yes, see Section VI.   No

3. Does the State "Prevention of Significant Deterioration" (PSD) requirements apply to this source? If yes, see Sections VI and VII.   No

4. Do "Standards of Performance for New Stationary Sources" (NSPS) apply to this source?   No

5. Do "National Emission Standards for Hazardous Air Pollutants" (NESHAP) apply to this source?   No

Attach all supportive information related to any answer of "Yes". Attach any justification for any answer of "No" that might be considered questionable.

SECTION III: AIR POLLUTION SOURCES & CONTROL DEVICES (Other than Incinerators)

A. Raw Materials and Chemicals Used in your Process, if applicable: Utilization basis = 1800 LTPD ÷ 24

Description	Contaminants		Utilization Rate - lbs/hr	Relate to Flow Diagram
	Type	% Wt		
Prilled Sulfur	Dust	(.05 or less)	168,000	6-A
	H_2S	(.025 or less)		6-A

B. Process Rate, if applicable: (See Section V, Item 1)

1. Total Process Input Rate (lbs/hr): _____ 168,000

2. Product Weight (lbs/hr): _____ 167,998.86

Maximum Lb/Hr. Basis = 1800 LTon/Day ÷ 24

C. Airborne Contaminants Emitted: Actual T/Yr. Basis = 600,000 L Ton/Yr.

Name of Contaminant	Emission[1]		Allowed Emission[2] Rate per Ch. 17-2, F.A.C.	Allowable[3] Emission lbs/hr	Potential Emission[4]		Relate to Flow Diagram
	Maximum lbs/hr	Actual T/yr			lbs/hr	T/yr	
Particulate	1.14	4.57	34.11 Lb/Hr.*	34.11	1.14	4.57	6-A,B
H_2S	42	4.20	N/A	N/A	42	4.20	6-C,D

* Process Weight Table

D. Control Devices: (See Section V, Item 4)

Name and Type (Model & Serial No.)	Contaminant	Efficiency	Range of Particles[5] Size Collected (in microns)	Basis for Efficiency (Sec. V, It[5]
Wet Scrubber	H2S	95%	N/A	See Supplements 2 & 3

[1]See Section V, Item 2.

[2]Reference applicable emission standards and units (e.g., Section 17-2.05(6) Table II, E. (1), F.A.C. — 0.1 pounds per million BTU heat input)

[3]Calculated from operating rate and applicable standard

[4]Emission, if source operated without control (See Section V, Item 3)

[5]If Applicable

E. Fuels

Type (Be Specific)	Consumption*		Maximum Heat Input (MMBTU/hr)
	avg/hr	max./hr	

*Units Natural Gas, MMCF/hr; Fuel Oils, barrels/hr; Coal, lbs/hr

Fuel Analysis:

Percent Sulfur: _____ Percent Ash: _____

Density: _____ lbs/gal Typical Percent Nitrogen: _____

Heat Capacity: _____ BTU/lb _____ BTU/gal

Other Fuel Contaminants (which may cause air pollution): _____
_____

F. If applicable, indicate the percent of fuel used for space heating. Annual Average _____ Maximum _____

G. Indicate liquid or solid wastes generated and method of disposal.
   Spent scrubber liquor will go to recycle pond.
   _____
   _____

H. Emission Stack Geometry and Flow Characteristics (Provide data for each stack):

Stack Height: _____50_____ ft. Stack Diameter: _____2.5_____ ft.

Gas Flow Rate: _____125_____ ACFM Gas Exit Temperature: _150_ °F.

Water Vapor Content: Saturated % Velocity: _____41.67_____ FPS

SECTION IV: INCINERATOR INFORMATION

Type of Waste	Type O (Plastics)	Type I (Rubbish)	Type II (Refuse)	Type III (Garbage)	Type IV (Pathological)	Type V (Liq & Gas By-prod.)	Type VI (Solid By-prod.)
Lbs/hr Incinerated							

Description of Waste _____

Total Weight Incinerated (lbs/hr) _____ Design Capacity (lbs/hr) _____

Approximate Number of Hours of Operation per day _____ days/week _____

Manufacturer _____

Date Constructed _____ Model No. _____

	Volume (ft)^3	Heat Release (BTU/hr)	Fuel		Temperature (°F)
			Type	BTU/hr	
Primary Chamber					
Secondary Chamber					

Stack Height: _____ ft. Stack Diameter _____ Stack Temp. _____

Gas Flow Rate: _____ ACFM _____ DSCFM* Velocity _____ FPS

*If 50 or more tons per day design capacity, submit the emissions rate in grains per standard cubic foot dry gas corrected to 50% excess air.

Type of pollution control device: [ ] Cyclone [ ] Wet Scrubber [ ] Afterburner [ ] Other (specify) _____

Brief description of operating characteristics of control devices: _____

_____

_____

_____

_____

Ultimate disposal of any effluent other than that emitted from the stack (scrubber water, ash, etc.):

_____

_____

_____

_____

SECTION V: SUPPLEMENTAL REQUIREMENTS

Please provide the following supplements where required for this application.

1. Total process input rate and product weight — show derivation.

2. To a construction application, attach basis of emission estimate (e.g., design calculations, design drawings, pertinent manufacturer's test data, etc.,) and attach proposed methods (e.g., FR Part 60 Methods 1, 2, 3, 4, 5) to show proof of compliance with applicable standards. To an operation application, attach test results or methods used to show proof of compliance. Information provided when applying for an operation permit from a construction permit shall be indicative of the time at which the test was made.

3. Attach basis of potential discharge (e.g., emission factor, that is, AP42 test).

4. With construction permit application, include design details for all air pollution control systems (e.g., for baghouse include cloth to air ratio; for scrubber include cross-section sketch, etc.).

5. With construction permit application, attach derivation of control device(s) efficiency. Include test or design data. Items 2, 3, and 5 should be consistent: actual emissions = potential (1-efficiency).

6. An 8½" x 11" flow diagram which will, without revealing trade secrets, identify the individual operations and/or processes. Indicate where raw materials enter, where solid and liquid waste exit, where gaseous emissions and/or airborne particles are evolved and where finished products are obtained.

7. An 8½" x 11" plot plan showing the location of the establishment, and points of airborne emissions, in relation to the surrounding area, residences and other permanent structures and roadways (Example: Copy of relevant portion of USGS topographic map).

8. An 8½" x 11" plot plan of facility showing the location of manufacturing processes and outlets for airborne emissions. Relate all flows to the flow diagram.

9. An application fee of $20, unless exempted by Section 17-4.05(3), F.A.C. The check should be made payable to the Department of Environmental Regulation.

10. With an application for operation permit, attach a Certificate of Completion of Construction indicating that the source was constructed as shown in the construction permit.

SECTION VI: BEST AVAILABLE CONTROL TECHNOLOGY

A. Are standards of performance for new stationary sources pursuant to 40 C.F.R. Part 60 applicable to the source?
[ ] Yes [ ] No

Contaminant	Rate or Concentration

B. Has EPA declared the best available control technology for this class of sources (If yes, attach copy) [ ] Yes [ ] No

Contaminant	Rate or Concentration

C. What emission levels do you propose as best available control technology?

Contaminant	Rate or Concentration

D. Describe the existing control and treatment technology (if any).

1. Control Device/System:

2. Operating Principles:

3. Efficiency: *   4. Capital Costs:

5. Useful Life: 6. Operating Costs:

7. Energy: 8. Maintenance Cost:

9. Emissions:

Contaminant	Rate or Concentration

*Explain method of determining D 3 above.

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10. Stack Parameters

    a.   Height: ft.   b.   Diameter: ft.

    c.   Flow Rate: ACFM   d.   Temperature: °F

    e.   Velocity: FPS

E.   Describe the control and treatment technology available (As many types as applicable, use additional pages if necessary).

    1.

        a.   Control Device:

        b.   Operating Principles:

        c.   Efficiency*:   d.   Capital Cost:

        e.   Useful Life: f.   Operating Cost:

        g.   Energy*:   h.   Maintenance Cost:

        i.   Availability of construction materials and process chemicals:

        j.   Applicability to manufacturing processes:

        k.   Ability to construct with control device, install in available space, and operate within proposed levels:

    2.

        a.   Control Device:

        b.   Operating Principles:

        c.   Efficiency*:   d.   Capital Cost:

        e.   Useful Life: f.   Operating Cost:

        g.   Energy**:   h.   Maintenance Costs:

        i.   Availability of construction materials and process chemicals:

        j.   Applicability to manufacturing processes:

        k.   Ability to construct with control device, install in available space, and operate within proposed levels:

*Explain method of determining efficiency.

**Energy to be reported in units of electrical power — KWH design rate.

    3.

        a.   Control Device:

        b.   Operating Principles:

        c.   Efficiency*:   d.   Capital Cost:

        e.   Life: f.   Operating Cost:

        g.   Energy: h.   Maintenance Cost:

*Explain method of determining efficiency above.

i. Availability of construction materials and process chemicals:

j. Applicability to manufacturing processes:

k. Ability to construct with control device, install in available space and operate within proposed levels:

4.

  a. Control Device

  b. Operating Principles:

  c. Efficiency*:   d. Capital Cost:

  e. Life: f. Operating Cost:

  g. Energy: h. Maintenance Cost:

  i. Availability of construction materials and process chemicals:

  j. Applicability to manufacturing processes:

  k. Ability to construct with control device, install in available space, and operate within proposed levels:

F. Describe the control technology selected:

1. Control Device:

2. Efficiency*:   3. Capital Cost:

4. Life: 5. Operating Cost:

6. Energy: 7. Maintenance Cost:

8. Manufacturer:

9. Other locations where employed on similar processes:

  a.

    (1) Company:

    (2) Mailing Address:

    (3) City: (4) State:

    (5) Environmental Manager:

    (6) Telephone No.:

*Explain method of determining efficiency above.

    (7) Emissions*:

Contaminant	Rate or Concentration

    (8) Process Rate*:

  b.

    (1) Company:

    (2) Mailing Address:

    (3) City: (4) State:

*Applicant must provide this information when available. Should this information not be available, applicant must state the reason(s) why.

(5)   Environmental Manager:

(6)   Telephone No.:

(7)   Emissions*:

Contaminant	Rate or Concentration

(8)   Process Rate*:

10. Reason for selection and description of systems:

*Applicant must provide this information when available. Should this information not be available, applicant must state the reason(s) why.

SECTION VII – PREVENTION OF SIGNIFICANT DETERIORATION

A. Company Monitored Data

   1. _____ no sites _____ TSP _____ ( ) SO^{2*} _____ Wind spd/dir

   Period of monitoring _____/_____/_____ to _____/_____/_____
                              month day year   month day year

   Other data recorded _____

   Attach all data or statistical summaries to this application.

   2. Instrumentation, Field and Laboratory

     a) Was instrumentation EPA referenced or its equivalent? _____ Yes _____ No

     b) Was instrumentation calibrated in accordance with Department procedures? _____ Yes _____ No _____ Unknown

B. Meteorological Data Used for Air Quality Modeling

   1. _____ Year(s) of data from _____/_____/_____ to _____/_____/_____
                                      month day year   month day year

   2. Surface data obtained from (location) _____

   3. Upper air (mixing height) data obtained from (location) _____

   4. Stability wind rose (STAR) data obtained from (location) _____

C. Computer Models Used

   1. _____ Modified? If yes, attach description.

   2. _____ Modified? If yes, attach description.

   3. _____ Modified? If yes, attach description.

   4. _____ Modified? If yes, attach description.

   Attach copies of all final model runs showing input data, receptor locations, and principle output tables.

D. Applicants Maximum Allowable Emission Data

             Pollutant   Emission Rate

               TSP   _____ grams/sec

              SO^2 _____ grams/sec

E. Emission Data Used in Modeling

   Attach list of emission sources. Emission data required is source name, description on point source (on NEDS point number), UTM coordinates, stack data, allowable emissions, and normal operating time.

F. Attach all other information supportive to the PSD review.

*Specify bubbler (B) or continuous (C).

G. Discuss the social and economic impact of the selected technology versus other applicable technologies (i.e., jobs, payroll, production, taxes, energy, etc.). Include assessment of the environmental impact of the sources.

H. Attach scientific, engineering, and technical material, reports, publications, journals, and other competent relevant information describing the theory and application of the requested best available control technology.

APPENDIX A - PROJECT DESCRIPTION

The purpose of the project is to construct a handling facility at
the existing Agrico South Pierce Plant to receive and transfer
wetted prilled sulfur to a new sulfur melting system. The sulfur
will be received via trucks or railcar, at a rate of 1800 long tons
per day. The facility will process a maximum of 600,000 long tons
per year.

The trucks and/or railcars will be ████████████████████. The
unloaded sulfur will be conveyed to a 100 LT surge hopper. From the
hopper, the sulfur will be fed to the melting system by a ████████
████. The melting system consists of three 900 LT/Day melters.
One of the melters will provide spare capacity, however, the through-
put of the system will not exceed 1800 LT/Day. The potential H_2S
fumes generated from the melting of the sulfur will be controlled by
a wet scrubber. The scrubber will utilize a caustic solution as the
scrubbing liquor.

SUPPLEMENT #1

DERIVATION OF PROCESS INPUT
WEIGHT FROM OUTPUT WEIGHT

PRODUCT INPUT WEIGHT (1800 LTPD Design Rate)

$$1800 \ \frac{LT}{Day} \times \frac{1 \ Day}{24 \ Hrs} \times \frac{2240 \ Lb.}{1 \ Lt.} = 168,000 \ Lb./Hr.$$

DUST EMISSIONS

$$1800 \ \frac{L \ Tons}{Day} \times .0068 \ \frac{Lb}{Ton} \times 2 \ dumps \times 1.12 \ \frac{Ton}{L \ Ton} \times \frac{1 \ Day}{24 \ Hrs.} = 1.14 \ Lb./Hr.$$

DERIVATION

$$168,000 \ \frac{Lb}{Hr.} - 1.14 \ \frac{Lb}{Hr.} = 167,998.86$$

SUPPLEMENT #2 and #3

EMISSION ESTIMATES

I. PARTICULATES

On February 28, 1979, Dr. Dale A. Lundgren, of the University of Florida, issued a report entitled "Determination of Emission Factors for Fugitive Emission Sources". The paper summarized research conducted to determine the emission rate of dust in the movement of prilled sulfur. The results of the research indicated that for prilled sulfur with 2% moisture, an emission rate of .0068 lb. of particulate per ton of material could be expected in a transfer-convey operation. At South Pierce, the sulfur will be unloaded from trucks and/or railcars and transferred into a silo.

For a facility handling 600,000 long tons of material a year, the following emissions are expected:

Assume: .0068 Lb/Ton Emission Factor
         2 Transfer Locations

$$600{,}000 \; \frac{L \; Ton}{Yr.} \times .0068 \; \frac{Lb}{Ton} \times 2 \; dumps \times 1.12 \; \frac{Ton}{L \; Ton} \times \frac{1 \; Ton}{2000 \; Lb} = 4.57 \; Ton/Yr.$$

The attached photos are included to demonstrate the lack of dust. They were taken at a prilled sulfur installation in Canada. Notice that there are no visible emissions in the movement of the material.

II. HYDROGEN SULFIDES

Technical data obtained from Dr. Mike D. Raymont of the Sulfur Development Institute of Canada indicated that 25-50 PPM of H2S could normally be released during melting of the prilled sulfur. Occasionally some sulfur could release as much as 250 PPM, however, this would be rare.

The H2S scrubber will be designed to control the worst case situation of a release of 250 PPM H2S.

The maximum throughput of the three melters are 1800 LTPD. The emission rate would be:

$$1800 \; \frac{L \; Ton}{Day} \times .00025 \; \frac{L \; Ton \; H2S}{L \; Ton} \times \frac{1 \; Day}{24 \; Hr.} \times \frac{2240 \; Lb.}{1 \; L \; Ton} = 42 \; \frac{Lb \; H2S}{Hr.}$$

The design output of the scrubber (per Barnard & Burk) will
be 1.9 Lb/Hr. The efficiency will be:

$$\frac{42-1.9}{42} \times 100 = 95\%$$

Yearly emissions rate:

$$600{,}000 \frac{L\ Ton}{Yr.} \times .00025 \frac{L\ Ton\ H2S}{L\ Ton} \times .05 \times 1.12 \frac{Ton}{L\ Ton} = 8.4\ Ton/Yr.\ H_2S$$

TYPICAL PRILLED SULFUR OPERATION
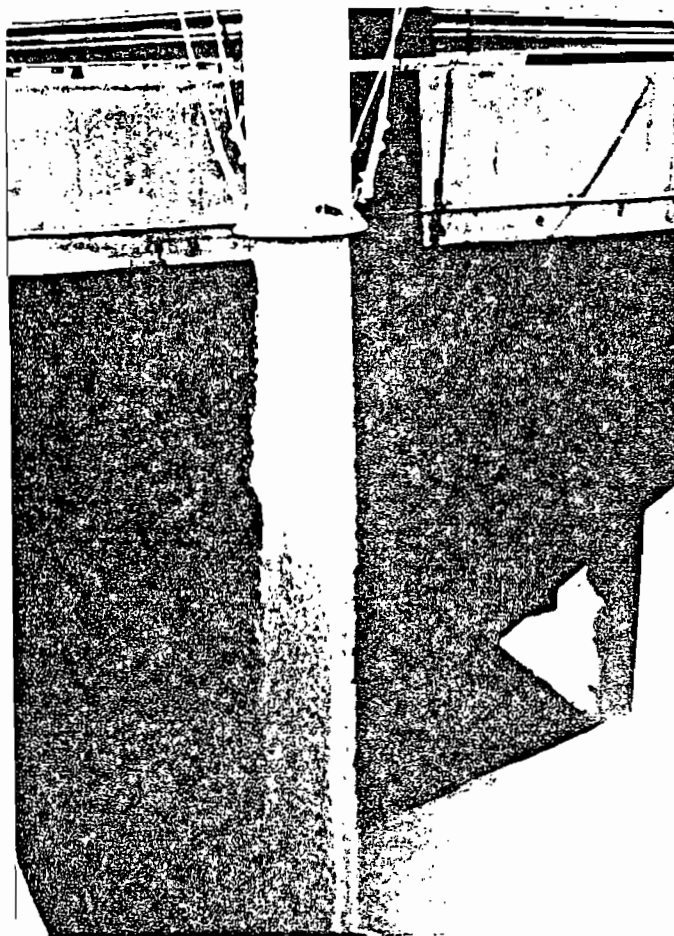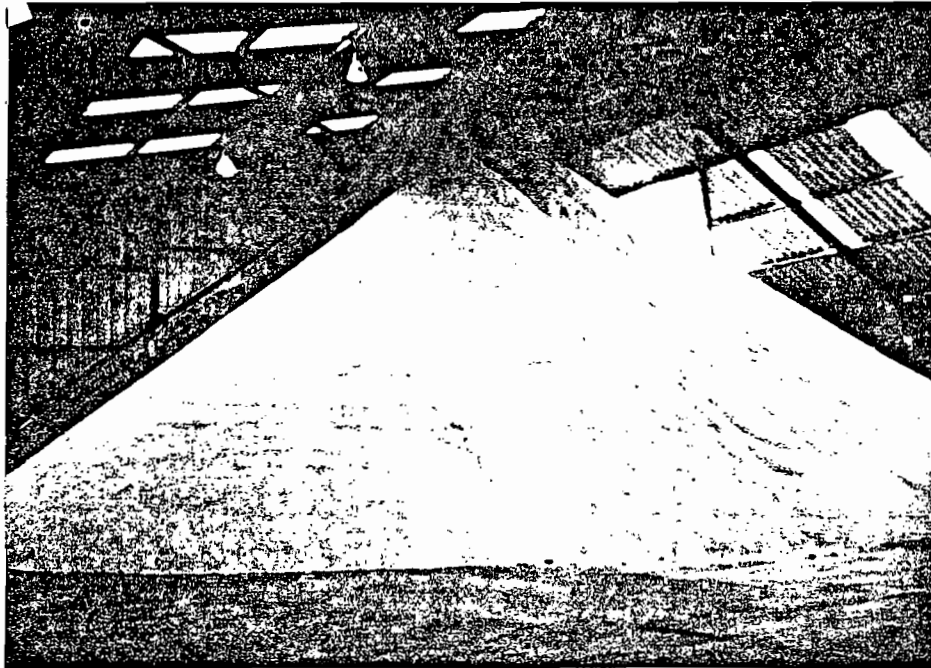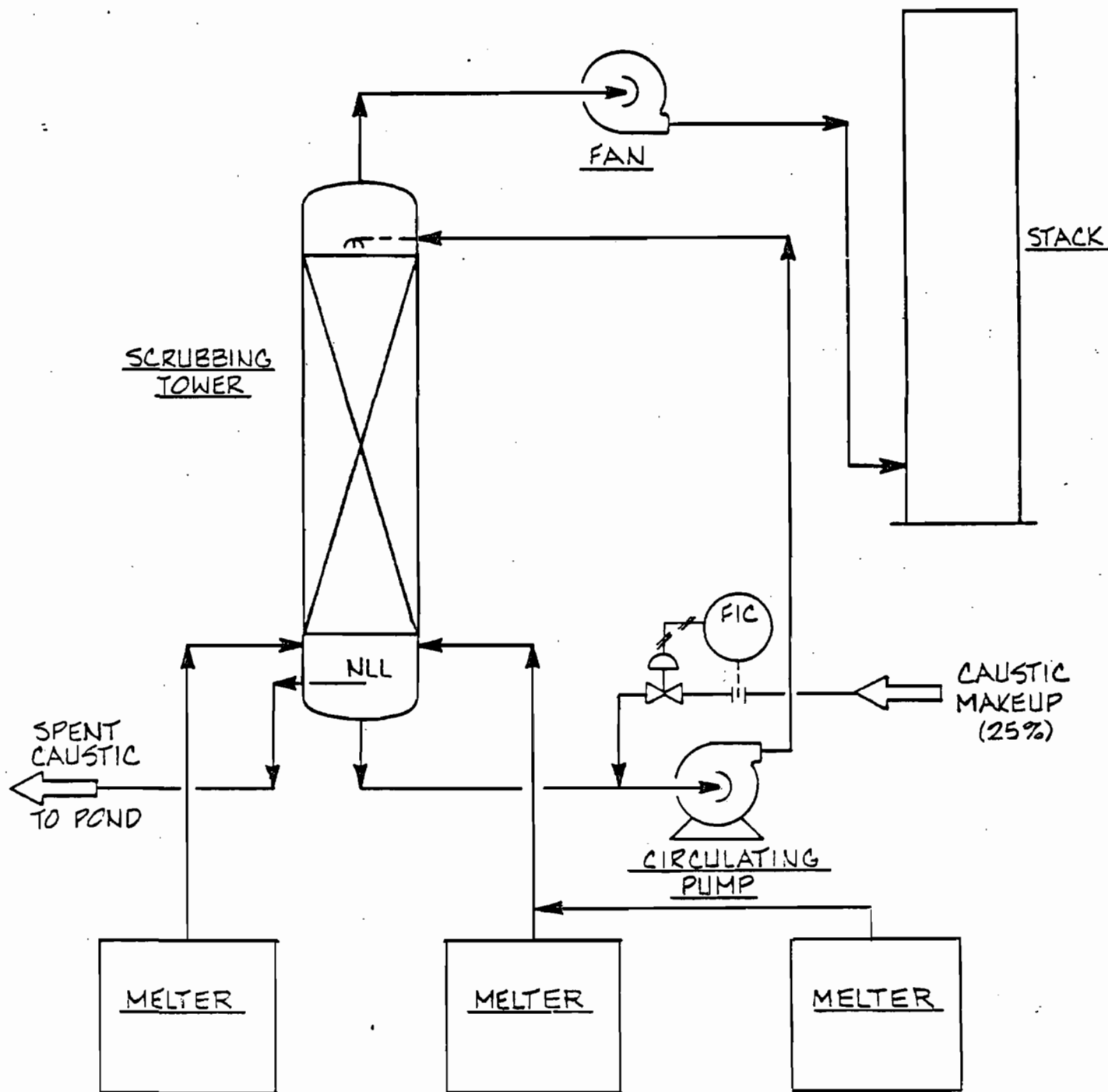
FAN

STACK

SCRUBBING
TOWER

FIC

NLL

CAUSTIC
MAKEUP
(25%)

SPENT
CAUSTIC

TO POND

CIRCULATING
PUMP

MELTER

MELTER

MELTER

SUPPLEMENT #4

SUPPLEMENT #6
FLOW DIAGRAM
PRILLED SULFUR - S.P.C.W.

CONVEYOR
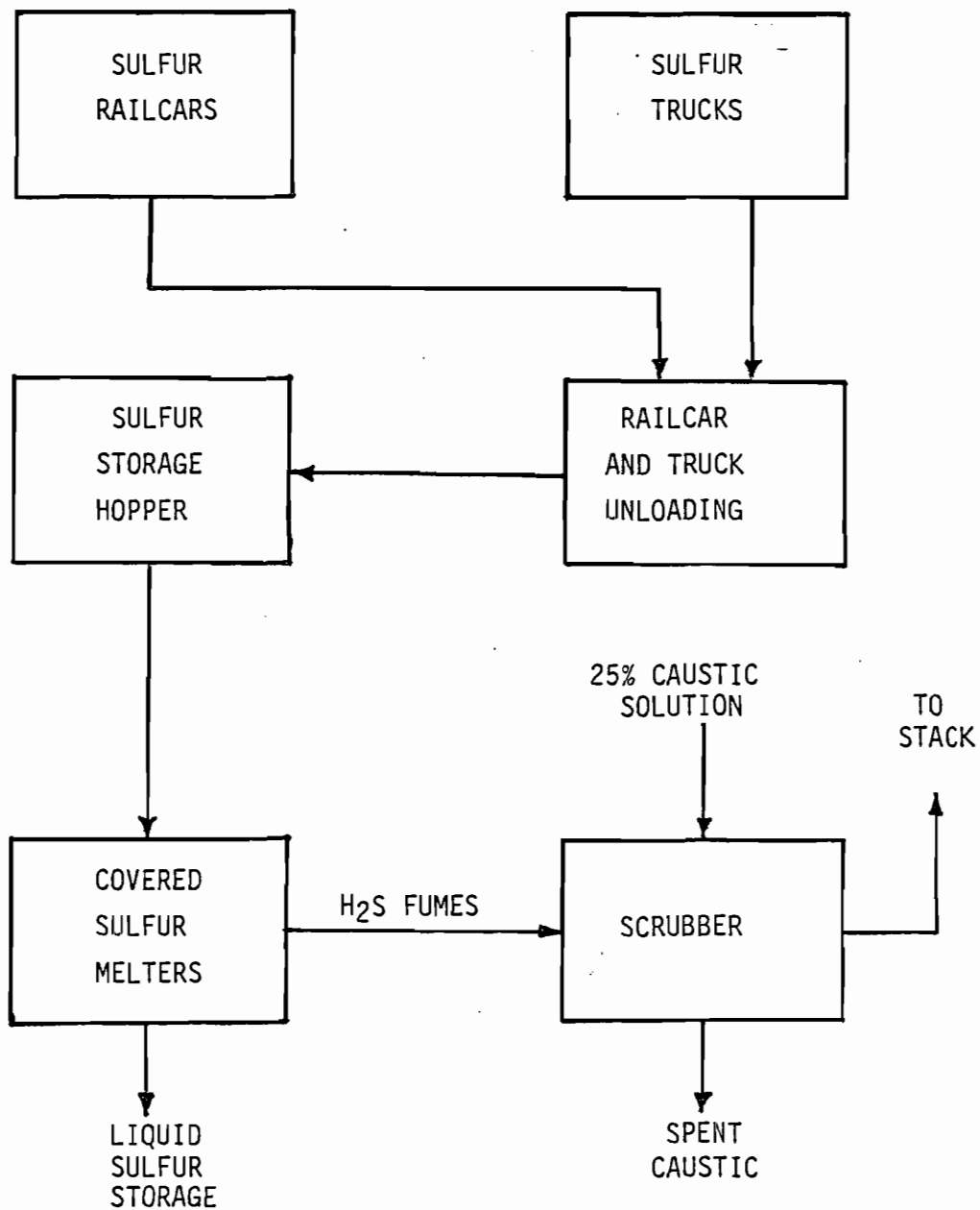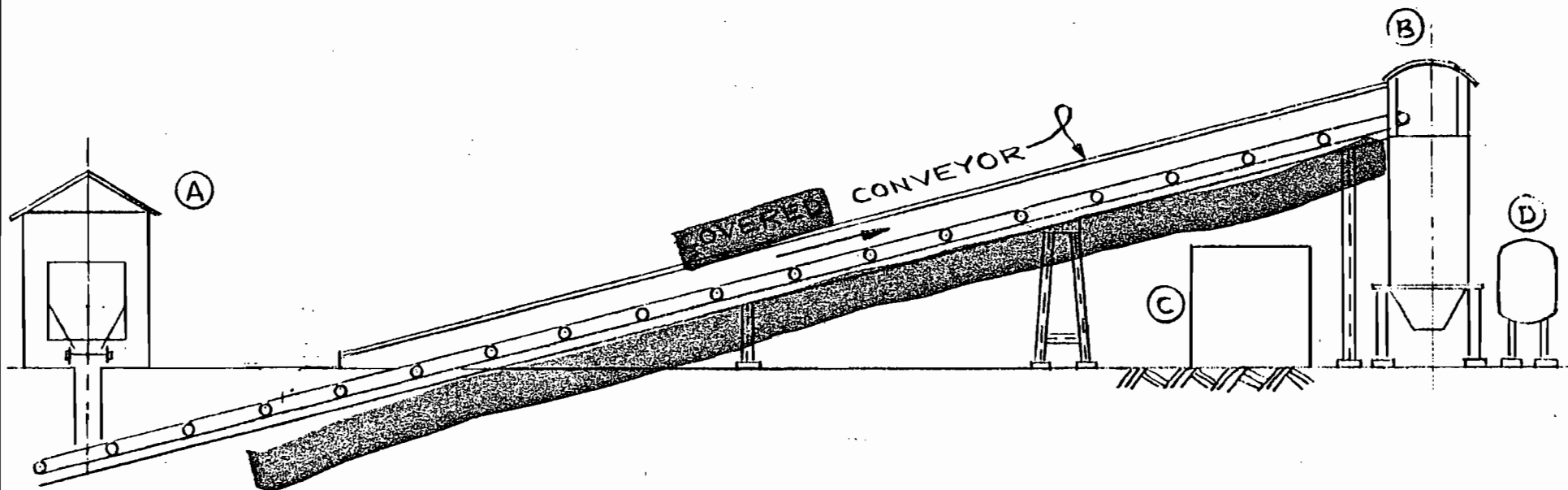
COVERED

Ⓐ RAILCAR AND TRUCK UNLOADING SHED
Ⓑ COVERED STORAGE HOPPER
Ⓒ COVERED MELTERS
Ⓓ H_2S SCRUBBER

SUPPLEMENT #6

IB®
IB
BARNARD AND BURK ENGINEERS
& CONSTRUCTORS, INC.

TITLE
FLOW DIAGRAM
PRILLED SULPHUR HANDLING
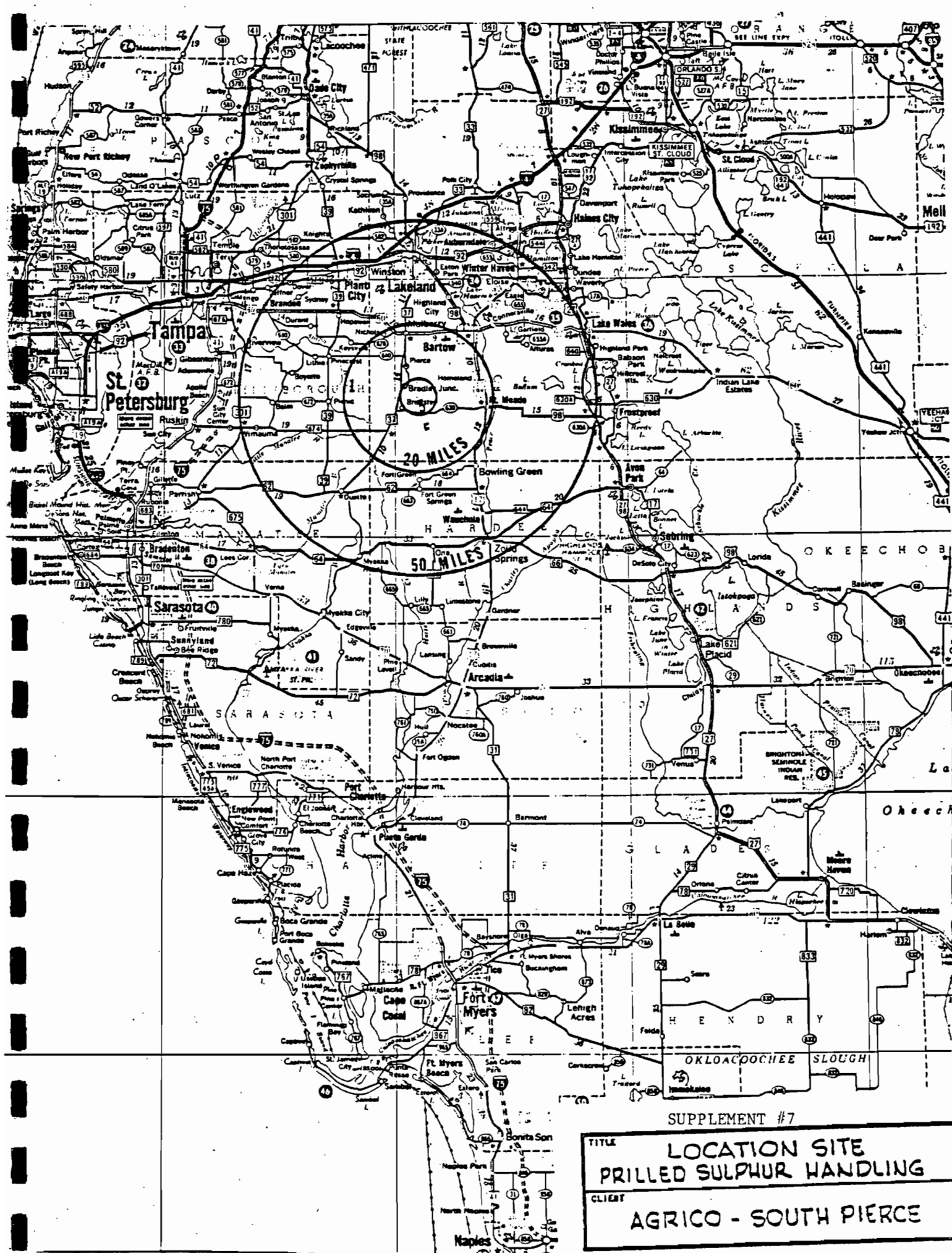
CLIENT
AGRICO - SOUTH PIERCE

TITLE
LOCATION SITE
PRILLED SULPHUR HANDLING
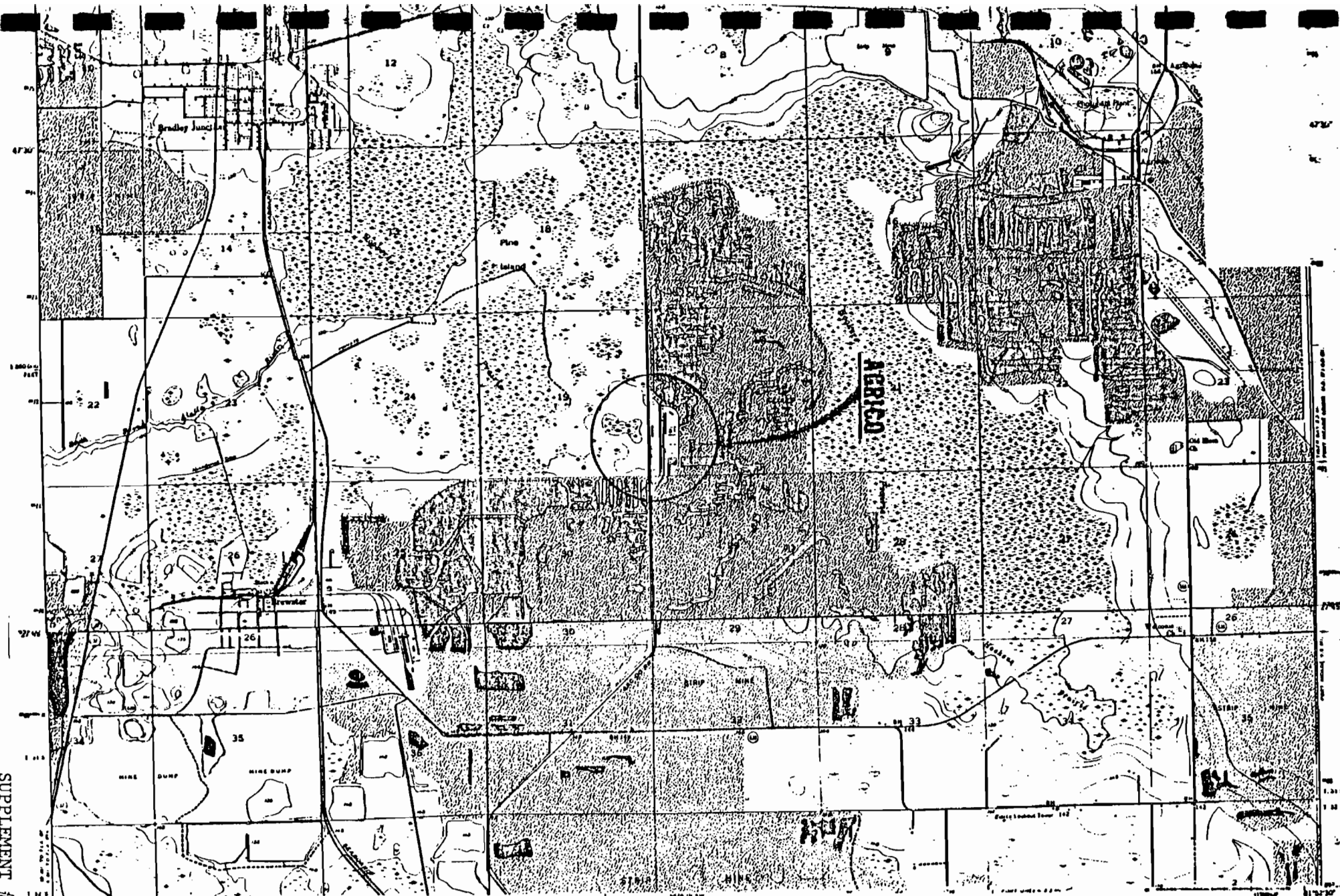
CLIENT
AGRICO - SOUTH PIERCE

20 MILES

50 MILES

SUPPLEMENT #7

SCALE 1:24 000
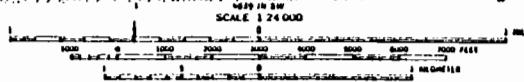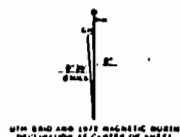
CONTOUR INTERVAL 5 FEET
DATUM IS MEAN SEA LEVEL

FLORIDA

QUADRANGLE LOCATION

ROAD CLASSIFICATION

Heavy duty _____   Light duty _____
Medium duty _____   Unimproved dirt ......

U S Route   State Route

BAIRD, FLA.

N2737.5—W8152.5/7.5

1955
PHOTOREVISED 1972

NORTH

EXIST. R.R. TRACK 9
EXIST. R.R. TRACK 10

TRUCK AND RAILCAR SHED

EXTENDED CONCRETE SLAB

CONVEYOR

HOPPER

EXIST. BLDG.

MELTER

SCRUBBER

MELTER

EXIST.

EXIST. AIR COMP. BLDG.

LUNCH ROOM

AMB. GARAGE

WAREHOUSE

PROPOSED PROJECT

SUPPLEMENT #8

IB ® BARNARD AND BURK ENGINEERS & CONSTRUCTORS, INC.

TITLE
LOCATION PLAN
PRILLED SULPHUR HANDLING

CLIENT
AGRICO - SOUTH PIERCE

Bill

Mr. C. H. Fancy, P.E.
Deputy Bureau Chief
Bureau of Air Quality Management
Department of Environmental Regulation
Towers Office Building
Blairstone Road
Tallahassee, Florida 32301

RE: Air Pollution Source
     Construction Application -
     South Pierce Chemical Works,
     AC53-55780

Dear Mr. Fancy:

Agrico Chemical Company is in receipt of your June 9, 1982
letter which stated that the permit application for a prilled sulfur
receiving and melting facility at our South Pierce Chemical Works
was deemed incomplete. In your letter you requested information on
eight areas in order to complete processing of our permit. In the
order in which the questions were asked, we respond with the following
information:

We have enclosed a copy of Dr. Lundgren's "Determination of
Emission Factors for Fugitive Emission Sources", per your request.
We have also included Dr. Ramont's technical data on hydrogen sulfide
emissions.

Regarding Agrico's rationale behind the choice of the number of
dumps in the calculation of particulate emission, we maintain that only
two locations for air emissions are involved, not five. The wet-prilled
sulfur is ▒▒▒ hopper
▒▒▒
▒▒▒▒▒▒▒▒▒ source. From the hopper, it is ▒▒▒▒▒▒▒▒▒▒▒▒ a covered ▒▒▒▒
▒▒▒▒▒. Since this discharge is totally enclosed, no particulate emissions
are generated. The ▒▒▒▒▒▒ conveyor ▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒ surge hopper
▒▒▒▒▒▒▒▒▒▒▒▒ designed so that ▒▒▒▒▒▒▒▒▒▒▒▒ will escape out of the ▒▒▒▒
▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒. The design of the surge hopper results in the ▒▒▒▒
▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒▒. The storage hopper then discharges into enclosed
vibrating feeders. Thus, the discharge from the enclosed hopper to the
vibrating feeders does not generate fugitive dust.

-1-

From the vibrating feeders, the wet-prilled sulfur dumps into covered melters. The covers on the tops of the melters prevent any potential generation of fugitive dust. It should also be mentioned that the fumes from the melters will be scrubbed to remove any H_2S. Thus, because of the enclosed design of the system, only two transfers can be considered potential sources of particulate emissions.

In complying with the requirement of 17-2.610(3), FAC, Unconfined Emissions of Particulate Matter, it appears that compliance depends upon the interpretation of ▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓ Agrico maintains that handling wet-prilled sulfur at approximately 2% moisture, fines particles are very effectively held to the prill. Thus, the moisture content prevents the release of particulates to the ambient air; and, as such, constitutes a reasonable precaution. This reasonable precaution was approved as adequate in the recent air construction permit issued by the Department for Agrico's prilled sulfur terminal at Big Bend, Hillsborough County, Florida.

In addition, FAC Rule 17-2.650 (2) (c) 5b, (i) establishes a reasonable emission limit of 0.30 pounds of particulate per ton of product for unit operations in a phosphate processing plant. The manu-facturing of sulfuric acid is an integral part of the process to produce G.T.S.P. so, therefore, this limitation could be considered reasonable. The three sulfuric acid plants will produce 250 tons per hour of product and the sulfur unloading facility will produce 1.14 lbs./hr. of particulate. This results in a .0046 pound per ton emission rate or 1.5% of the allow-able for unit operation. If the process is limiting fugitive emissions to within 1.5% of what controlled emissions are allowed, then Agrico contends that the intent of 17-2.610 (3) is being met.

In response to your question regarding process rates from the surge hopper and truck unloading conveyor, preliminary design calls for a maximum vibrating feeder rate of 60 tons per hour (actual rate will vary depending on plant consumption). The truck unloading rate is considerably faster in order to maintain a minimum turnaround time on the trucks. As such, ▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓

Regarding supplemental information concerning the wet scrubber, we have attached design information from the firm of Bernard and Burk Engineers and Constructors, Inc.

In regard to the flow characteristics of the wet scrubber stack, we have enclosed a revised Page 4 of 10.

Mr. C. H. Fancy
Page Three

In regard to the airborne contaminants emitted, we have enclosed
a revised Page 3 of 10. The changes made in Section III C are explained
below:

1. The allowed emission rate for particulate is changed from
   the process weight table limitations to the unconfined
   emission statement of 17-2.610(3).

2. The maximum lb./hr. and T/Yr. emission H_2S is changed to
   1.9 and 8.4 respectively, to reflect the information
   submitted in Supplement 3.

3. The potential T/Yr. H_2S emission is changed to 1680.
   This number is calculated by using the equation quoted
   in Supplement 3, with removal of the .05 control factor.

During the melting process minute amounts of SO_2 will be generated.
The ratio of H_2S to SO_2 is approximately 800 to 1. The uncontrolled
amount of H_2S emitted is 1680 tons per year, therefore, the SO_2 emissions
will be approximately 2.1 tons per year. The SO_2 fumes will be evacuated
through the fume system and will be fed to the scrubber before release
into the atmosphere. There are no other criteria pollutants emitted
during the operation.

Agrico believes the above responses sufficiently respond to the
questions raised in your July 9, 1982 memo, and the processing of our
air construction permit can now be finalized. If there are any questions
concerning this matter, please contact ██████████████████████

                              Sincerely,

                              L. C. Lahman,
                              Plant Manager

Enclosure

LCL/lgm

Determination of Emission Factors for Fugitive Emission Sources

February 28, 1979

Dale A. Lundgren

Calculation of fugitive emissions from industrial processes involving the transfer, conveying, loading and unloading of bulk materials generally following the procedures outlined in EPA document AP-42 titled "Compilation of Air Pollutant Emission Factors" February 1976 or the document titled "Technical Guidance for Control of Industrial Process Fugitive Particulate Emissions". (EPA-450/3-77-010, March 1977). In both documents the "emission factor" for the given bulk material is basic to making an emission estimate. Only for a few materials have emission factors been obtained. Emission factors are given for transfer and conveying of coal, coke, dry phosphate rock, sand, grain, iron ore, and lead ore. Among these materials, dry phosphate rock has a factor reliability of "below average" or "D" while all other materials have a factor reliability of "poor" or "E". Loading and unloading operations have emission factors listed for dry phosphate rock, taconite pellets, coal and grain. The phosphate rock has an emission factor reliability of "average" or "C". All other materials are in the below average or poor reliability factor categories.

Emission factor data for prilled sulfur is needed to make a valid estimate of the dust emission rate from a prilled sulfur unloading facility such as the Agrico Chemical Company, Big Bend Terminal in Hillsborough County, Florida. A careful literature search failed to find any emission factor data for any form of prilled sulfur. This lack of data was confirmed by Mr. Gilbert Wood, EPA Project Officer for the cited EPA report on fugitive particulate emissions - a study conducted for EPA by PEDCo Environmental, Inc. (Mr. Gilbert's recommendation was to obtain field or laboratory test data for the prilled sulfur).

The complete lack of a reasonable emission factor for prilled sulfur has been recognized and stated by most persons involved in the problem of estimating emissions from the proposed Agrico sulfur unloading facility. This lack of knowledge has not prevented about five different firms or persons (including the writer) from calculating over 10 different dust emission rate estimates.

In an attempt to resolve this emission factor uncertainty and to determine the effect of moisture content on the dustiness of prilled sulfur, a test procedure was developed and tests run on both phosphate rock and prilled sulfur at various moisture contents. These tests were run in a specially built wind tunnel which allowed the aerosolized dust to be collected and measured. A standard Hi-Vol motor, blower and filter holder and an 8x10 inch glass fiber filter paper were used for efficient collection of the dust. A sketch of the test chamber is shown in Figure 1.

In operation, the Hi-Vol is fitted with a pre-weighed filter, set in place and operated at an air flow rate of about 60 cfm. A pre-weighed sample of product is discharged into the center of an 8-inch vertical duct. The downward air velocity in the duct is about 170 fpm. The sample is gradually and uniformly dumped in a rate of about 10 pounds per minute and allowed a free fall of five feet onto a cement slab (covered with Kraft paper or plastic for ease of product recovery). Dust generated is blown from the product under test by the downward direction of the air stream. Cross-sectional area and air flow rate of the vertical wind tunnel were selected so that all particles less than about 60 um aerodynamic diameter would be drawn up and collected onto the filter paper. Particles greater than -100 um aerodynamic diameter would have sufficient settling velocity (-60 fpm) to resist the upward air motion and settle downward. These collection characteristics are comparable to the standard Hi-Vol air sampler operating in a shelter of approved design. Data is therefore obtained

on the quantity of dust that is capable of being collected by a Hi-Vol (the sampling instrument used for determination of compliance with the national ambient air quality standard for suspended particulate matter).

In order to relate this measurement of dust emission factor with available published data in AP-42, a total of eight tests were run on dry phosphate rock (duplicate tests on four samples). Dry phosphate rock was selected as the best material for comparison purposes because it has the highest assigned reliability factor for any material listed in the EPA Technical Guidance Document EPA-450/3-77-010. Dry phosphate rock was assumed to be rock allowed to equilibrate for several days at 70-75°F temperature and 40-50% relative humidity. The reference or comparison test run on dry phosphate rock produced an average product emission factor (or dustiness) of 1.5 pounds per ton (average of 0.9, 2.0, 1.5 and 1.5 pounds per ton). This suggests that the proposed wind tunnel tests produce data comparable to that presented in AP-42 and EPA-450/3-77-010.

The sequence of testing for both the phosphate rock and the sulfur prill first involved air drying the material in a thin layer on a table top for three days (72 hours) at an average room temperature of 75°F and room air humidity of 45 to 50% RH. Moisture tests were run on 100 gram samples of each material. The weight loss upon heating to 105°C in a drying oven for 60 minutes was determined and considered to be the percent moisture.

Ten pound samples of each material (4540 grams) were weighed out and used for the wind tunnel drop test (a 5 foot drop onto a cement floor covered with a sheet of Kraft paper) using the test chamber shown in Figure 1. Each sample of each material was used twice. Separate pre-weighed filters were used for each test. On completion of each test, the filter was weighed on a standard analytical balance to the nearest 0.1 mg. Filters were not desiccated or otherwise dried before weighing. All filters were marked and saved.

After the initial dry product tests, the air dried phosphate rock and sulfur prill were each wet with about 600 ml of ordinary tap water (no wetting agent used). These samples were carefully mixed, spread out onto a sheet of plastic, and allowed to dry or equilibrate for 15 hours. Moisture analysis was run as previously described (100-gram samples dried at 105°C for 60 minutes) and weight loss used to calculate percent moisture. The remaining material was weighed and used for emission factor tests as described. Duplicate tests were run on each material.

Samples were air dried further and tested as described. Additional phosphate rock samples were air dried and tested.

The original phosphate rock and sulfur prill samples were completely dried to original (first test) moisture conditions and re-tested. The object was to determine if the product dustiness had changed significantly. As indicated on the following table as "initial" and "final" the percent dust produced was nearly unchanged. All test data is summarized in the following table. Duplicate tests were reproducible to within ± 20% of the average in almost all cases.

Test results for sulfur prill are 0.0037 pounds dust per ton of product at 2.6% moisture and 0.0098 pounds dust per ton of product at 1.6% moisture. These data are averaged and the emission factor for a 2% moisture sulfur prill is estimated to be 0.0068 pounds per ton. Using this emission factor for 2% moisture prilled sulfur, an estimate of the uncontrolled dust emission rate can be calculated. A water spray control efficiency factor of 50% or a wetting agent control efficiency factor of 90% can then be applied. If the Emission Estimate table prepared by PEDCo is used with the 0.0068 pounds per ton dustiness factor, the following emission rate valves are determined.

Uncontrolled emission rate	10.2 lb/hour
Water control at 50%	5.1 lb/hour
Wetting agent control @ 90%	1.0 lb/hour

The above values are from the table on the following page. On a yearly average basis the respective rates are all reduced by a factor of about 10 to values of 1, 0.5, and 0.1 pounds per ton.

Because of the uncertainty of such estimates, it is likely that the actual emission rate is somewhere between one-half and twice that calculated and may be as little as one-fourth or as much as four times the calculated values for the control conditions given.

Figure 1 - Test Chamber

60 cfm air flow rate

Hi-Vol Blower

Product Inlet

Air Inlet

8"X10" filter paper
(7"X9" filter area
giving a filter
inlet velocity
= 140 fpm.)

24"

8"D.

Product and air.
Air Velocity = 170fpm

60"

floor covered
with Kraft paper.

25"

25"

Emission Estimates

Using PEDCo listed Activities and a 0.0068 #/ton emission factor

Activity	Uncontrolled Emission Factor #/ton	Material Throughput tons/hour	Emission Rate-#/hour Uncontrolled	Emission Rate-#/hour 50% Control	Emission Rate-#/hour 90% Control
Ship Unloading	0.0068	600	4.1	2.05	0.41
Transfer-convey	0.0068	600	4.1	2.05	0.41
Storage(0.0068)					
-onto pile	0.0008	600	0.5	0.25	0.05
-veh. traffic	0.0027	75	0.2	0.1	0.02
-wind erosion	0.0022	75	0.2	0.1	0.02
-loadout	0.0010	75	0.1	0.05	0.01
Transfer-convey	0.0068	75	0.5	0.25	0.05
Truck loadout	0.0068	75	0.5	0.25	0.05
Total			10.2	5.1	1.0

Summary of Wind Tunnel Tests on
Phosphate Rock and Sulfur Prill

by

Dale A. Lundgren

January 26, 1979

Sulphur Prill

% H_2O	% Dust	# Dust/ Ton Product
10.7	0.00014	0.0028
3.5	0.00018	0.0036
2.6	0.00019	0.0037
1.6	0.00049	0.0098
0.1 - initial	0.15	3.0
0.1 - final	0.19	3.8

Phosphate Rock

% H_2O	% Dust	# Dust/ Ton Product
10.6	0.00022	0.0044
3.5	0.00072	0.014
2.2	0.039	0.78
1.3 - new sample	0.045	0.90
1.2 - initial	0.10	2.0
1.2 - final	0.076	1.5
1.6 - new sample	0.077	1.5

Sulphur Development Institute of Canada (SUDIC)
#1702 Canada Trust Building
505 Third Street, S.W.
Calgary, Alberta

May 19, 1982

Mr. R. W. Curtis
Agrico Chemical Company
P.O. Box 3166
Tulsa, OK 74101

Dear Mr. Curtis:

Pursuant to our telephone conversation in March concerning hydrogen sulphide emissions, I would like to confirm the following:

1. Total levels of hydrogen sulphide present as both dissolved hydrogen sulphide and combined hydrogen polysulphide in solid sulphur product from gas plants will generally lie in the 50-250 ppm range depending on the thermal history and age of the product. Most product levels will lie at the lower end of the range (50-100 ppm H_2S).

2. Remelting of this product will release part but not all of this total hydrogen sulphide content. Free dissolved hydrogen sulphide will be released on melting whereas the hydrogen sulphide present as combined hydrogen polysulphide will not be readily emitted. If held in the molten state for long periods, the hydrogen polysulphides will grad-ually decompose, slowly releasing more hydrogen sulphide. In any event the maximum release of hydrogen sulphide on melting can clearly not exceed the total content and will generally be of lower quantity.

3. The actual concentration of hydrogen sulphide both in process units (e.g., melters) and in the surrounding ambient air will clearly depend on melt rate, tonnage, and the dilution of the released gases.

I will try to find some papers in the literature which will support these state-ments on my return to Calgary and forward them to you in due course.

Yours sincerely,

Michael Raymont by R.Tom L

M. E. D. Raymont
Director, Research and Development.
SUDIC

General Background
See especially pp. 24-25

INTERCONVERSION RATES AND EQUILIBRIA IN

THE SULPHUR-HYDROGEN SULPHIDE SYSTEM

W. Schwalm and J.B. Hyne
Fundamental Sulphur Research Group

Almost any sulphur sample, especially sulphur recovered from sour natural gas, is an example of a sulphur-H_2S system. H_2S-free sulphur probably exists only when H_2S is deliberately removed from sulphur, Thus, the behaviour of sulphur can hardly be understood without reference to its H_2S content and for a number of reasons this understanding is crucial.

Because of the toxicity of H_2S, safety is a prime consideration. H_2S is lost from sulphur over a period of time. As will be shown later this loss is slow so build-up of H_2S concentration in the adjoining air space is often not a problem. High H_2S concentrations arise primarily with liquid sulphur in areas with inadequate ventilation. Examples of such situations could include sulphurcrete manufacture, sulphur remelters and liquid sulphur shipment. The last of these has been discussed by Williams et al[1] and by Hyne[2]. In addition an explosion hazard exists if the H_2S concentration in the air rises above 3.36% or 33,600 ppm[3]. These conditions can occur in localised volumes even with bulk sulphur containing only 10 - 15 ppm of H_2S[4].

ASR's interest in the study of the sulphur-H_2S system originated with the problem of sulphur deposition in sour natural gas collecting systems. This deposition was explained in terms of the formation and decomposition of hydrogen polysulphides or sulphanes, H_2S_x[5]. Sulphanes are also believed to be among the species responsible for the rapid corrosion of steel in the presence of sulphur and water.

It is also well-known that the presence of H_2S can have a dramatic effect on the properties of elemental sulphur. The effect of H_2S on the viscosity of liquid sulphur is particularly marked due to a decrease in the average length of the sulphur chains in the polymeric form. This viscosity modification by the H_2S was investigated by Fanelli in 1943-1946[6,7] and by Rubero in 1964[8]. It was found that 0.3% (3,000 ppm) H_2S increased the temperature of maximum viscosity of sulphur by 100°C and reduced the maximum viscosity by a factor of 1,000. Another property of pure sulphur which is affected by the small quantities of H_2S which can be incorporated is its flexure strength[9]. Saturation with H_2S makes sulphur 50% weaker and even very low concentrations have a marked effect. This, of course, would make sulphur less suitable as a construction material or for paving roads. Fortunately, the effect on sulphur composites is much less dramatic and additives have been identified that virtually eliminate the weakening effect.

Historical Development

In 1949, Fanelli investigated the apparent solubility of H_2S in

sulphur and found that it _increased_ with increasing temperature going through a broad maximum[10]. This behaviour is in contrast to most gases whose solubility in liquids _decreases_ with increasing temperature. From this and the effect of H_2S on sulphur's viscosity he inferred that a chemical reaction must be taking place resulting in the formation of sulphanes. However, the necessary techniques for distinguishing between H_2S and the H_2S_x species were not available. Feher and Winkhaus, in 1957, found H_2S_x species to be thermodynamically unstable with respect to H_2S and sulphur[11]. The solubility of sulphur in gaseous H_2S was investigated by Willand in 1958[12]. He found that more sulphur dissolved at higher temperatures and pressures but the formation of sulphanes in this H_2S rich system was uncertain.

In the mid 1960's two new techniques were used to investigate the sulphur-H_2S system - infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. Discussion of the former will be left to a later section. The NMR spectrum of sulphanes was first published by Schmidbaur and co-workers in 1964[13]. He found a distinct peak for each individual sulphane up to 5 sulphur atoms ($x = 5$ in H_2S_x). Higher sulphanes could not be resolved but formed one broad peak. This new tool allowed Hyne, Muller and Wiewiorowski to study the lower members of the sulphane family[14] and their thermal decomposition was investigated by Hyne and Muller[15,16]. In the course of these studies NMR spectra were run of sulphur in which H_2S had been dissolved and equilibrated. These spectra showed a virtual absence of sulphanes with less than 6 sulphur atoms. A thermodynamic treatment yielded an average chain length of 27 sulphur atoms at 127°C, increasing with rising temperature.

Meyer and his associates investigated the solubility of sulphur in liquid H_2S at elevated pressures in 1969[17,18]. They also found that in the presence of H_2S, the melting point of sulphur is depressed by about 20°C meaning that H_2S must also dissolve in solid sulphur. However, they found no evidence for sulphane formation up to 80°C (176°F). This was confirmed by Parthasarathy at ASR, who found that no sulphanes are formed up to 200°F[19]. Hyne and co-workers also confirmed that sulphane formation is favored by higher temperatures and pressures[20] and proposed a free radical mechanism for their formation[20,21]. A short review of solubility aspects of the sulphur-H_2S system by Wiewiorowski appeared in 1970[22].
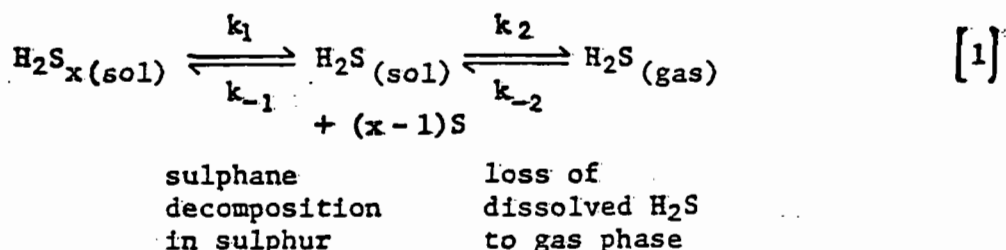
The formation of sulphanes, by the reaction of H_2S with liquid sulphur makes the removal of H_2S from sulphur more difficult. H_2S removal was studied by Rennie at ASR using a variety of catalysts to help break down the sulphanes[23]. Patents for removal of H_2S from liquid sulphur obtained in 1974[24] and 1975[25,26] show that this is a continuing concern. Analytical methods for measuring the total H_2S content of sulphur samples must also make allowance for the presence of sulphanes. Both the older method of Tuller[27] and the refinement by ASR[28] involve the use of a catalyst to break down the sulphanes and extended purge times.

The System

Most of the previous work on the sulphur-H_2S system has involved

static or equilibrium situations and little is said about the rates of the various processes. It is for this reason that the study to be described was undertaken. The sulphur-H_2S system can be described by the following set of reactions:

$$H_2S_{x(sol)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2S_{(sol)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2S_{(gas)} \qquad [1]$$
$$+ (x-1)S$$

sulphane   loss of
decomposition   dissolved H_2S
in sulphur   to gas phase

$H_2S_{x\ (sol)}$ represents all sulphanes present and dissolved in the sulphur; $H_2S_{(sol)}$ is the hydrogen monosulphide dissolved in the sulphur and $H_2S_{(gas)}$ is the H_2S present in the gas phase in contact with the sulphur. Examination of this set of reactions shows that the H_2S can be lost from the system to the gas phase only as the monosulphide. The sulphanes must first decompose to reform H_2S which can then be lost. This is a key consideration in any degassing technique for removal of H_2S from sulphur.

The k's in [1] represent the rate constant for the processes in the indicated directions. In addition, when at equilibrium, the system is constrained by the following equilibrium expressions:

$$K_1 = \frac{[H_2S_x]}{[H_2S_{(sol)}]} \qquad [2]$$

$$K_2 = \frac{[H_2S_{(sol)}]}{[H_2S_{(gas)}]} \qquad [3]$$

It should be noted that the concentration of sulphur does not appear in expression [1] since it is present in such large excess that it is essentially unchanged by the formation or decomposition of H_2S_x. Therefore, it has been incorporated into K_1. It should also be noted that at the very low concentrations of H_2S and H_2S_x considered here (ppm level) concentration units can be used instead of the more rigorous thermodynamic activity values in calculating rates and equilibrium constants. An additional equilibrium constant can be defined as:

$$K_3 = \frac{[H_2S_{(sol)}] + [H_2S_x]}{[H_2S_{(gas)}]} \qquad [4]$$

i.e. K_3 is the ratio of total H_2S concentration (both mono and poly-sulphide forms) in the sulphur to the concentration of H_2S in the gas phase.

The rate and equilibrium constants are related because equilibrium exists when the rates of the forward and reverse reactions are equal. For example, for equilibrium between H_2S_x and $H_2S_{(sol)}$

$$k_1\left[H_2S_x\right] = k_{-1}\left[H_2S_{(sol)}\right]$$

$$\frac{k_{-1}}{k_1} = \frac{\left[H_2S_x\right]}{\left[H_2S_{(sol)}\right]} = K_1 \qquad [5]$$

Likewise:

$$K_2 = \frac{k_{-2}}{k_2} \qquad [6]$$

K_3 can be related to the rate constants by making the appropriate substitutions into expresion [4] and rearranging to give:

$$K_3 = \frac{k_{-2}}{k_2}\left(1 + \frac{k_{-1}}{k_1}\right) \qquad [7]$$

Expressions [5], [6] and [7] are useful because if all the constants but one are known for any of the expressions the remaining one can be calculated. If all of the constants are known, the expressions can be used as a check for self-consistency. In this study, the equilibrium constants were first determined. A knowledge of these values is of importance in estimating maximum free H_2S concentrations likely to be found in equilibrium with liquid sulphur in enclosed systems (e.g. rail tank cars). A sulphur sample was allowed to degas (left to right in expression [1]) while the concentrations of H_2S_x and $H_2S_{(sol)}$ were monitored. This allowed k_1 and k_2 to be calculated and expressions [5] and [6] were used to calculate k_{-1} and k_{-2}. Expression [7] was then used to make sure that all values were internally consistent.

The Method

The data required to obtain rate and equilibrium constants were the concentrations of H_2S_x and $H_2S_{(sol)}$ in liquid sulphur. To obtain the K's the concentrations had to be known for equilibrium situations while for obtaining the k's the concentrations had to be followed over a period of time as a sulphur sample with high total H_2S concentration was degassed.

The tool best suited for obtaining these data is infrared

spectroscopy. The use of liquid sulphur as a solvent for IR was first reported by Wiewiorowski and co-workers in 1965[29]. Shortly thereafter, they described the use of IR in determining the hydrocarbon content of sulphur[30]. In another paper they described the use of IR in an investigation of the sulphur-H_2S system including a break down of the "solubility" of H_2S into its components ($H_2S_{(sol)}$ and H_2S_x) over the temperature range from $125 - 182^\circ C$[31]. All H_2S_x's appear in one peak and are, therefore, indistinguishable in the infrared. Fig. 1 is based on their data.

In this study, the infrared cell used is similar to that described in reference 29 except that a path length of 3 cm was used. This was achieved by replacing the teflon spacer with another aluminum block 3 cm in thickness, machined to accommodate 2 more heaters. The disassembled cell is seen in Fig. 2. Fig. 3 shows the assembled cell and the temperature controller and Fig. 4 shows the cell mounted in a Beckman IR-20 infrared spectrophotometer which was used for recording the spectra used in this investigation. All data were obtained at $125^\circ C$ or $257^\circ F$.

Determination of Equilibrium Constants

K_1 (the ratio of the concentration of H_2S_x to that of $H_2S_{(sol)}$) was taken from the data of Wiewiorowski and Touro (Fig. 1)[31]. Its value at $125^\circ C$ is 0.21 meaning that most of the H_2S content of sulphur at this temperature is present as hydrogen monosulphide. Wiewiorowski's data was obtained under an atmosphere of pure H_2S.

K_2 and K_3 were evaluated from an experiment in which sulphur charged with H_2S was placed in a closed IR cell. The spectrum was run numerous times over a period of 1 week at which time the concentrations of H_2S_x and $H_2S_{(sol)}$ had become constant. The concentration of H_2S in the air space was obtained by calculating the decrease in the total H_2S content in the sulphur and dividing by the volume of the air space. The initial total H_2S concentration of the sulphur was 34.5 ppm and the final value was 26.7 ppm, the volume of sulphur in the cell was 29.5 ml and the volume of the space was 3.7 ml. Therefore, the pressure of H_2S in the air space was 52 mm and the concentration was 7.8% or 78,000 ppm. This is well over the lower explosion limit of 3.36% quoted in reference 3. This supports the contention of reference 4 that the lower explosion limit can be reached with sulphur containing as little as 10 - 15 ppm total H_2S, if adequate ventilation of the system is not provided.

If the values for the concentrations in the liquid and gas phases are left expressed in ppm, one obtains a K_3 of 3.4×10^{-4} at Calgary's atmospheric pressure of 660 mm. Converting the data to moles/litre yields a $K_3 = 0.47$. The large numerical difference arises because of the difference in the densities of the gas and liquid phases. The equilibrium concentration of $H_2S_{(sol)}$ in this experiment was 22.6 ppm and, converting again to moles/litre, K_2 is found to be 0.40. Finding K_2 and K_3 to be less than 1 seems intuitively correct since H_2S is a gas at 125° and one would, therefore expect the gas phase to be favored.

FIG. 1

"SOLUBILITY" OF H_2S IN LIQUID SULPHUR

○ Composite curve — true H_2S solubility and equilibrium amount of H_2S_x

△ H_2S_x in equilibrium with H_2S

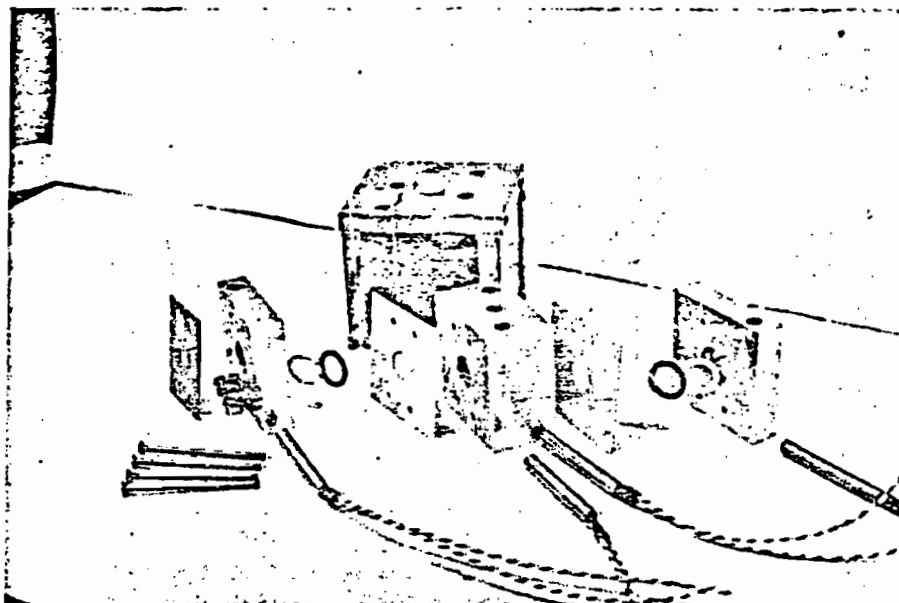✕ true H_2S solubility in S_x

H_2S %

Temp. ^oC ⟶

18.

Fig. 2
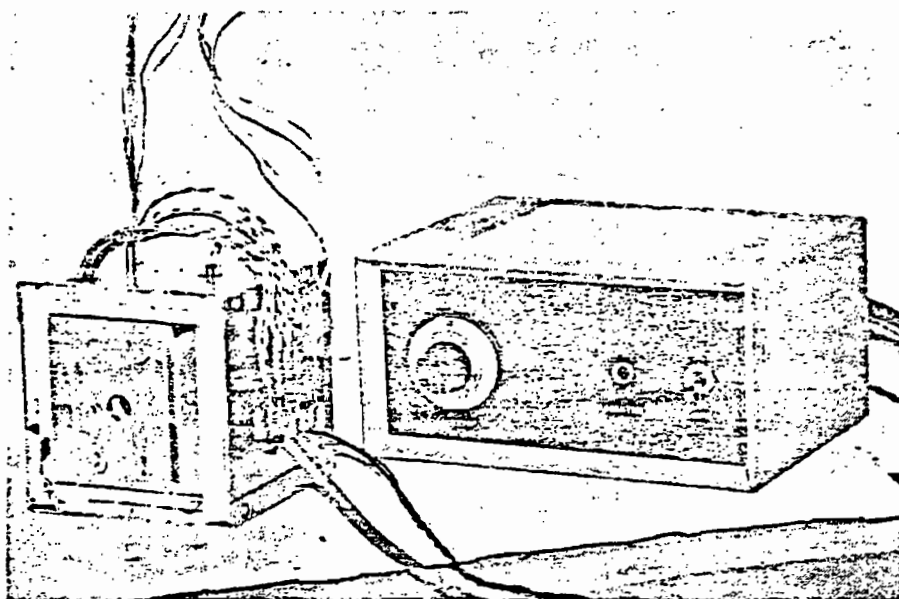

Fig. 3
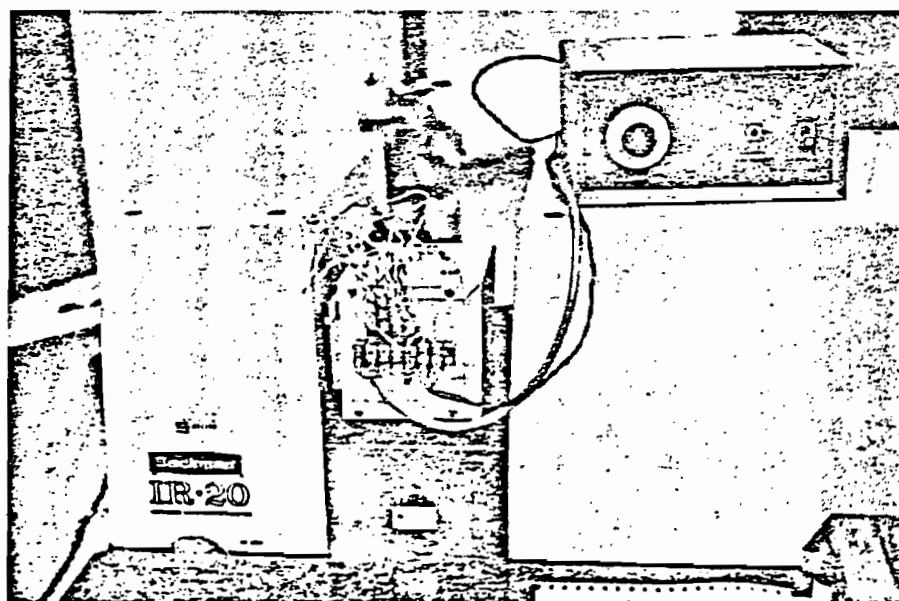

Fig. 4

Determination of Rate Constants

Rate constants were determined from an experiment in which a sulphur sample with high H_2S content was placed in an IR cell open to atmosphere i.e. evolved H_2S was free to escape from the system. The spectrum was run repeatedly until $H_2S_{(sol)}$ and H_2S_x were no longer dectectable in the sulphur. The lower limit of detectability (about 1 ppm) was reached in $4\frac{1}{2}$ days. Fig. 5 shows how the IR spectrum changed as the H_2S was lost from the sulphur. The H_2S peak is at 2570 cm^{-1} and the H_2S_x peak at 2498 cm^{-1}. Although the response for H_2S_x is much greater than that for $H_2S_{(sol)}$ the concentration of $H_2S_{(sol)}$ is actually greater than that of H_2S_x. This arises because the extinction coefficient for H_2S_x is greater than that for $H_2S_{(sol)}$, i.e. H_2S_x absorbs infrared radiation more strongly. Concentrations of both $H_2S_{(sol)}$ and H_2S_x were obtained from spectra such as those shown in Fig. 5 by application of Beers Law. As mentioned previously, H_2S_x cannot be lost from sulphur directly - it must first decompose to produce $H_2S_{(sol)}$. Thus, the rate of decrease of total H_2S concentration $\left[H_2S_t\right] = \left[H_2S_x\right] + \left[H_2S_{(sol)}\right]$) is directly proportional to the concentration of $H_2S_{(sol)}$

i.e.
$$\frac{-d\left[H_2S_t\right]}{dt} = k_2\left[H_2S_{(sol)}\right] \qquad [8]$$

or
$$k_2 = \frac{-d\left[H_2S_t\right]}{dt} \Big/ \left[H_2S_{(sol)}\right] \qquad [9]$$

This holds as long as $\left[H_2S_{(gas)}\right] = 0$ i.e an open system, so that there is no opposing process where H_2S redissolves in the sulphur. In this experiment the system was open allowing the H_2S to diffuse away as it was released from the sulphur and relationhsip [9] was valid. The indicated calculation was performed a number of times throughout two different runs resulting in a value which was essentially constant except for a sharp rise near the end of each run. At this time the concentration of $H_2S_{(sol)}$ became very small and the rate of decrease of $\left[H_2S_t\right]$ became dependent on the rate of decomposition of H_2S_x whose concentration was still relatively high (see Fig. 6). The average value for k_2 obtained from the two runs was 0.035 hr^{-1}. This is a typical first order rate constant containing no concentration units. Since K_2 was known, k_{-2} could be calculated from relationship [6] and was found to be about 0.014 hr^{-1} - another pseudo first order rate constant.

k_1 and k_{-1} could not be obtained in such a direct manner. Since formation and decomposition of H_2S_x are taking place at all times, the observed decrease in the concentration of H_2S_x depends on the difference between the two rates. However, when the concentration of $H_2S_{(sol)}$

FIG. 5

H_2S H_2S_x

2 ppm
135 HR.

70 ppm
61 HR.

164 ppm
24 HR.

398 ppm
1.4 HR.

IR spectra as a function of time showing decrease
in concentration (ppm) of both H_2S (2570 cm^{-1})
and H_2S_x (2498 cm^{-1}).

becomes very small, the rate of re-formation of H_2S_x becomes negligible. We then have:

$$\frac{-d\left[H_2S_x\right]}{dt} = k_1\left[H_2S_x\right] \qquad [10]$$

or

$$\frac{-d\left[H_2S_x\right]}{\left[H_2S_x\right]} = k_1 dt \qquad [11]$$

Integration gives:

$$\ln\left[H_2S_x\right] = k_1 t + c \qquad [12]$$

The concentration of $\left[H_2S_x\right]$ or $\left[H_2S\right]$ can be expressed in terms of Beers Law relationship e.g. $\log I_0/I = \left[H_2S_x\right]$. Therefore, a log log I_0/I plot for each species as a function of time should yield the linear relationship indicated by equation $[12]$. These plots are shown in Fig. 6. Both the H_2S_x and H_2S plots are good linear relationships during the initial degassing period. This is because the ratio of the concentrations of H_2S_x and $H_2S_{(sol)}$ remains fairly constant and the apparent rate of loss of H_2S_x is due to the difference between the rates of formation and decomposition. However, as the degassing proceeds, $H_2S_{(sol)}$ is depleted faster than H_2S_x since there is no H_2S redissolving. Thus, the net rate of loss of H_2S_x increases as shown by the increase in slope and it is the slope of the steep line at the end which was used to calculate k_1. An average value of 0.065 hr^{-1} was obtained. Equation $[5]$ then yielded a value for $k_{-1} = 0.014 \ hr^{-1}$.

At first glance it would appear that k_2 could also be obtained from Fig. 6, since the plot for $H_2S_{(sol)}$ is a fairly straight line. However, the change in concentration depends on the balance between the rate of loss of H_2S from the system, the rate of reaction with sulphur to form H_2S_x and the rate of decomposition of H_2S_x. If k_2 is calculated from the slope of the line in Fig. 6 a value of about 0.014 hr^{-1} is obtained, compared with the value of about 0.035 hr^{-1} found as described above.

In summary, the values found for the various constants are:

$k_1 \approx 0.065 \ hr^{-}$ $\qquad\qquad$ $k_2 \approx 0.035 \ hr^{-}$

$k_{-1} \approx 0.014 \ hr^{-}$ $\qquad\qquad$ $k_{-2} \approx 0.014 \ hr^{-}$

$K_1 \approx 0.21$ $\qquad\qquad$ $K_2 \approx 0.40$

$K_3 \approx 0.47$ $\qquad\qquad$ $K_3 \approx 0.49$ (calc. from eq. $[7]$)

$\qquad\qquad \approx 3.4 \times 10^{-4} \ \dfrac{ppm \ in \ liquid}{ppm \ in \ gas}$

FIG. 6

Change in log log $\left(\frac{I_0}{I}\right)$ during run

H_2S_x

H_2S

log log $\left(\frac{I_0}{I}\right)$

Time (hr.)

23.

The use of approximation signs is intended to indicate
uncertainty of values quoted. Due to the low concentrations of the species
being measured, great accuracy is difficult to achieve. Errors involved in
the IR determinations of $\left[H_2S_{(sol)}\right]$ and $\left[H_2S_x\right]$ may be as great as 3%. This
makes precise rate constants difficult to obtain. The uncertainty for values
for k_1 and k_2 were $\pm$ 15%. K_1 , which was taken from the data of Wiewiorowski
and Touro is probably accurate to within $\pm$ 5%. However, K_2 and K_3,
calculated from their data, are 0.53 and 0.64 respectively, or about 35%
greater than our values of 0.40 and 0.47. This difference could be
explained if H_2S escaped slowly from the closed cell in these experiments.
If so, k_{-2} which was calculated from K_2 would be in error by the same
percentage. The fact that the calculated K_3 differs from the experimentally
determined value by only 4%, however, shows that the rate and equilibrium
constants quoted above are at least self-consistent.

Implications for the Rate of Degassing

This work and other experience point out a number of factors
which affect the rate of loss or removal of the total H_2S content of
sulphur. One very important factor is temperature. Almost all processes
speed up as the temperature is raised and this case is no exception.
In a complex system of coupled forward and reverse reactions such as that
indicated in equation [1] the effect of temperature on all of the rate
constants must be considered before arriving at a conclusion about the
effect of temperature on the overall process. Generally speaking, however,
both the rate of decomposition of H_2S_x and the rate of loss of H_2S from
solution will both increase with temperature. Therefore, provided that
the system is open and the released H_2S can escape higher temperatures
will favour faster degassing of the sulphur as far as H_2S is concerned.
However, at 159°C, the viscosity of sulphur rises sharply as it polymerises.
This rise in viscosity slows down the rate of diffusion within the sulphur
and, consequently, slows down the rate at which H_2S escapes. A high
concentration of H_2S greatly lowers the viscosity of sulphur in this
temperature range, allowing a greater rate of loss than would be expected.
However, as the concentration of H_2S decreases, the viscosity will increase
and the loss of H_2S will become much slower. The time required for sulphur
with 100 ppm total H_2S to approach 0 ppm is about 4 days at 125°C but at
160°C this increases to about 10 days.

Purging with an inert gas, such as nitrogen, also speeds the loss
of H_2S. Our experience in degassing sulphur samples while using nitrogen
sweep indicates that it takes approximately 24 hours to reduce total H_2S
content from 100 to 10 ppm. A recent Japanese patent involves removing
H_2S from sulphur by blowing countercurrently with waste gas[25].

Since the rate controlling step in H_2S degassing of liquid
sulphur is the decomposition of H_2S_x catalysts can greatly reduce degassing
times. Tuller's method for determining total H_2S content of sulphur[27]
and ASR's refinement[28] involve use of a lead sulphide catalyst and purging
with nitrogen to remove all the H_2S from the sulphur. This can be
accomplished in about 1 hour even if the sample initially contains 200 ppm

total H_2S. Ammonia and various amines are also effective catalysts for the decomposition of H_2S_x. The objection to use of a catalyst is that another contaminant is added to the sulphur which may be undesirable in itself (e.g. lead). The possibility of using alumina or spent bauxite, has been suggested by Rennie[23]. A recent British patent[26] employs addition of SO_2, along with an amine, to remove H_2S.

Surface area of the liquid sulphur being degassed is another factor. Although a preliminary examination suggested that the effect might be minimal, one would expect faster loss of H_2S if the sulphur is allowed to stand in a very wide, shallow container. Stirring should also help, presumably by increasing the effective surface area by continually bringing fresh sulphur to the surface. This would prevent establishment of a gradient with low H_2S sulphur at the surface and high H_2S sulphur trapped below. This idea has also resulted in a patent involving liquid sulphur being passed over a series of baffles in a vented tower[24]. However, from 1 to 9 days are required. The effect of purging with an inert gas may also be due to an increase in effective surface area with each bubble representing a fresh surface.

The above considerations all deal with liquid sulphur. Solidification of sulphur results in the immediate loss of about 20 to 30% of the total H_2S content, this being almost exclusively H_2S in solution. Melting of solid sulphur also results in the loss of considerable H_2S (20-50%), the amount depending on the thermal history of the solid. Any H_2S_x trapped in the solid sulphur matrix on solidification will slowly decompose in the solid state to yield H_2S which will be released on remelting. The rate of H_2S decomposition in the solid will be temperature dependent. This, of course, is the reason sulphur remelters and sulphurcrete production areas should have good ventilation.

In the solid state, loss of H_2S becomes extremely slow. Loss of 100 ppm total H_2S content would take years at 70°F and would become even slower at lower temperatures. This is not to say that the processes involved stop - they still take place, but at much slower rates. H_2S_x still decomposes and $H_2S_{(sol)}$ still comes out of solution resulting in H_2S gas. The gas, however, becomes trapped in the crystals matrix unless it happens to be at the surface. All of this implies that the longer a solid sulphur sample is stored, the easier it should be to degas, although temperature of storage is also very important[32].

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THE ASR INFRARED LIQUID SULPHUR ANALYZER
DETERMINATION OF H_2S, H_2S_x & HYDROCARBON CONTENT

by
W.J. Schwalm and J.B. Hyne

INTRODUCTION

Over the last several years, Alberta Sulphur Research has gained considerable experience in the analysis of liquid sulphur. By 1975, it had become obvious to us that Tuller's accepted method for determination of the H_2S content of sulphur [1] often gave results which were too low by 20 - 35%. As a result, a modification of this method was adopted and published in ASR's Quarterly Bulletin [2]. However, the slowness of the method, the skill level required and the fact that it does not distinguish between H_2S and H_2S_x make this "wet chemical" method less than ideal for routine analysis.

The pioneering work of Wiewiorowski and his co-workers [3,4] in the infrared analysis of liquid sulphur has been followed up in ASR's research laboratory. Modifications were made in the length of the heated cell and a custom-made temperature control unit was designed and built. The resulting system has proved very satisfactory for H_2S/H_2S_x analysis both in the lab and in the field and has been described in the Quarterly Bulletin [5] as well as at Chalk Talks presented to member companies of ASR.

The article to follow is a written version of the presentation given at the Chalk Talk on June 25, 1980. It represents an update on the system including recent technical improvements and field experience. In addition, the recent extension of the method to the analysis of liquid sulphur for hydrocarbons is described. This makes the ASR Infrared Analyzer even more valuable, especially in view of the increasing amounts of block sulphur (undoubtedly contaminated over the years) being remelted, reformed and shipped to market.

COMPONENTS

The major components of the system are contained in two boxes about the size of small suitcases, weighing 20 to 30 lbs each (see Figure 1). One box contains the infrared spectrometer, the heated sulphur cell, the temperature control unit and a few minor accessories. The second box contains an external recorder.

The infrared spectrometer is a Wilks Miran 1A-CVF Infrared Analyzer, the centre light-colored component in Figure 2. This is a relatively inexpensive instrument which can, with slight modification, accomodate the rather bulky heated cell. An important feature of this particular spectrometer is that absorbance readings can be obtained directly, eliminating the need for conversion of the results to logarithms. The detector is mounted at the opposite end of the cell and its electrical signals are fed back to the spectrometer.

The heated cell has been shown previously [5] and is the small square metallic box on the left side of the spectrometer in Figure 2. Basically, it is an insulated block of aluminum fitted with rod heaters. An internal cavity 4.5 cm in length and 2.5 cm in diameter contains the sulphur sample. A recent improvement consists of incorporation of a siphon system to facilitate unloading. In many cases, the sulphur drains from the cell as soon as the teflon plug is removed from the outlet. Otherwise, application of pressure by means of a rubber bulb is required. Loading is facilitated by use of a small aluminum funnel.

The temperature controller is custom-made and supplies power to the rod heaters in short pulses. The actual temperature of the cell is sensed by a thermocouple. This signal is fed to the controller which modifies the power supplied to the heaters accordingly. The necessity of good temperature control will be outlined in due course. The controller is the dark rectangular object nestled in the right-hand side of the carrying case in Figure 2.

The second box contains a Deluxe Laboratory Chart Recorder, Single Channel Model, from Linear Instruments. As will be seen later, one of the more important features of this recorder is that a number of attenuations of the signal from the spectrometer are available. A portion of the recorder is seen to the left of the opened carrying case in Figure 2.

The last piece of apparatus is a sampling pot, slightly larger than a two-litre container (see Figure 3). The capacity of the pot is only about 50 ml but it has very thick aluminum walls and a layer of insulation. The heat loss is thus very slow and, once heated electrically, this pot is capable of keeping a sulphur sample in the liquid state for 15 - 30 minutes without further heating. Solidification must be prevented if accurate results are to be obtained for the H_2S and the H_2S_x contents of the liquid sulphur samples. The reason for this will be explained later.

It can be seen, from the above description, that the entire system is very portable. It can easily be carried about in a car and set up in a minimal amount of space (about 4 ft x 2 ft). Analyses can be performed anywhere that 115V AC power is available.

OPERATION

The heated cell reaches the set temperature in about 10 minutes. However, the infrared analyzer and the recorder are allowed to warm up for about 30 minutes before running any spectra. Therefore, just over one half hour elapses before the first spectrum is obtained.
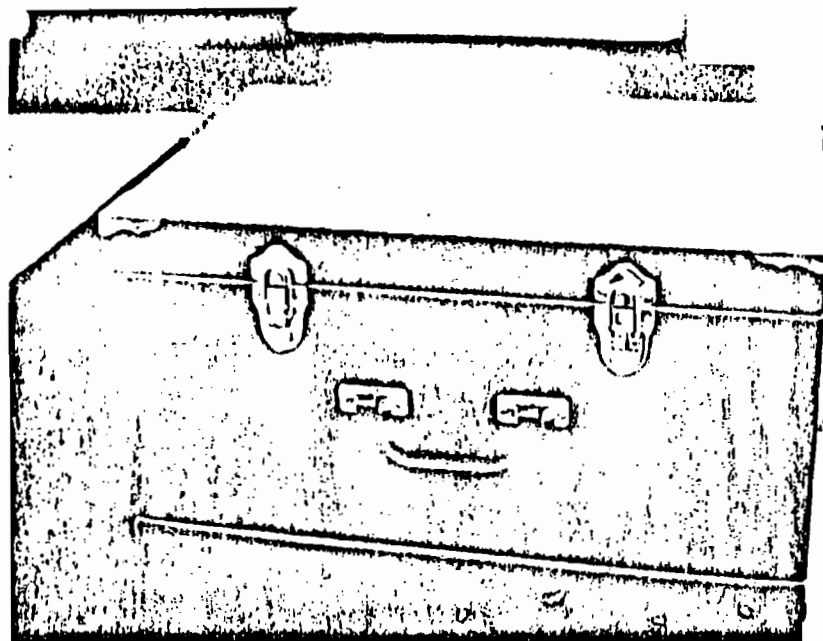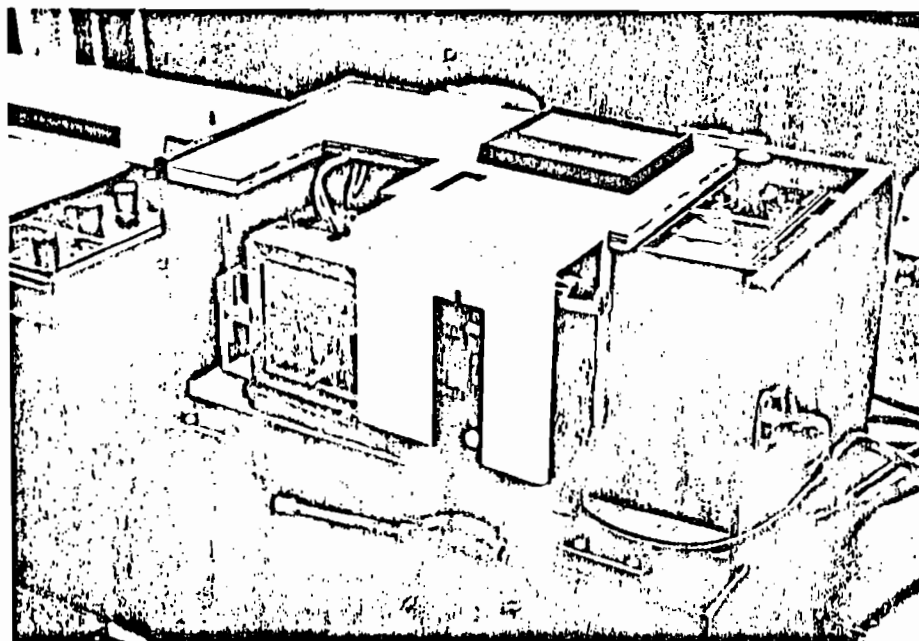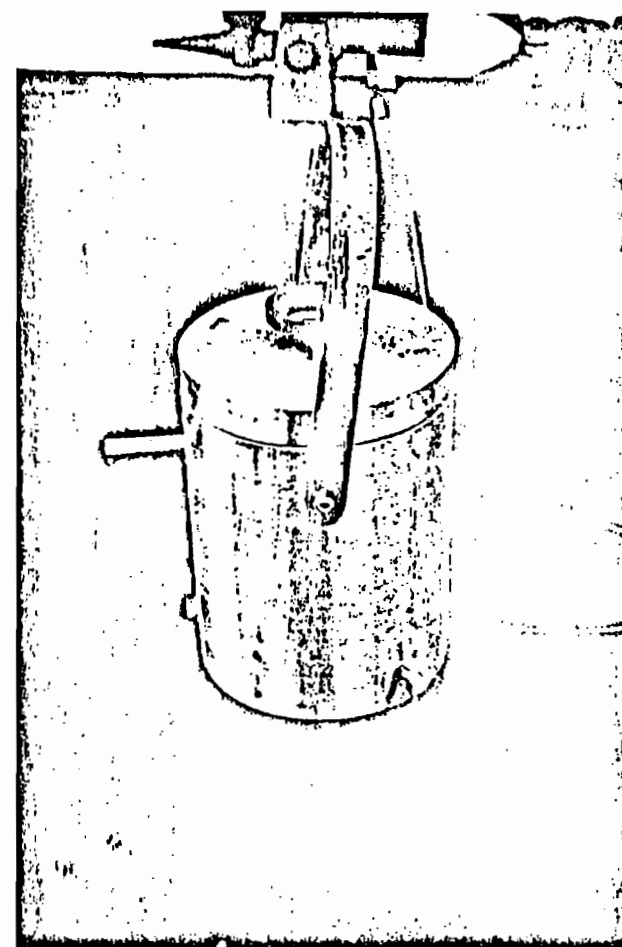
Figure 1

Figure 2

Figure 3

Spectra can now be obtained more quickly than samples can be brought to the instrument from the sampling points in a gas plant. The cell is filled with sulphur from the sampling pot using the aluminum funnel. Appropriate settings are selected for the spectrometer and the recorder and the desired portion of the spectrum is scanned. For H_2S/H_2S_x analysis alone, the region from 3.5 - 4.2 μm (microns) is scanned which takes less than 50 seconds. After unloading the cell using the rubber bulb to force out the last drops of the sample, a new sample can be introduced. The entire procedure takes about 5 minutes per sample.

ANALYSIS FOR H_2S AND H_2S_x

The spectra shown in Figures 4 and 5 were obtained in the field at Alberta sulphur plants. Figure 4 shows the spectra of two samples with very high H_2S/H_2S_x concentrations. In fact, the total H_2S contents of these samples are among the highest ever seen by ASR. Figure 5 shows the spectra of three samples with lower concentrations. Attenuation on the recorder is varied from spectrum to spectrum.

The first four spectra show two peaks each. The peak on the left in each spectrum is at 3.89 microns (2580 cm^{-1}) and is due to H_2S. The peak on the right occurs at 4.00 μm (2498 cm^{-1}) and is due to H_2S_x. This ability to distinguish between the two is one of the great advantages of the infrared method. For a comprehensive discussion of the H_2S-H_2S_x-sulphur system see reference 5.

It may seem rather odd that the peak for H_2S_x is often larger than that for H_2S even though the concentration of the latter is greater. This occurs because the extinction coefficient for H_2S_x is several times greater than for H_2S. In other words, the infrared technique is more sensitive to H_2S_x than to H_2S.

The large size of the H_2S_x peak sometimes makes it rather wide as well as high. This width may affect the separation of the two peaks. In these cases, the H_2S peak becomes a shoulder, rather than a distinct peak but measurement of the H_2S concentration is still possible.

The importance of the attenuation feature of the recorder employed is demonstrated in these spectra. The input factor (I.F.= 2V, 1V or 0.5V) chosen is shown on each spectrum. The readout on the spectrometer is only 0 - 1V. However, the output is 0 - 2.5V and use of the 2V setting on the recorder kept the large H_2S_x peaks of the spectra on Figure 4 on-scale. Had this not been possible, these peaks would have gone off-scale making measurement of the H_2S_x concentrations of the corresponding samples impossible. Only minimum values can be quoted for off-scale peaks.

FIGURE 4

TOTAL – 413 ppm

TOTAL – 405 ppm

H_2S_x
178

H_2S_x
115

I.F. = 2V
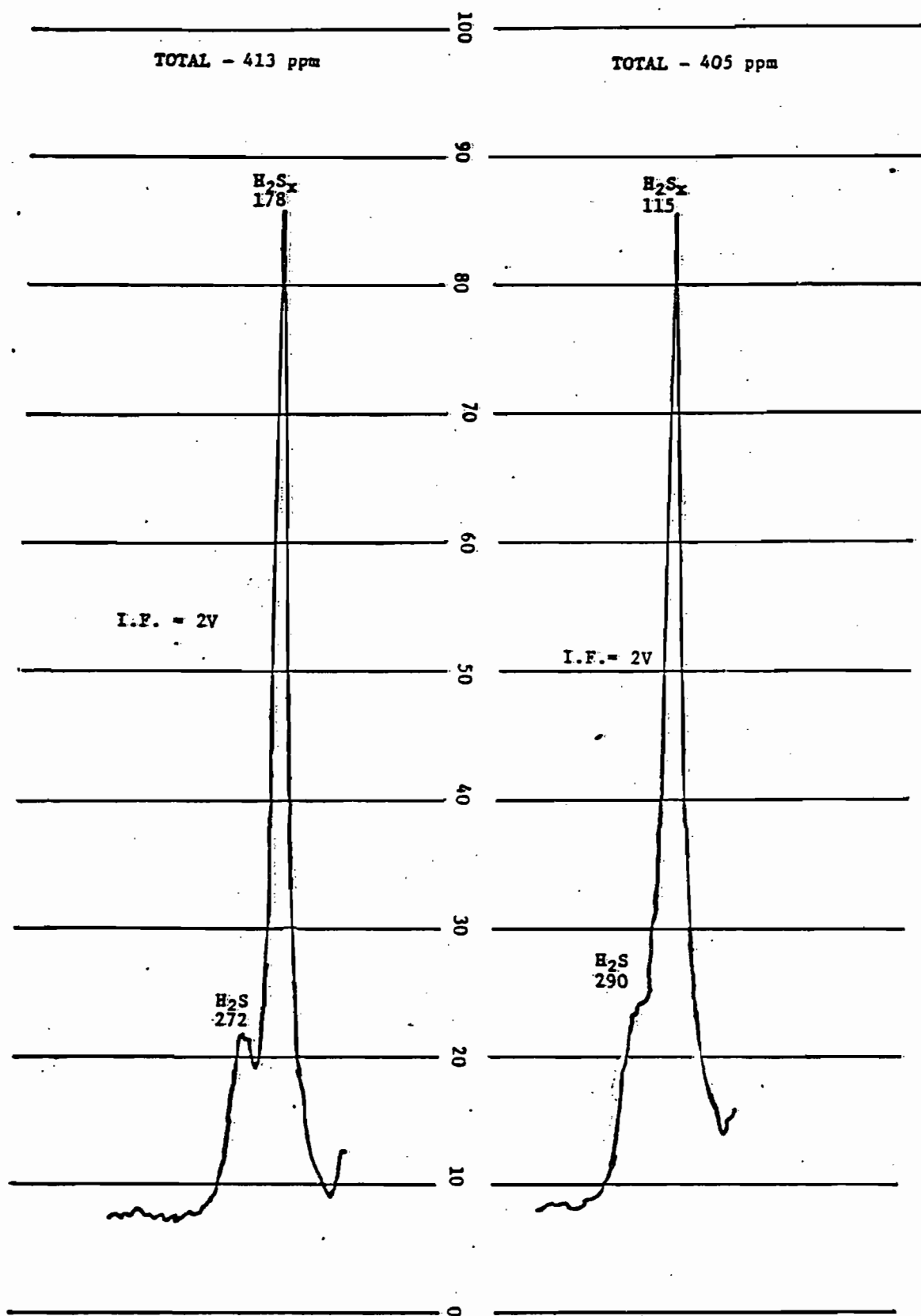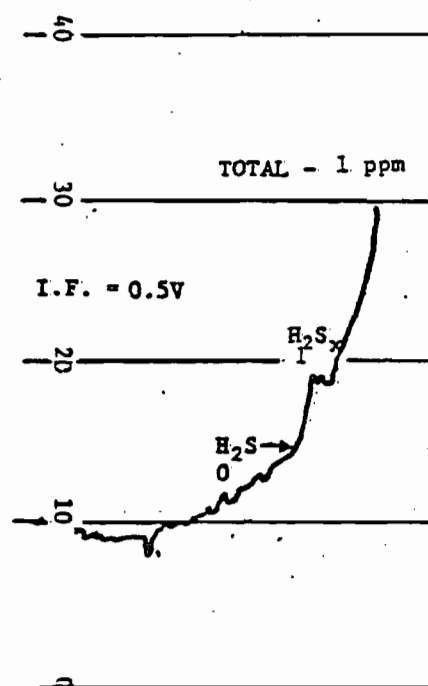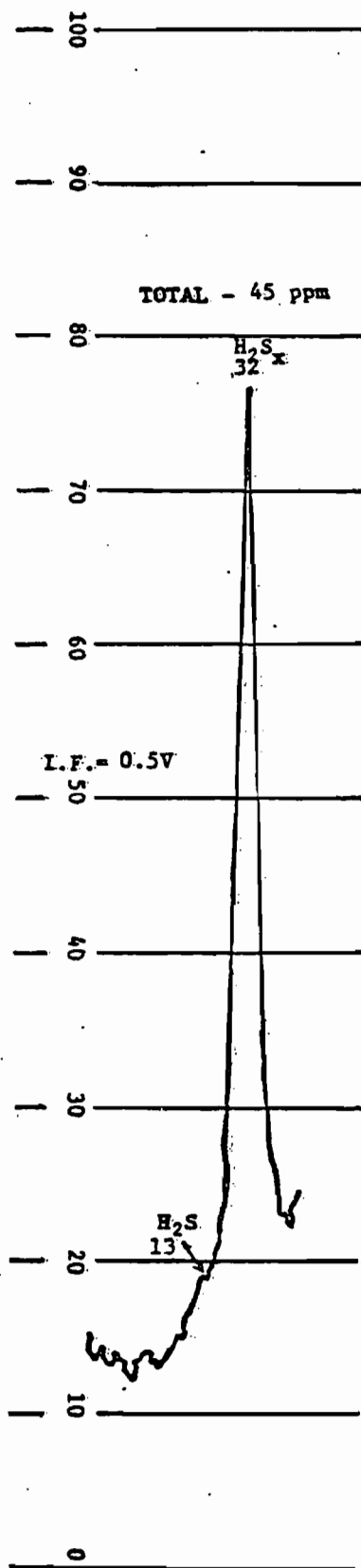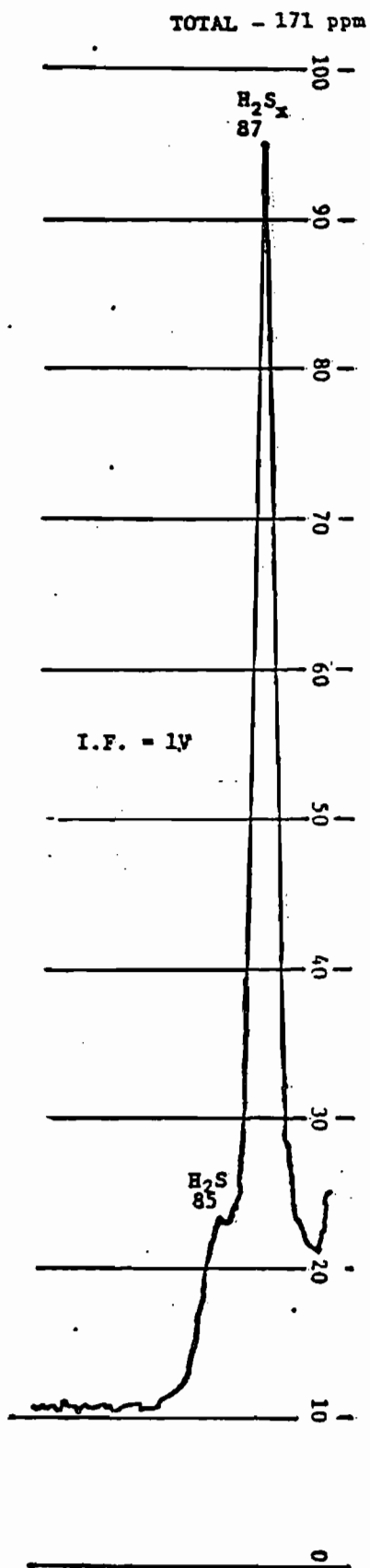
I.F.= 2V

H_2S
272

H_2S
290

FIGURE 5

The first spectrum on Figure 5 was run with an input factor of lV and the last two with 0.5V. By decreasing the attenuation, the peaks are kept as large as possible, thereby increasing the accuracy of the measurements. (Decreasing the input factor below 0.5V usually does not help because electrical noise is also magnified).

The last two spectra on Figure 2 give an idea of the lower limits of detection for H_2S and H_2S_x using the ASR Infrared Analyzer. At 13 ppm, the H_2S peak has almost disappeared, but this is partly due to the width of the H_2S_x peak on this particular spectrum. Normally, one can measure H_2S concentrations down to about 10 ppm. On the last spectrum, the H_2S peak has completely disappeared but the peak due to H_2S_x can still be seen even though it corresponds to only 1 ppm. H_2S_x can be measured down to about 1 ppm in most cases.

Thus we can quote the following values for the range of the ASR Infrared Analyzer, with respect to total H_2S:

Detect to 1 ppm (if in the form of H_2S_x)
Measure quantitatively; 10 - 1300 ppm

This is a very wide range, considering the fact that a constant path length is employed - the entire range can be measured with one cell. Selection of a recorder with a number of attenuation factors has helped to make this wide range possible.

The accuracy of the ASR Infrared Analyzer can be quoted, somewhat conservatively, as:

at 10 ppm - ± 2 ppm (±20%)
at 100 ppm - ± 5 ppm (±5%)
at 1,000 ppm - ± 20 ppm (±2%)

In practice, the accuracy is usually better than indicated. Considering the speed of the method and the low concentrations being measured (100 ppm is only 0.01%), these levels of accuracy are very good. As would be expected, accuracy becomes relatively better at higher concentrations.

The calculations involved are very simple, which is another advantage of this particular system. As pointed out before, the infrared instrument incorporated in this package can give absorbance values directly, eliminating the need for logarithmic conversions. In addition, absorbance (i.e. peak height) is directly proportional to concentration over the entire concentration range. Therefore, one needs only to multiply peak height by a pre-determined calibration factor. One such factor is obtained for H_2S, and another for H_2S_x, by scanning the infrared spectrum of a liquid sulphur sample saturated with H_2S and H_2S_x. Saturation is achieved by bubbling in H_2S for at least 24 hours under an atmosphere of H_2S.

PLANT MONITORING

The ASR Infrared Analyzer has thus far (September 1980), been used to measure the H_2S content of sulphur at seven Alberta plants. One of these plants has an analyzer permanently on-site. Figure 6 shows some of the results obtained.

One of the most obvious features in these results is the decrease in H_2S and H_2S_x content in the sulphur samples as one progresses through each plant. This is, of course, due to the fact that H_2S is removed from the gas stream at each stage in the plant. As the H_2S content decreases in the gas phase in contact with the liquid sulphur being formed, the H_2S and H_2S_x levels in that sulphur decrease. Thus, sulphur from the front end furnace has the highest total H_2S content in a given plant and that from the last condenser, the lowest.

The "Sulphur to Slater" and "Fresh Slate" analyses on Figure 6 (Plant 1) show the importance of keeping liquid sulphur samples from solidifying before analysis for H_2S and H_2S_x. This is why the heated, insulated sampling pot is needed. On solidification, there is an immediate loss of at least 20% of the total H_2S content. In fact, if the H_2S content of the sulphur is high enough, bubbles of H_2S can be seen escaping from the sulphur during the solidification process. Because of the equilibrium between H_2S and H_2S_x, however, the the loss shows up as a loss in H_2S_x due to displacement of the equilibrium i.e.

$$H_2S_x \longrightarrow H_2S \uparrow + S_{x-1}$$
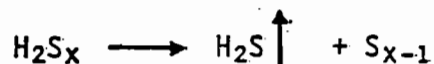
Thus, allowing sulphur to solidify, then remelting it for analysis will result in a measured total H_2S level which is too low. For this reason, in-plant analyses are to be greatly preferred over delivering solidified samples to a lab for analysis. As a consequence, a portable package, such as the ASR Infrared Analyzer, is not only desirable, but necessary. It should be pointed out that it is total H_2S and H_2S_x which decrease with phase changes. The amount of H_2S may increase (as in the Plant 1 example) if the amount of H_2S lost to the gas phase is outweighed by the amount of H_2S_x decomposing to reform H_2S.

The sample from the remelter at Plant 1 shows no detectable H_2S but 6 ppm of H_2S_x. Degassing is greatly slowed, but not stopped when sulphur is solidified. H_2S_x continues to decompose and H_2S is lost, although much of it is trapped in the spaces between the crystals. When the sulphur is remelted, the trapped H_2S is lost but the remaining H_2S_x can still be measured. This confirms ASR's experience with degassing - the H_2S is easy to remove but getting rid of the H_2S_x is very difficult. Removal of H_2S can be achieved by merely purging

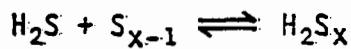## Figure 6

ACTUAL PLANT ANALYSES (ppm)

Plant 1	H₂S	H₂Sₓ	TOTAL
1st CONDENSER RUNDOWN	82.6	127	210
2nd CONDENSER RUNDOWN	20	52	72
3rd CONDENSER RUNDOWN	8	11	19
SULPHUR TO SLATER	23	53	76
FRESH SLATE	25	35	60
SULPHUR FROM REMELTER	--	6	6

Plant 2			
W.H.B. RUNDOWN	200	132	332
CONVERTER #1 RUNDOWN	50	57.2	107
CONVERTER #2 RUNDOWN	8	19	27
RUNDOWN PIT	72	69.4	141

with an inert gas, but removal of the H_2S_x requires a catalyst to aid in its decomposition. The sulphur from the rundown pit of Plant 2 (Figure 6) could easily be reduced to about 70 ppm but further degassing, in the absence of a catalyst, could take days. Reference 5 contains a much more complete discussion of the topic of degassing. The ASR Infrared Analyzer is obviously useful for monitoring a degassing process.

The real value of H_2S/H_2S_x analysis in the plant is not so much in the values obtained at a given time but in <u>changes</u> detected by regular monitoring at various points in the plant. Changes in the H_2S and/or H_2S_x levels may be the first indication of changes occurring in the plant. In particular, a change in temperature and/or conversion efficiency should be accompanied by a change in the $H_2S_x:H_2S$ ratio of the sulphur produced. This application is presently being examined.

Figure 7 shows the saturation levels of H_2S and H_2S_x in sulphur as a function of temperature. The true solubility behaviour of free H_2S in sulphur is that of a normal gas-liquid system since there is a slight decrease in solubility with increasing temperature as indicated by the line labelled "H_2S". However, matters are complicated by the reaction of H_2S with sulphur to form H_2S_x. The effect of temperature on this process is twofold.
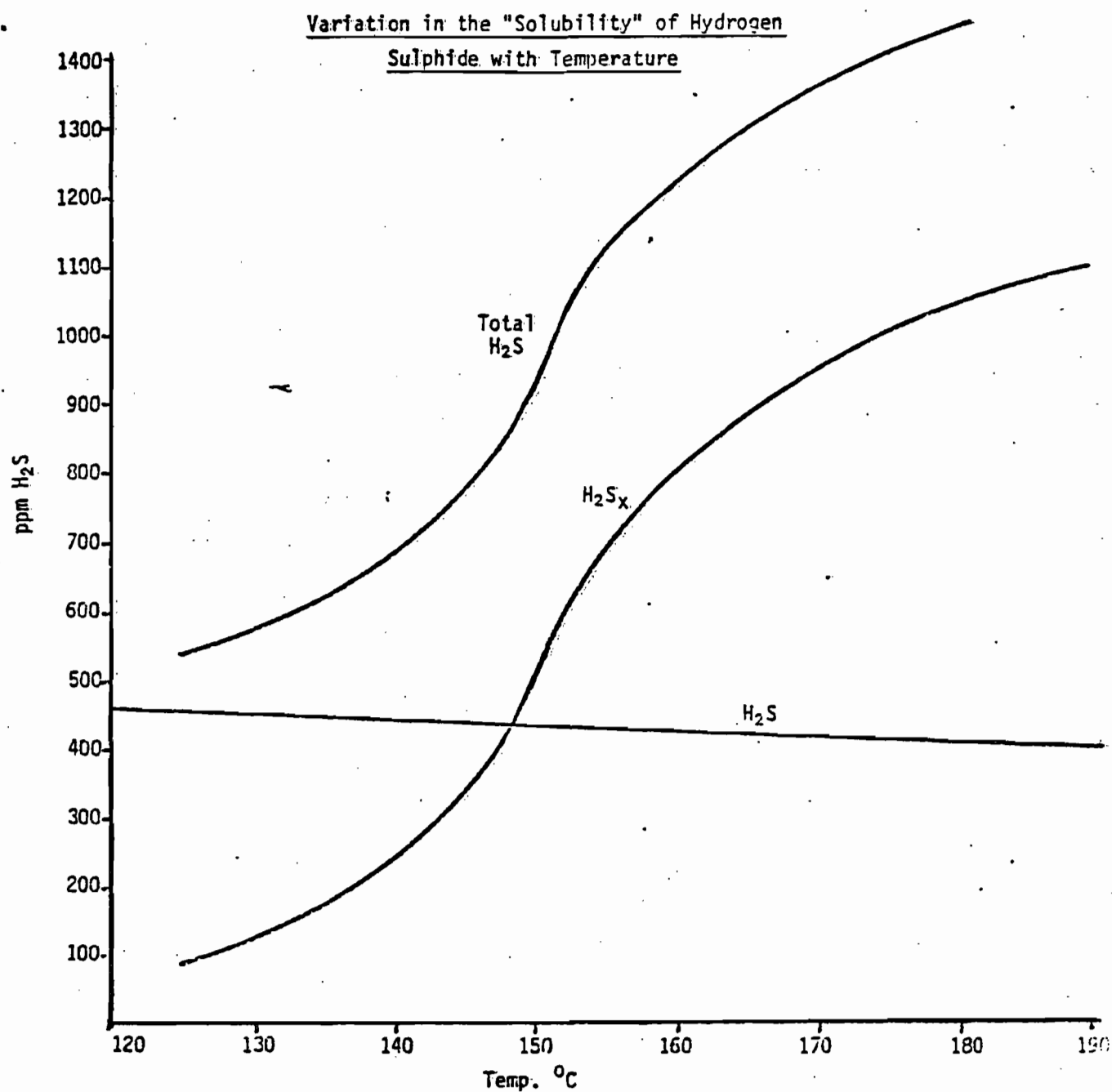
$$H_2S + S_{x-1} \rightleftharpoons H_2S_x$$

$$\xrightarrow{\hspace{2cm}}$$
formation

Firstly, H_2S_x formation occurs at a greater rate at higher temperature. Secondly, at higher temperature, equilibrium favors a greater concentration of H_2S_x as shown by the "H_2S_x" curve on Figure 7. An increase in temperature, therefore, favors a higher $H_2S_x:H_2S$ ratio. The fact that this ratio changes with temperature is the most important reason for provision of good temperature control for the cell. It should be noted that Figure 7 is based on data obtained at a normal sea-level atmospheric pressure. The lower pressures encountered at the altitudes of Alberta sulphur plants would result in a lowering of both the "H_2S" and the "H_2S_x" curves but the ratio should remain unchanged.

In view of the above, an increase in the $H_2S_x:H_2S$ ratio at a certain point in a sulphur plant would likely indicate that the temperature has increased or that the H_2S content of the gas stream has increased at that point. It should be pointed out that the data of Figure 7 represent equilibrium situations, whereas samples taken from the various rundowns in a sulphur plant would not have had time to reach equilibrium. Despite this, any increase in temperature

Figure 7

Variation in the "Solubility" of Hydrogen
Sulphide with Temperature

Data Taken from T. K. Wiewiorowski and F. J. Touro,
J. Phys. Chem., 70, 234 (1966)

should still result in an increase in the $H_2S_x:H_2S$ ratio (i.e. any change would be in the direction indicated by the equilibrium data).

The analyses of samples from Plant 2 (Figure 6) can be used to illustrate one further point regarding sulphur plant monitoring. If the rundown pit contains only fresh sulphur which has not had a chance to equilibrate and degas, analysis of the various rundowns being collected and of the sulphur in the pit may make possible an estimation (or confirmation) of the amounts of sulphur coming from these various sources. If all points are sampled at about the same time, the weighted averages of both the H_2S and H_2S_x contents of the various sulphur sources should be close to the H_2S and H_2S_x concentrations of the sulphur in the rundown pit.

HYDROCARBON CONTENT

Thus far the discussion has dealt exclusively with H_2S and H_2S_x determinations. However, with no modifications whatsoever, the hydrocarbon content of liquid sulphur can also be determined using techniques previously described by Wiewiorowski and co-workers.

This information is important for two basic reasons. Sulphur, to meet export specifications, must contain no more than 250 ppm of hydrocarbons. Figure 8 shows the spectrum of a sulphur sample containing 242 ppm of an aliphatic hydrocarbon mixture. This spectrum was run using the 5V input factor of the recorder which is the least sensitive setting for this recorder. The fact that the recorder had to be attenuated so much shows that the extinction coefficient for hydrocarbons is even larger than that for H_2S. However, even with the long path length of the heated sulphur cell, the peak height was only 2.3 absorbance units. Thus, the upper specification limit for hydrocarbons is just within the maximum range of the instrument (0 - 2.5 volts which corresponds to 0 - 2.5 absorbancs units).

The second major reason for analyzing sulphur hydrocarbon content is the reaction between liquid sulphur and hydrocarbons:
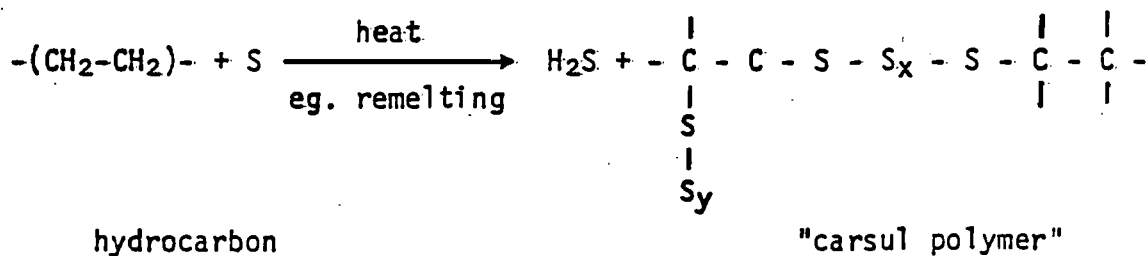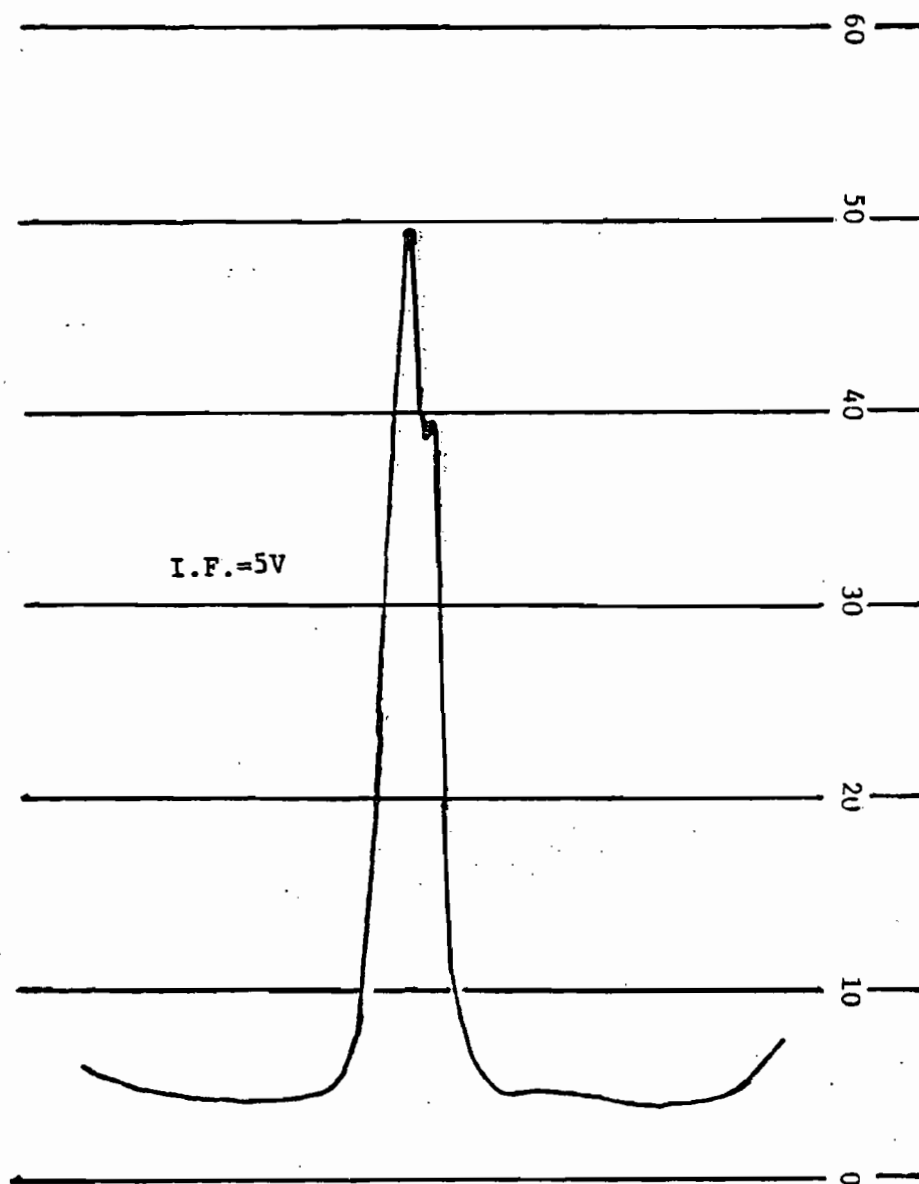
$$-(CH_2-CH_2)- + S \xrightarrow[\text{eg. remelting}]{\text{heat}} H_2S + -\overset{\displaystyle |}{\underset{\displaystyle \underset{\textstyle S_y}{\overset{|}{\underset{|}{S}}}}{C}} - C - S - S_x - S - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} -$$

hydrocarbon   "carsul polymer"

FIGURE 8

EXPORT SPECIFICATION

MAXIMUM HYDROCARBON CONTENT = 250 ppm

HYDROCARBON CONTENT OF THIS SAMPLE = 242 ppm

I.F.=5V

Although the reaction has been illustrated for an aliphatic hydrocarbon, aromatic hydrocarbons also react. In the early stages of the reaction, only a few of the hydrogen atoms are replaced by sulphur chains. However, as the reaction continues, more hydrogens are replaced until a high molecular weight polymer consisting largely of carbon and sulphur atoms is formed. This "carsul" is a typical polymer in having high viscosity and it can cause problems in handling and forming sulphur. Of course, the higher the concentration of hydrocarbons at the start, the more "carsul" can be formed. The reaction is a fairly slow one and can be minimized by keeping the temperature of the liquid sulphur as low as possible and keeping the sulphur in the liquid state for as short a time as possible. Removal of dissolved hydrocarbons from sulphur, unfortunately, is very difficult, requiring boiling it over magnesium oxide for many hours [6] or contacting it with sulphuric acid [7].

The hydrogen removed from the hydrocarbon combines with sulphur to produce H_2S and H_2S_x. This slow production of H_2S can influence analyses for H_2S and H_2S_x, especially if the sulphur is in an enclosed space (such as a rail car) where significant loss of H_2S to atmosphere cannot take place. Since the atomic weight of sulphur is 32 and that of carbon is only 12, conversion of 100 ppm of aliphatic hydrocarbon to carsul and H_2S could give rise to a theoretical increase of over 250 ppm in total H_2S content. Aromatic hydrocarbons should cause less problems than aliphatics, partly because the reaction should be slower and partly because aromatics contain proportionately less hydrogen which would mean a lower production of H_2S.

An additional problem caused by the reaction of hydrocarbons with sulphur is the resulting discoloration of the sulphur. The color of the sulphur becomes brown and, under extreme conditions, a black color may result. In fact, this color change can be used for a qualitative evaluation of the hydrocarbon content of sulphur. If a sulphur sample containing hydrocarbon is heated to $210^{\circ}C$ for two hours the color of the solid on resolidification gives a rough idea of the hydrocarbon content. However, the length of time required and the non-quantitative nature of the results obtained make this method very unsatisfactory.

Four oxidation and heat-treatment methods are available [8] for determination of the hydrocarbon content of sulphur. Unfortunately, all share the disadvantage of lengthy procedures requiring considerable operator skill.

ANALYSIS FOR HYDROCARBON, H_2S AND H_2S_x

The ASR Infrared Analyzer can be used, without modification, to obtain hydrocarbon concentrations as well as H_2S/H_2S_x contents of liquid sulphur samples. Only one very minor change in procedure is

required - the spectrum is run from 3.0 to 4.2 μm to obtain both hydrocarbon and H_2S/H_2S_x analyses whereas for H_2S/H_2S_x alone the narrower range from 3.5 to 4.2 μm is scanned. This adds less than one minute to the time required.

Figure 9 shows the spectrum of a sulphur sample over the wider range. It is obvious that the response of the instrument to aliphatic hydrocarbons is much stronger than even the response to H_2S_x. The extinction coefficient for aromatic hydrocarbons is about the same as for H_2S_x. Because of the differences in response factors and because the hydrocarbon and H_2S/H_2S_x contents are normally independent of each other, it will often prove desirable to change attenuations between the aliphatic hydrocarbon peak and the H_2S peak. One half of the spectrum may require higher attenuation (a higher input factor) to keep the peak(s) on-scale whereas lower attenuation is desirable for the other half of the spectrum for greater accuracy.

The shoulder on the side of the aliphatic hydrocarbons peak is typical - all aliphatics show two peaks in this region, a strong peak at about 3.4 μm and a somewhat weaker peak at about 3.5 μm. Only the larger of the two peaks is used in calibrations and in the determination of concentrations. Usually, only one peak at about 3.25 μm is seen for aromatic hydrocarbons.

There is a major difference between the calculations for H_2S/H_2S_x content and those for aliphatic hydrocarbon content. The response of an infrared instrument to aliphatic hydrocarbons is not related to concentration in a linear manner as it is for H_2S and H_2S_x. Therefore a single calibration factor cannot be determined for aliphatics content. A calibration curve, such as that shown in Figure 10 must be used. The curve is obtained by plotting the absorbances of several samples of known hydrocarbon content. This curve will then give the hydrocarbon concentration of an unknown sample once its absorbance has been determined (provided that its concentration is within the range of concentrations covered by the calibration curve).

If the identities of the hydrocarbons in the sulphur to be analyzed are known, these should be used in the calibration. Most sulphur samples, unfortunately, contain complex mixtures of hydrocarbons. Thus, it is preferrable to use a typical aliphatic hydrocarbon (or a mixture of aliphatics) to calibrate the instrument for aliphatic hydro- carbons and an aromatic hydrocarbon (or a mixture) to calibrate for aromatics. We have found Nujol (a complex mixture of high molecular weight aliphatics commonly used in infrared work) to be satisfactory for calibration in the aliphatic region although Tuller [9] has recommended decahydronaphthalene. He recommends naphthalene for the aromatic region.
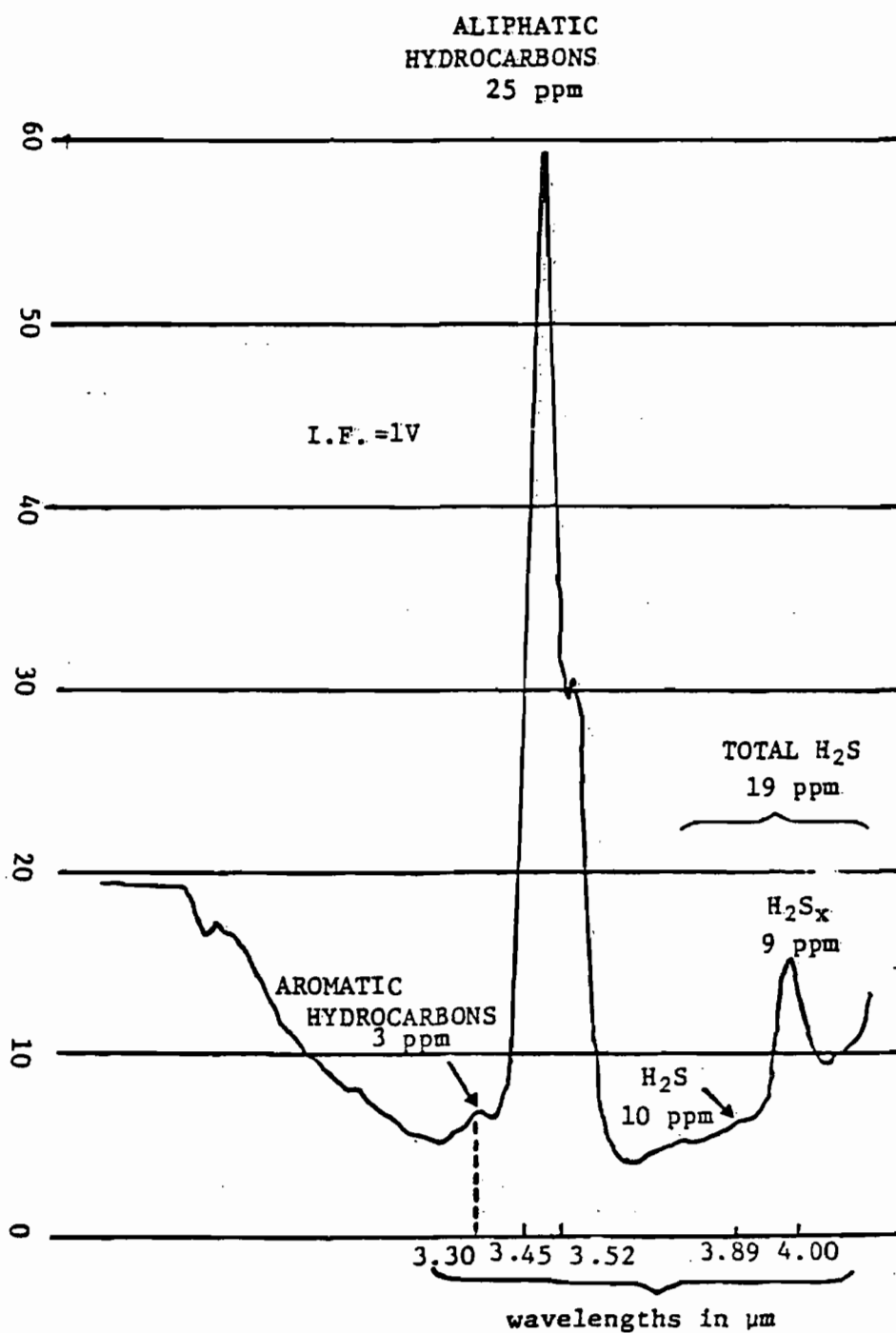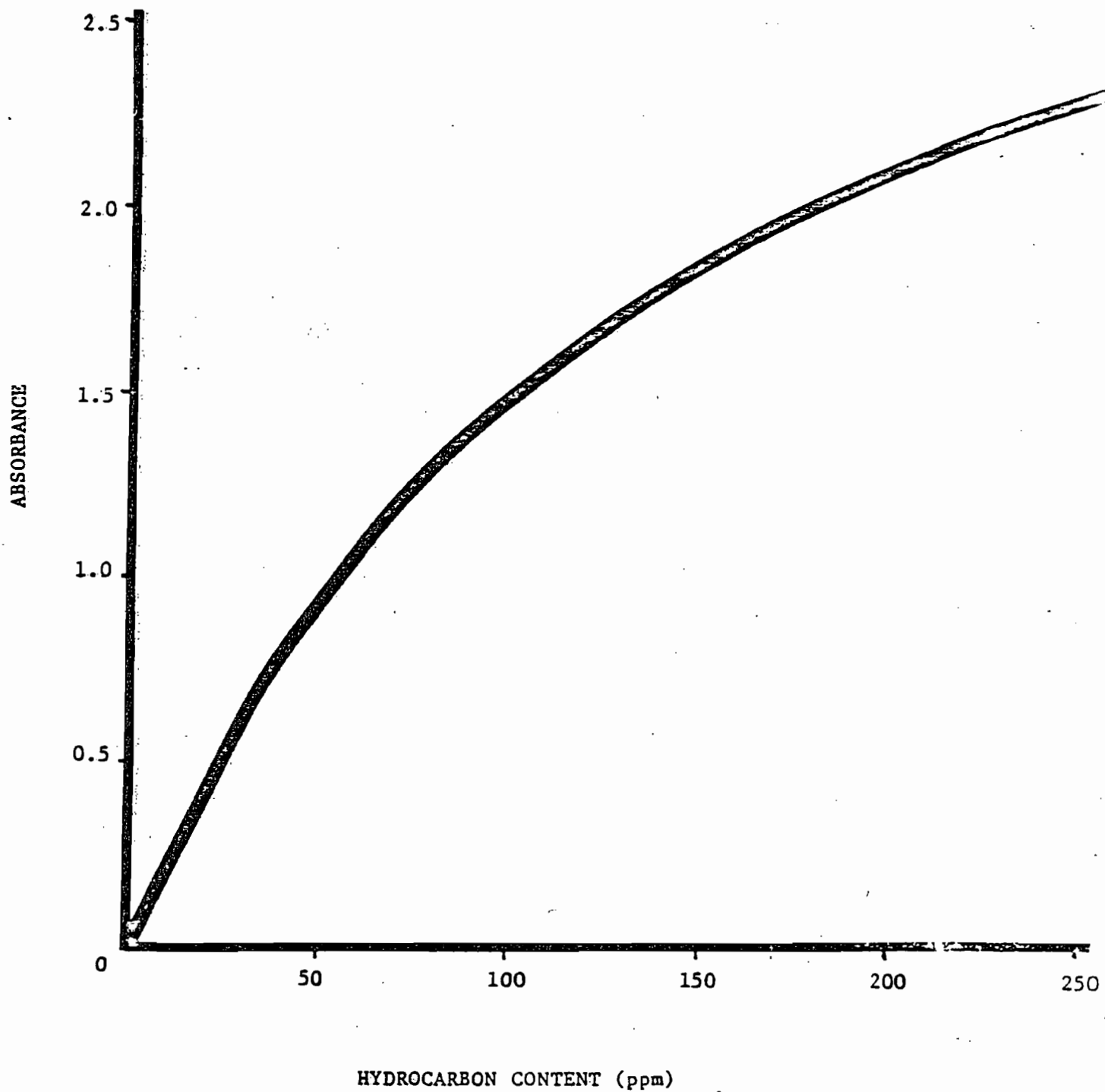
FIGURE 9

H_2S AND HYDROCARBON CONTENT

ALIPHATIC
HYDROCARBONS
25 ppm

I.F. =1V

TOTAL H_2S
19 ppm

H_2S_x
9 ppm

AROMATIC
HYDROCARBONS
3 ppm

H_2S
10 ppm

3.30 3.45 3.52   3.89 4.00

wavelengths in µm

Figure 10

HYDROCARBON CONTENT CALIBRATION CURVE

HYDROCARBON CONTENT (ppm)

As far as aliphatic hydrocarbons are concerned, the capabilities of the ASR Infrared Analyzer can be quoted as follows:

Detect down to 0.5 ppm or lower
Measure quantitatively; 1 - 300 ppm with same cell
Accuracy - at   1 ppm - ±0.5 ppm
          at   50 ppm - ±2 ppm
          at 250 ppm - ±5 ppm

The range of the instrumental package has not been well-defined as yet. The lower end of the range will probably not be checked because it is very difficult to remove hydrocarbons from sulphur. A sample boiled over magnesium oxide for more than 30 hours (Bacon and Fanelli's method [6]) was still found to contain more than 2 ppm of aliphatic hydrocarbon. The upper limit may be only slightly higher than 300 ppm since the maximum output of the infrared instrument utilized is only 2.5V. Extrapolation of the calibration curve (Figure 7) would indicate that this limit of 2.5V or 2.5 absorbance units would be reached at 310 ppm. Sulphur samples of higher aliphatic content could still be measured if they were diluted with known amounts of sulphur containing low, known levels of aliphatic hydrocarbon.

The accuracies quoted are again conservative estimates. The accuracy with which aliphatic concentrations can be measured is better than that with which aromatics, H_2S and H_2S_x concentrations can be measured because of the greater extinction coefficient for aliphatics. Aromatics can be measured about as accurately as H_2S_x. Again, considering the low concentrations being measured and the speed with which analyses can be performed, the accuracy is very good.

Because the extinction coefficient for aromatics is two to three times smaller than that for aliphatics, the range quoted should be correspondingly larger. Unfortunately, the errors in concentration measurements will also be correspondingly larger. However, it appears that the concentrations of aromatic hydrocarbons in Alberta sulphur are normally very low (less than 10 ppm). Since aliphatic hydrocarbons are present in larger quantities, measurement of their concentrations is more important.

SUMMARY OF CAPABILITY OF THE ASR INFRARED ANALYZER

1) Measurements of the H_2S and H_2S_x contents of liquid sulphur are easily and quickly done. These measurements are important for a number or reasons. The release of H_2S into the gas phase in closed or poorly ventilated spaces can easily give rise to toxic atmospheres. In a closed rail car explosive gas mixtures could arise. Of course, the higher the levels of H_2S and H_2S_x in the liquid sulphur, the higher the level of H_2S in the gas phase. Degassing procedures are being implemented in some gas plants and the system described would be ideal for monitoring such procedures. In addition, regular measurement of the total H_2S levels

and the H_2S/H_2S_x ratios at various points in a gas plant could provide useful information on the performance of the relevant components of the plant. H_2S is also known to affect the physical properties of sulphur, especially the strength of the solid [10] and the viscosity of the liquid [11, 13].

2) With no modifications to the equipment and without a major increase in analysis time, hydrocarbon levels can also be determined. The export specification for sulphur is a maximum of 250 ppm of hydrocarbon. The reaction between hydrocarbons and sulphur to form the "carsul" polymer plus more H_2S makes knowledge of the hydrocarbon level of sulphur still more desirable. As more block sulphur is remelted, after several years of exposure to possible contamination, a fast and accurate determination of its hydrocarbon content will become more and more valuable.

Calibrations must be done from time to time as the instrumental response can change. The method is not absolute and reference to one or more standards is, therefore, required. Measurement of very low levels of H_2S is not possible due to the low extinction coefficient of H_2S in the infrared. These levels, however, are of little concern at this time.

The advantages to use of the ASR Infrared Analyzer easily outweigh the disadvantages mentioned above. This package is a compact, highly portable system ideal for routine analyses of liquid sulphur for H_2S, and H_2S_x and both aromatic and aliphatic hydrocarbon concentrations. Results are obtained quickly and easily and a high degree of accuracy is the norm.

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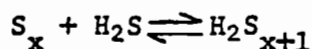
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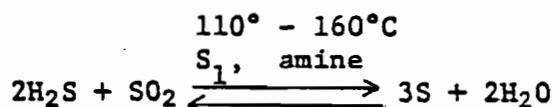# The Removal of H₂S "dissolved" in Liquid Sulphur

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Introduction

Elemental sulphur produced by the Claus Process from sour natural gas always contains some dissolved hydrogen sulphide. The hot, liquid sulphur stream is in contact with a gaseous phase containing hydrogen sulphide resulting in dissolution of the hydrogen sulphide in the sulphur. This in itself would not be a serious problem if the dissolution was the only absorption process. However the hydrogen sulphide also combines chemically with the sulphur to form hydrogen polysulphides.

$$S_x + H_2S \rightleftharpoons H_2S_{x+1}$$

The problems associated with hydrogen polysulphides in the production of sour gas wells have long been recognised (1), and the above equilibrium reaction has been extensively studied (2, 3, 4). If hydrogen sulphide was merely dissolved in the sulphur, it could be readily stripped from the sulphur by an inert gas stream, such as nitrogen or even air. Also on first sight one would expect, as hydrogen sulphide is removed from the sulphur in an inert gas stream, the above equilibrium would be driven to the right, resulting in the breakdown of hydrogen polysulphides with the subsequent release of more hydrogen sulphide. This is in fact true, as has been demonstrated by Wiewiorowski (3) but the rate of the reaction is not instantaneous and extremely long purge times would be required. This explains why hydrogen sulphide release is not a serious problem at the plant in the area of the liquid sulphur storage pits, although an odour of H₂S is generally obvious in this area. Where sulphur is transported as a liquid in tank cars however, sufficient hydrogen sulphide may have been degassed by the time the shipment reaches its destination to present a definite hazard to personnel involved in the unloading operations if the prescribed safety procedures are not observed. There are potentially increasing markets for liquid sulphur, but it is probable that both customers and governmental agencies will regulate the allowed amount of hydrogen sulphide in the head space of liquid sulphur tank cars. It is therefore important to do something about the problem if these markets are to be taken advantage of and to ensure the retention of present markets for liquid elemental sulphur. The industry is aware of these problems and has been successful in some instances in removing the hydrogen sulphide from the liquid sulphur during the loading operation. For example one such method is to carry out a Claus reaction in liquid sulphur (5). Nitrogen containing compounds such as amines are known to catalyse the reaction between hydrogen sulphide and sulphur dioxide in liquid sulphur.

$$110° - 160°C$$
$$2H_2S + SO_2 \xrightleftharpoons[]{S_1, \quad amine} 3S + 2H_2O$$

The removal of all the hydrogen sulphide from elemental sulphur produced by the Claus Process is likely to become more important as new uses are found for sulphur. In particular, it would obviously be undesirable to have seepage of hydrogen sulphide from such materials as sulphur concretes and ashphalts. The decomposition of the hydrogen polysulphides would be very slow in the solid state and the hydrogen sulphide released would be largely trapped in the solid matrix and released slowly to the atmosphere. Also it would be advantageous to remove the hydrogen sulphide from the sulphur prior to the slating operation as hydrogen sulphide is known to reduce the strength of elemental sulphur (6).

The purpose of this research project is to develop a cheap, efficient method for the removal of hydrogen sulphide from liquid sulphur as it is produced at the plant. As was mentioned earlier one method used at the present time is to add an organic base to the sulphur to promote decomposition of the hydrogen polysulphides and also to act as a catalyst for reaction between the liberated hydrogen sulphide and sulphur dioxide which is added to the system. This procedure does not remove all the hydrogen sulphide and adds another contaminant, namely the organic base which can adversely effect strength of solid sulphur (7). The approach used in the work reported here is to replace the organic base with an inert basic material which will not dissolve in or chemically react with the sulphur.

Experimental Results

In any examination of the efficiency of various techniques for the removal of H_2S from liquid sulphur it is essential that an effective and reliable analytical technique be available for determining the H_2S content before and after treatment.

Molten sulphur at 140°C is saturated with hydrogen sulphide. A sample of this sulphur (100 – 200 g) is then analysed for hydrogen sulphide content by the procedure outlined below which is based on a published method (8). A sample of this sulphur (∿250 g) is also added to a heated vessel (160°C) containing 40 g of the catalyst to be tested. (Approximate depth of catalyst bed 1" and height of sulphur column 4"). The sulphur is allowed to stand over the catalyst with occasional agitation for 10 minutes. The sulphur (∿200 g) is then transferred to a heated (140°C) pre-weighed purge vessel containing 2 g of lead sulphide to catalyse the release of the remaining hydrogen sulphide. The system is purged 2 hours with nitrogen, the off gases being passed through two traps containing 100 mls of 3% zinc acetate solution in each trap.

After 2 hours the absorption flasks are removed from the system and the contents transferred to a 500 ml Erlenmeyer flask. The flask is then cooled in an icebath to below 10°C. Formaldehyde solution (5 mls) and 10% acetic acid (20 mls) are added to prevent any sulphur dioxide present consuming iodine. Maintaining the temperature below 10°C, 0.1N standard iodine is pipetted into the solution until a deep iodine colour persists after allowing the solution to stand for 5 minutes. (Usually 20 mls of 0.1N iodine is sufficient). Maintaining the temperature below 10°C, the solution is titrated with a standard thio-sulphate solution (0.1N) using a starch solution as indicator.

A blank determination is carried out on the reagents.

Calculations

$$\% \ H_2S = \frac{1.7N}{W} \frac{(\nu_B V_D - \nu_D)}{V_B}$$

Where

W = Wt. of sulphur sample in grams
V_D = ml. of standard iodine solution used in the determination
ν_D = ml. of standard sodium thiosulphate used in determination
V_B = mls. of standard iodine used in the blank
ν_B = mls. of standard sodium thiosulphate solution used in blank
N = normality of standard sodium thiosulphate solution

Results

Table I

Catalyst	BLANK (ppm $H_2S \pm 2$)	SAMPLE (ppm $H_2S \pm 2$)	% REDUCTION
Limestone	85	65	23.5
PbS[a]	108	56	48
Soda Glass	40	46	-
Soda Glass (acid washed)	84	71	-
Kaiser Alumina (KA-201)	117	37	68.4
Spent Bauxite[b] (2nd Bed)	101	34	66.3
Spent Bauxite[c] (1st Bed)	94	86	-
Spent Bauxite[c] (1st Bed)	101	99	-
Spent Bauxite[c] (2nd Bed)	75	49	34.5
Fire Brick[d]	87	79	-

a - prepared using Kaiser Alumina KA-201 as a support
b - the catalyst was not dried prior to use
c - catalyst predried for 2 hours at 140°C before use
d - high alumina - 90%

Each of the several catalysts for H_2S release were examined first measuring the H_2S content of a sample of the H_2S loaded sulur (BLANK) and then determining the residual H_2S in the remainder the sample after treatment with catalyst - (SAMPLE). The results Table I are therefore relative and demonstrate the degree of removal of H_2S achieved (% REDUCTION).

The results shown in Table I indicate that the catalysts ailer Alumina (KA-201) and spent bauxite (2nd Bed) merit further investigation. In the case of the lead sulphide catalyst, it was necesary to coat the sulphide on a support to prevent contamination of the ulhur. The support used in this case was Kaiser Alumina KA-201 and s better results were obtained with uncoated KA-201 (Table I) it would e pointless to continue experimenting with this particular system.

The experiments using spent bauxite (2nd catalyst bed) showed an improvement in the ability to promote the removal of hydrogen sulphde when the catalyst was not predried. This is probably due to a combination of the purging action of the stream and a catalysed Claus reaction. The spent bauxite catalyst from the 2nd Bed is obviously superior to that from the 1st Bed which operates under heavier loads ard consequently may be more deactivated (sulphated) than the 2nd Bed (i.e. less basic sites).

The results obtained with the high alumina (90%) fire brick are interesting in that very little surface area active alumina (KA-201) promoted a substantial hydrogen sulphide release. This could in part be due to the vast differences in surface areas but may be due to the alumina in the fire brick being a different modification to that in the KA-201.

The system being used in the laboratory is a static system in that the sulphur, saturated with hydrogen sulphide stands over the catalyst for a short time prior to being analysed for hydrogen sulphide. This is an inefficient method of contacting the sulphur and catalyst and could be improved by allowing the sulphur to pass down a heated column packed with the catalyst. A further improvement should be achieved f an inert gas is used to purge the system.

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METHODS FOR ANALYSIS OF H_2S IN SULPHUR

W. J. Schwalm and M.E.D. Raymont
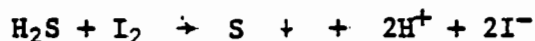Fundamental Sulphur Research Group

Introduction

For various reasons a knowledge of the amount of hydrogen sulphide in sulphur is often needed. Since H_2S is a very toxic gas, safety aspects must be considered. The release of H_2S from solid sulphur is slow, so this seldom becomes a problem in open spaces. However, in confined areas, especially if the sulphur is remelted, dangerously high concentrations of H_2S in the air can arise (e.g. head spaces of railway tank cars (1)). In addition, the presence of even 10 ppm of H_2S can substantially reduce the strength of elemental sulphur (2) or of sulphur composites. This is currently an active area of research by workers in the sulphurcrete field. This strength reduction aggravates an already serious dusting problem and, of course, released H_2S is itself a pollutant.

It is now well established that H_2S does not simply dissolve in sulphur, but also reacts to form hydrogen polysulphides or sulphanes (H_2S_x) (3,4,5). This complicates analysis because one must decompose the polysulphides in order to remove all of the H_2S (6). Thus, methods such as the use of lead acetate tape are susceptible to errors, since they only detect the free H_2S. One approach is to look at the H_2S and H_2S_x directly by an in situ technique such as the IR method recently developed by Alberta Sulphur Research Ltd. The other approach is to remove the H_2S and H_2S_x from the sulphur and analyze chemically to obtain a total H_2S value. This is the basis of the "wet chemical" techniques also employed by ASR.

Search for an Accurate Method

Until the summer of 1974 ASR employed the method described by Tuller (7). This method involved bubbling nitrogen through liquid sulphur to purge out the free H_2S and that arising from the H_2S_x. The nitrogen stream was passed through two scrubbing towers containing zinc acetate solution which removed the H_2S by forming the insoluble zinc sulphide, ZnS. This was then treated with acetic acid to liberate the H_2S and a known excess of iodine was added, giving rise to the reaction:

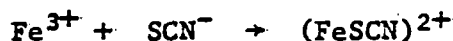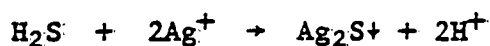$$H_2S + I_2 \rightarrow S + + 2H^+ + 2I^-$$

Finally, the remaining iodine was titrated with thiosulphate and from this, the amount of H_2S in the sample was calculated.

Although this is a widely accepted method, results were frequently obtained which were too low by 20 - 35%. It was suspected that the problem arose from the loss of H_2S on reliberation from the ZnS. Small bubbles were sometimes observed at this stage, indicating that some of the H_2S was escaping before reacting with the iodine. In addition, the solutions involved are subject to bacterial degradation so that their concentrations can change over a period of time.

A literature search for a more reliable method was then launched. One method which seemed to show promise involved the formation of methylene blue on the reaction of the zinc sulphide, formed as in the above method, with p-aminodimethylaniline in the presence of acid and ferric chloride. The amount of H_2S present in the sample is calculated from the absorbance of the solution at 670 nm. in the red end of the visible spectrum (8,9). This method is widely used for the determination of small quantities of H_2S in gas streams. Unfortunately, this method is very sensitive to slight variations in conditions such as small quantities of impurities and the dielectric constant of the solution. Since this method is designed for very small amounts of H_2S, analysis of sulphur samples from gas plants would require considerable dilution of solutions, introducing another source of error. In addition, many standards would have been required for calibration of the method. For these reasons, it was decided not to proceed in adapting this method for our H_2S analyses.
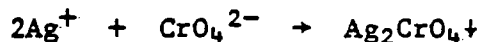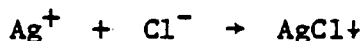
The literature search also produced a method (10) using silver nitrate, $AgNO_3$, as the absorbent for H_2S, forming silver sulphide, Ag_2S, which is exceedingly insoluble in water. The Ag_2S is then filtered off and washed thoroughly and the filtrate is titrated with ammonium thiocyanate using ferric ion as the indicator. This is a standard method for the determination of silver ion (11,12). From the difference between the amount of silver in the solution before and after purging the sample, the amount of H_2S in the sample can be calculated. The reactions involved are:

$$H_2S + 2Ag^+ \rightarrow Ag_2S\downarrow + 2H^+$$

$$Ag^+ + SCN^- \rightarrow AgSCN\downarrow$$

$$Fe^{3+} + SCN^- \rightarrow (FeSCN)^{2+}$$

(deep red brown)

The thiocyanate is standarized by titrating with $AgNO_3$ which is standardized against a sodium chloride solution whose concentration is accurately known, using chromate ion as the indicator:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4\downarrow$$

(red)

This method was tested for accuracy by analyzing a known weight of H_2S dissolved in water with the following results:

Actual Weight of H_2S	From Analysis	Error	Corresponding ppm
0.01660 g.	0.01652 g.	-0.48%	83
0.01659 g.	0.01656 g.	-0.18%	83
0.04532 g.	0.04607 g.	+1.65%	227
0.04523 g.	0.04581 g.	+1.28%	226

This method appears to be a very significant improvement over that involving the iodine-thiosulphate titration. We believe that we can analyze to a precision of ±1 ppm up to at least the 100 ppm level, although the uncertainty rises at higher H_2S contents. $AgNO_3$ seems to remove H_2S from the purge stream more efficiently than does zinc acetate. Up to concentrations of 100 ppm of H_2S, no Ag_2S appears in the second scrubbing tower, meaning that the first tower removes all the H_2S.

In the past year, this method has been used to analyze a wide variety of sulphur samples, generated both in our laboratories and supplied by outside sources. Some typical results are given below:

lab degassed sulphur	0.1 ppm
lab produced H_2S - containing sulphur	12 - 274 ppm
sulphur from Claus 1st condenser	336 - 494 ppm
sulphur from Claus 2nd condenser	38 - 73 ppm
sulphur from Claus 3rd condenser	12 ppm
liquid sulphur storage pit	108 - 190 ppm
gas plant degassed sulphur	61 - 240 ppm
bulk sulphur stockpile	92 - 132 ppm

Experimental Details for Silver Nitrate Method

Solutions: -

$AgNO_3$ - approximately 0.05M solution made by dissolving 32g. of solid $AgNO_3$ in 4 ℓ. of distilled water. 2 ml. of conc. HNO_3 added to prevent formation of silver oxide.

NH$_4$SCN - approximately 0.21M solution made by dissolving 62 g. of solid NH$_4$SCN in 4 ℓ. of distilled water.

NaCl - approximately 0.086M solution made by drying 5 g. of solid NaCl at 110°C for 1 hr., weighing accurately and dissolving in enough distilled water to make exactly one liter of solution. Molarity calculated to 4 significant digits.

Fe^{3+} - approximately 1M solution made by dissolving 482 g. of ferric alum [FeNH$_4$(SO$_4$)$_2$ · 12 H$_2$O] in the minimum amount of distilled water, filtering the resulting solution and making it up to one liter with concentrated nitric acid.

CrO$_4$$^{2-}$ - approximately 0.1M solution made by dissolving 2 g. of potassium chromate (K$_2$CrO$_4$) in 100 ml. of distilled water.

Standardizations: -

AgNO$_3$ - 20.0 ml. of NaCl solution of accurately known molarity, 30 ml. of distilled water, 2 ml. of CrO$_4$$^{2-}$ solution and 0.5 g. of solid calcium carbonate (CaCO$_3$) are placed in a 200 ml. Erlenmeyer flask. The solution is titrated with the AgNO$_3$ solution being standardized until the red precipitate of silver chromate (Ag$_2$CrO$_4$) can be detected. About 36 ml. is required. Under these conditions one overshoots the true end point by up to 0.25 ml., so an indicator blank must be subtracted. The blank is determined by titrating a solution containing 80 ml. of distilled water, 2 ml. of CrO$_4$$^{2-}$ solution and 0.5 g. of solid CaCO$_3$ (i.e. no NaCl).

NH$_4$SCN - 100.0 ml. of the standardized AgNO$_3$ solution, 250 ml. of distilled water and 20 ml. of Fe^{3+} solution in a 500 ml. Erlenmeyer flask are titrated with NH$_4$SCN solution until the first lasting tinge of red-brown colour appears. The solution must be stirred or shaken well just prior to the end point to dispel the non-permanent colour which appears before the end point is actually reached. In this case no indicator blank need be subtracted. About 23 ml. is required.

Analysis Procedure: -

Solid samples - 2 g. of PbS and 200.0 g. of sulphur are weighed into a 500 ml. round bottom flask with a 45/50 ground glass joint. This is fitted with an open-ended glass tube reaching to the bottom and provision is made for gases to exit from the top. A slow stream of nitrogen gas is passed through the sample and through two scrubbing towers each containing 100.0 ml. of AgNO$_3$ solution by means of open-ended glass tubes reaching close to the bottom of the towers. The sulphur sample is

heated to 125 - 130°C and purged at this temperature for
2 hrs. after melting is complete. The Ag_2S is then filtered
off and the scrubbing towers and the solid on the filter paper
are washed repeatedly with distilled water (total of at least
100 ml.). To the filtrate is added 20 ml. of Fe^{3+} solution
and the resulting solution is titrated with standardized NH_4SCN
solution until the first lasting tinge of red-brown colour appears.

Liquid samples - analysis flask and inlet tube and PbS are weighed and
warmed to 125° - 130°. The inlet tube is removed, sample is
poured in and the inlet tube is replaced. Nitrogen purge is
carried out for 2 hrs. The analysis flask, PbS, sample and
inlet tube are weighed to determine weight of sulphur by
difference. The remaining $AgNO_3$ in the scrubbing towers is
filtered and titrated as above.

Calculation -

$$\text{ppm } H_2S = \frac{V(Ag^+) \times C(Ag^+) - V(SCN^-) \times C(SCN^-)}{2,000} \times \frac{34.1 \times 10^6}{Ws}$$

where $V(i)$ and $C(i)$ are the volumes and concentrations,
respectively, of solutions containing species i and Ws is
the weight of the sulphur sample.

Cleanup - the scrubbing towers and glassware used for filtrations and
titrations present no problem (soap and water). The sulphur
in the round bottom flask is poured out as thoroughly as possible.
The flask, with its film of solid sulphur, is allowed to stand
until the next day or longer, if possible, to allow the sulphur
to age (13). Chloroform is run over the sulphur film which can
then be easily scraped off.

Precautions to be Taken

The major source of error arises from the adsorption of Ag^+ ions
on the surface of the Ag_2S precipitate (14). This tends to make the H_2S
levels calculated too high and becomes more serious at higher H_2S levels
because there are more, and larger, particles of Ag_2S present. As shown
before, our analyses of known samples of H_2S in water were about 0.2 to
0.5% low at the 80 ppm level but about 1.5% high at the 230 ppm level.
One must, therefore, wash the precipitate thoroughly after filtering.
Thorough washing of the scrubbing towers is also essential to ensure that
all of the unconsumed Ag^+ is transfered into the titration flask. Any
lost Ag^+ will again give high values for the H_2S determination.
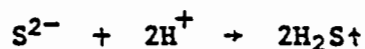
Another difficulty is the standardization of the AgNO$_3$. Chromate ion in solution tends to mask the colour of the red Ag$_2$CrO$_4$ precipitate, so the end point is not a sharp one. This difficulty, however, is alleviated by the determination of an indicator blank. Provided that one is consistent in observing the colour change, the error should be greatly diminished. It has been our experience that differences in the calculated molarities are in the fourth significant digit, making the errors in the determined H$_2$S levels less than the errors due to the Ag$^+$ ion adsorption.

It is important that the titrations of silver solutions with thiocyanate be very accurate, both in the standardizations and in H$_2$S determinations. This is because of the indirect nature of the method resulting in a calculation based on the difference between two terms. In cases where the H$_2$S level is low, this difference will be small and any errors in volumes or concentrations will be magnified. The volumes of Ag$^+$ and SCN$^-$ must, of course, be accurately known. Titrations can be consistently made within 0.03 ml. of SCN$^-$ solution or ±0.5 ppm of H$_2$S in a 200 g. sample. One advantage of an indirect titration is that overshooting the end point is no problem. One simply adds more AgNO$_3$, continues the titration and inserts the appropriate volumes into the equation.

Finally there is one difficulty common to all methods for analysis of H$_2$S levels in solid sulphur - avoiding loss of H$_2$S on sample preparation. Some of the H$_2$S will be present in the gas phase within the interstices of the solid and this will be lost from each new surface produced in reducing the sulphur to a suitable size for introduction into the analysis vessel. The losses will be especially serious with old samples where 30% of the H$_2$S may be present as the gas. For this reason, a wide mouthed round bottom flask is used and one must work quickly in weighing the sulphur and start the gas purge as soon as possible. The loss of H$_2$S becomes more rapid with higher H$_2$S content. This is partially compensated for by the fact that at high concentrations one tends to get results which err on the high side due to Ag$^+$ ion adsorption on the Ag$_2$S precipitate. Liquid sulphur samples are best analyzed without allowing them to solidify. 20% of the H$_2$S present may be lost on solidification and up to 30% on remelting (15). It is important, therefore, that solid samples be melted in the analysis vessel.

Applications

Although the procedures outlined above have been designed for the analysis of H$_2$S levels in sulphur, they could be readily adapted to any system from which H$_2$S could be liberated and purged. Such a system could be the determination of sulphide (or hydrosulphide) which would release H$_2$S on reaction with acid:

$$S^{2-} + 2H^+ \rightarrow 2H_2S\uparrow$$

This might include analysis of the sulphide content of ores. The procedure could also be modified by adding $AgNO_3$ directly to sulphide solutions to give the Ag_2S precipitate in situ. This would eliminate the necessity of purging out the H_2S which would be difficult or impossible if the concentration of sulphide were very low (e.g. waste water sulphide determinations).

The lower limit of measurement using solutions of the concentrations recommended above is $\sim$ 1 ppm of H_2S in 200 g. sample, i.e. 0.0002 g. of H_2S. We have worked with samples containing up to 500 ppm H_2S. The only limitations to working at higher levels could be those mentioned previously - loss of H_2S on sample preparation and adsorption of Ag^+. The latter could be alleviated by reducing the sample size and the former by modification of the apparatus to accommodate large samples without breakup.

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13. J. B. Hyne and J. G. Shawchuk, Report to the Members of Alberta Sulphur Research Ltd. on Sulphur Slates and Pellet, November (1972).

14. F. Peter and R. Rosset, Analytica Chimica Acta, Vol. 70, p. 149 (1974).

15. J. B. Hyne, Memorandum to Members of Alberta Sulphur Research Ltd. on Evolution of H_2S on Melting Recovered Sulphur, May 26, (1974).

SECTION III: AIR POLLUTION SOURCES & CONTROL DEVICES (Other than Incinerators)

A. Raw Materials and Chemicals Used in your Process, if applicable:

Description	Contaminants		Utilization Rate - lbs/hr	Relate to Flow Diagram
	Type	% Wt		
Prilled Sulfur	Dust	(.05 or less)	168,000	6-A
	H_2S	(.025 or less)		6-A

B. Process Rate, if applicable: (See Section V, Item 1)

1. Total Process Input Rate (lbs/hr): _____ 168,000

2. Product Weight (lbs/hr): _____ 167,998.86

Maximum Lb./Hr. Basis = 1800 L Ton/Day ÷ 24

C. Airborne Contaminants Emitted: Actual T/Yr. Basis = 600,000 L Ton/Yr.

Name of Contaminant	Emission[1]		Allowed Emission[2] Rate per Ch. 17-2, F.A.C.	Allowable[3] Emission lbs/hr	Potential Emission[4]		Relate to Flow Diagram
	Maximum lbs/hr	Actual T/yr			lbs/hr	T/yr	
Particulate	1.14	4.57	17-2.610 (3)		1.14	4.57	6-A,B
H_2S	1.9	8.40	N/A	N/A	42	1680	6-C,D

D. Control Devices: (See Section V, Item 4)

Name and Type (Model & Serial No.)	Contaminant	Efficiency	Range of Particles[5] Size Collected (in microns)	Basis for Efficiency (Sec. V, It[5]
Wet Scrubber	H_2S	95%	N/A	See Supple-
				ments 2 & 3

[1]See Section V, Item 2.

[2]Reference applicable emission standards and units (e.g., Section 17-2.05(6) Table II, E. (1), F.A.C. — 0.1 pounds per million BTU heat input)

[3]Calculated from operating rate and applicable standard

[4]Emission, if source operated without control (See Section V, Item 3)

[5]If Applicable

E. Fuels

Type (Be Specific)	Consumption*		Maximum Heat Input (MMBTU/hr)
	avg/hr	max./hr	

*Units Natural Gas, MMCF/hr; Fuel Oils, barrels/hr; Coal, lbs/hr

Fuel Analysis:

Percent Sulfur: _____ Percent Ash: _____

Density: _____ lbs/gal Typical Percent Nitrogen: _____

Heat Capacity: _____ BTU/lb _____ BTU/gal

Other Fuel Contaminants (which may cause air pollution): _____

_____

F. If applicable, indicate the percent of fuel used for space heating. Annual Average _____ Maximum _____

G. Indicate liquid or solid wastes generated and method of disposal.

_____

_____

_____

H. Emission Stack Geometry and Flow Characteristics (Provide data for each stack):

Stack Height: _____50_____ ft. Stack Diameter: _____2.5_____ ft.

Gas Flow Rate: _____12,300_____ ACFM Gas Exit Temperature: _____105_____ °F.

Water Vapor Content: __Saturated (150°F)__ % Velocity: _____41.66_____ FPS

SECTION IV: INCINERATOR INFORMATION

Type of Waste	Type O (Plastics)	Type I (Rubbish)	Type II (Refuse)	Type III (Garbage)	Type IV (Pathological)	Type V (Liq & Gas By-prod.)	Type VI (Solid By-prod.)
Lbs/hr Incinerated							

Description of Waste _____
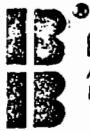
Total Weight Incinerated (lbs/hr) _____ Design Capacity (lbs/hr) _____

Approximate Number of Hours of Operation per day _____ days/week _____

Manufacturer _____

Date Constructed _____ Model No. _____

BARNARD AND BURK ENGINEERS & CONSTRUCTORS, INC.
A SUBSIDIARY OF BARNARD AND BURK GROUP, INC.
P. O. BOX 15648 / 10252 MAYFAIR DRIVE / BATON ROUGE, LA 70895-5648

Telephone: (504) 293-4000
TWX: 5109933463

April 1, 1982

Agrico
P. O. Box 3166
Tulsa, OK 74101

ATTENTION: Mr. William Banner

Gentlemen:

We have completed the design for the H_2S scrubber as requested. The design is based on 900 tons per day from each of the two sulfur melting pits. The pits are 12' x 60' in size. The scrubber is described as follows:

1. Scrubber tower, 5'-6"Ø x 30' high packed with ceramic raschig rings. Reservoir at bottom to collect caustic solution for recirculation to top of scrubber. Single fan taking suction on top of scrubber and discharging air through stack. Inlets to scrubber from each covered melting pit.

2. Air flow through scrubber - 125 cfm.

3. Water vapor content - air at discharge saturated at 150°F.

4. Stack dimensions - 30" x 50' high.

5. Exit velocity - 2500 ft/min. at 105°F.

We are enclosing a schematic of the above described unit. The lime to be added will be at a rate of 1 lb. per hour. The material will be dry and can be dispensed with augar or star valve. The quantities required are small and we see no possibility of reaching the 25 tons per year allowable to atmosphere.

We wish to thank you for allowing us to help you further in this phase of your work.

Very truly yours,
BARNARD AND BURK ENGINEERS &
CONSTRUCTORS, INC.

H. W. Allen
Project Manager

HWA/gw

ATTACHMENT   2

BOB GRAHAM
GOVERNOR

VICTORIA J. TSCHINKEL
SECRETARY

June 9, 1982

Mr. L. C. Lahman, Plant Manager
Agrico Chemical Company
P. O. Box 1969
Bartow, Florida 33830

Dear Mr. Lahman:

RE: Air Pollution Source Construction Application-
South Pierce Chemical Complex, AC 53-55780

Your construction permit application for a prilled
sulfur receiving and melting facility at your South Pierce
Chemical Complex has been transferred to the Bureau of Air
Quality Management for processing. The information submitted
has been reviewed and is deemed incomplete. The following
information is required to complete processing of the permit.

For both the particulate emission estimate and the
hydrogen sulfide emission estimate, the basis of potential
discharge is required as stated in the supplemental require-
ments. Therefore, a copy of Dr. Lundgren's "Determination of
Emission Factors for Fugitive Emission Sources" and a copy of
Dr. Raymont's technical data of hydrogen sulfide emissions
during melting is required.

In the calculation of annual particulate emissions a
factor of two dumps is used. The process diagram indicates
there are five drop points for this facility, the truck/rail
dump to conveyor, the conveyor to surge bin, the surge bin to
vibrating feeder, and the vibrating feeder to two melting pits
at one time. Therefore, provide the rationale behind the choice
of the number of dumps in the calculation of particulate emissions.

Since no emission control equipment is contained in
this application, the application must comply with the require-
ments of 17-2.610(3), FAC, Unconfined emissions of particulate
matter. This section requires that reasonable precaution be
applied to control such sources. Therefore reasonable precau-
tions to prevent particulate emissions from the truck/rail dump,

the conveyors system, the surge hopper, the vibrating feeder and the melting pits must be proposed in accordance with this section.

Is the process rate from the surge hopper to the melting pits the same as the truck unloading rate? If it is different, specify the maximum feed rate of the vibrating feeder.

In the supplemental requirement section of the application form, design details for all pollution control systems is required for construction permit applications. Therefore, more information is needed concerning the wet scrubber. Information on the type of wet scrubber, scrubbing liquor, liquor flow rates, scrubber dimensions and estimate of efficiency should be included. A brochure from the manufacturer would be extremely helpful.

In the emission stack geometry and flow characteristics section, the gas flow rate does not correspond to the stack diameter and velocity. This section should be changed if any of these items were incorrect.

In supplement #3, maximum hydrogen sulfide emissions after controls is listed as 1.9 pounds per hour and 8.4 tons per year. In section III c. maximum emissions of hydrogen sulfide is indicated as 42. pounds per hour and 4.20 tons per year. What is the maximum controlled hydrogen sulfide emission rate that Agrico is proposing?

During the melting process, would emissions of the other criteria pollutants occur? If yes, what will the emission rate be? Submit detailed information and calculations showing how this information was derived.

When the above questions are answered, the processing of the construction permit can be finalized. If there are any questions concerning this matter, please contact John Svec at (904) 488-1344.

Sincerely,

C. H. Fancy, P.E.
Deputy Bureau Chief
Bureau of Air Quality
Management

CHF/JS/bjm

ATTACHMENT   3

Bill

September 22, 1982

D E R

SEP 24 1982

BAQM

Mr. C. H. Fancy, P.E.
Deputy Bureau Chief
Bureau of Air Quality Management
Department of Environmental Regulation
Towers Office Building
Blairstone Road
Tallahassee, Florida 32301

RE: Air Pollution Source
     Construction Application –
     South Pierce Chemical Works,
     AC53-55780

Dear Mr. Fancy:

Agrico Chemical Company is in receipt of your June 9, 1982
letter which stated that the permit application for a prilled sulfur
receiving and melting facility at our South Pierce Chemical Works
was deemed incomplete. In your letter you requested information on
eight areas in order to complete processing of our permit. In the
order in which the questions were asked, we respond with the following
information:

We have enclosed a copy of Dr. Lundgren's "Determination of
Emission Factors for Fugitive Emission Sources", per your request.
We have also included Dr. Ramont's technical data on hydrogen sulfide
emissions.

Regarding Agrico's rationale behind the choice of the number of
dumps in the calculation of particulate emission, we maintain that only
two locations for air emissions are involved, not five. The wet-prilled
sulfur is received either by rail or truck and is discharged into a hopper
at the unloading shed. This constitutes the first transfer as an air
emission source. From the hopper, it is discharged onto a covered con-
veyor. Since this discharge is totally enclosed, no particulate emissions
are generated. The covered conveyor discharges into a 100 LT surge hopper.
The surge hopper is designed so that displaced air will escape out of the
top sides of the unit. The design of the surge hopper results in the
second emission point. The storage hopper then discharges into enclosed
vibrating feeders. Thus, the discharge from the enclosed hopper to the
vibrating feeders does not generate fugitive dust.

-1-

From the vibrating feeders, the wet-prilled sulfur dumps into covered melters. The covers on the tops of the melters prevent any potential generation of fugitive dust. It should also be mentioned that the fumes from the melters will be scrubbed to remove any H_2S. Thus, because of the enclosed design of the system, only two transfers can be considered potential sources of particulate emissions.

In complying with the requirement of 17-2.610(3), FAC, Unconfined Emissions of Particulate Matter, it appears that compliance depends upon the interpretation of "reasonable precaution". Agrico maintains that handling wet-prilled sulfur at approximately 2% moisture, fines particles are very effectively held to the prill. Thus, the moisture content prevents the release of particulates to the ambient air; and, as such, constitutes a reasonable precaution. This reasonable precaution was approved as adequate in the recent air construction permit issued by the Department for Agrico's prilled sulfur terminal at Big Bend, Hillsborough County, Florida.

In addition, FAC Rule 17-2.650 (2) (c) 5b, (i) establishes a reasonable emission limit of 0.30 pounds of particulate per ton of product for unit operations in a phosphate processing plant. The manufacturing of sulfuric acid is an integral part of the process to produce G.T.S.P. so, therefore, this limitation could be considered reasonable. The three sulfuric acid plants will produce 250 tons per hour of product and the sulfur unloading facility will produce 1.14 lbs./hr. of particulate. This results in a .0046 pound per ton emission rate or 1.5% of the allowable for unit operation. If the process is limiting fugitive emissions to within 1.5% of what controlled emissions are allowed, then Agrico contends that the intent of 17-2.610 (3) is being met.

In response to your question regarding process rates from the surge hopper and truck unloading conveyor, preliminary design calls for a maximum vibrating feeder rate of 60 tons per hour (actual rate will vary depending on plant consumption). The truck unloading rate is considerably faster in order to maintain a minimum turnaround time on the trucks. As such, preliminary design requires a 200 ton per hour process rate.

Regarding supplemental information concerning the wet scrubber, we have attached design information from the firm of Bernard and Burk Engineers and Constructors, Inc.

In regard to the flow characteristics of the wet scrubber stack, we have enclosed a revised Page 4 of 10.
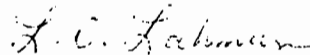
In regard to the airborne contaminants emitted, we have enclosed a revised Page 3 of 10. The changes made in Section III C are explained below:

1. The allowed emission rate for particulate is changed from the process weight table limitations to the unconfined emission statement of 17-2.610(3).

2. The maximum lb./hr. and T/Yr. emission H_2S is changed to 1.9 and 8.4 respectively, to reflect the information submitted in Supplement 3.

3. The potential T/Yr. H_2S emission is changed to 1680. This number is calculated by using the equation quoted in Supplement 3, with removal of the .05 control factor.

During the melting process minute amounts of SO_2 will be generated. The ratio of H_2S to SO_2 is approximately 800 to 1. The uncontrolled amount of H_2S emitted is 1680 tons per year, therefore, the SO_2 emissions will be approximately 2.1 tons per year. The SO_2 fumes will be evacuated through the fume system and will be fed to the scrubber before release into the atmosphere. There are no other criteria pollutants emitted during the operation.

Agrico believes the above responses sufficiently respond to the questions raised in your July 9, 1982 memo, and the processing of our air construction permit can now be finalized. If there are any questions concerning this matter, please contact Ed Mayer at (813) 428-1423.

Sincerely,

L. C. Lahman,
Plant Manager

Enclosure

LCL/lgm

Determination of Emission Factors for Fugitive Emission Sources

February 28, 1979

Dale A. Lundgren

Calculation of fugitive emissions from industrial processes involving the transfer, conveying, loading and unloading of bulk materials generally following the procedures outlined in EPA document AP-42 titled "Compilation of Air Pollutant Emission Factors" February 1976 or the document titled "Technical Guidance for Control of Industrial Process Fugitive Particulate Emissions". (EPA-450/3-77-010, March 1977). In both documents the "emission factor" for the given bulk material is basic to making an emission estimate. Only for a few materials have emission factors been obtained. Emission factors are given for transfer and conveying of coal, coke, dry phosphate rock, sand, grain, iron ore, and lead ore. Among these materials, dry phosphate rock has a factor reliability of "below average" or "D" while all other materials have a factor reliability of "poor" or "E". Loading and unloading operations have emission factors listed for dry phosphate rock, taconite pellets, coal and grain. The phosphate rock has an emission factor reliability of "average" or "C". All other materials are in the below average or poor reliability factor categories.

Emission factor data for prilled sulfur is needed to make a valid estimate of the dust emission rate from a prilled sulfur unloading facility such as the Agrico Chemical Company, Big Bend Terminal in Hillsborough County, Florida. A careful literature search failed to find any emission factor data for any form of prilled sulfur. This lack of data was confirmed by Mr. Gilbert Wood, EPA Project Officer for the cited EPA report on fugitive particulate emissions - a study conducted for EPA by PEDCo Environmental, Inc. (Mr. Gilbert's recommendation was to obtain field or laboratory test data for the prilled sulfur).

The complete lack of a reasonable emission factor for prilled sulfur has been recognized and stated by most persons involved in the problem of estimating emissions from the proposed Agrico sulfur unloading facility. This lack of knowledge has not prevented about five different firms or persons (including the writer) from calculating over 10 different dust emission rate estimates.

In an attempt to resolve this emission factor uncertainty and to determine the effect of moisture content on the dustiness of prilled sulfur, a test procedure was developed and tests run on both phosphate rock and prilled sulfur at various moisture contents. These tests were run in a specially built wind tunnel which allowed the aerosolized dust to be collected and measured. A standard Hi-Vol motor, blower and filter holder and an 8x10 inch glass fiber filter paper were used for efficient collection of the dust. A sketch of the test chamber is shown in Figure 1.

In operation, the Hi-Vol is fitted with a pre-weighed filter, set in place and operated at an air flow rate of about 60 cfm. A pre-weighed sample of product is discharged into the center of an 8-inch vertical duct. The downward air velocity in the duct is about 170 fpm. The sample is gradually and uniformly dumped in a rate of about 10 pounds per minute and allowed a free fall of five feet onto a cement slab (covered with Kraft paper or plastic for ease of product recovery). Dust generated is blown from the product under test by the downward direction of the air stream. Cross-sectional area and air flow rate of the vertical wind tunnel were selected so that all particles less than about 60 um aerodynamic diameter would be drawn up and collected onto the filter paper. Particles greater than -100 um aerodynamic diameter would have sufficient settling velocity (-60 fpm) to resist the upward air motion and settle downward. These collection characteristics are comparable to the standard Hi-Vol air sampler operating in a shelter of approved design. Data is therefore obtained

on the quantity of dust that is capable of being collected by a Hi-Vol (the sampling instrument used for determination of compliance with the national ambient air quality standard for suspended particulate matter).

In order to relate this measurement of dust emission factor with available published data in AP-42, a total of eight tests were run on dry phosphate rock (duplicate tests on four samples). Dry phosphate rock was selected as the best material for comparison purposes because it has the highest assigned reliability factor for any material listed in the EPA Technical Guidance Document EPA-450/3-77-010. Dry phosphate rock was assumed to be rock allowed to equilibrate for several days at 70-75°F temperature and 40-50% relative humidity. The reference or comparison test run on dry phosphate rock produced an average product emission factor (or dustiness) of 1.5 pounds per ton (average of 0.9, 2.0, 1.5 and 1.5 pounds per ton). This suggests that the proposed wind tunnel tests produce data comparable to that presented in AP-42 and EPA-450/3-77-010.

The sequence of testing for both the phosphate rock and the sulfur prill first involved air drying the material in a thin layer on a table top for three days (72 hours) at an average room temperature of 75°F and room air humidity of 45 to 50% RH. Moisture tests were run on 100 gram samples of each material. The weight loss upon heating to 105°C in a drying oven for 60 minutes was determined and considered to be the percent moisture.

Ten pound samples of each material (4540grams) were weighed out and used for the wind tunnel drop test (a 5 foot drop onto a cement floor covered with a sheet of Kraft paper) using the test chamber shown in Figure 1. Each sample of each material was used twice. Separate pre-weighed filters were used for each test. On completion of each test, the filter was weighed on a standard analytical balance to the nearest 0.1 mg. Filters were not desiccated or otherwise dried before weighing. All filters were marked and saved.

-3-

After the initial dry product tests, the air dried phosphate rock and sulfur prill were each wet with about 600 ml of ordinary tap water (no wetting agent used). These samples were carefully mixed, spread out onto a sheet of plastic, and allowed to dry or equilibrate for 15 hours. Moisture analysis was run as previously described (100-gram samples dried at 105°C for 60 minutes) and weight loss used to calculate percent moisture. The remaining material was weighed and used for emission factor tests as described. Duplicate tests were run on each material.

Samples were air dried further and tested as described. Additional phosphate rock samples were air dried and tested.

The original phosphate rock and sulfur prill samples were completely dried to original (first test) moisture conditions and re-tested. The object was to determine if the product dustiness had changed significantly. As indicated on the following table as "initial" and "final" the percent dust produced was nearly unchanged. All test data is summarized in the following table. Duplicate tests were reproducible to within ± 20% of the average in almost all cases.
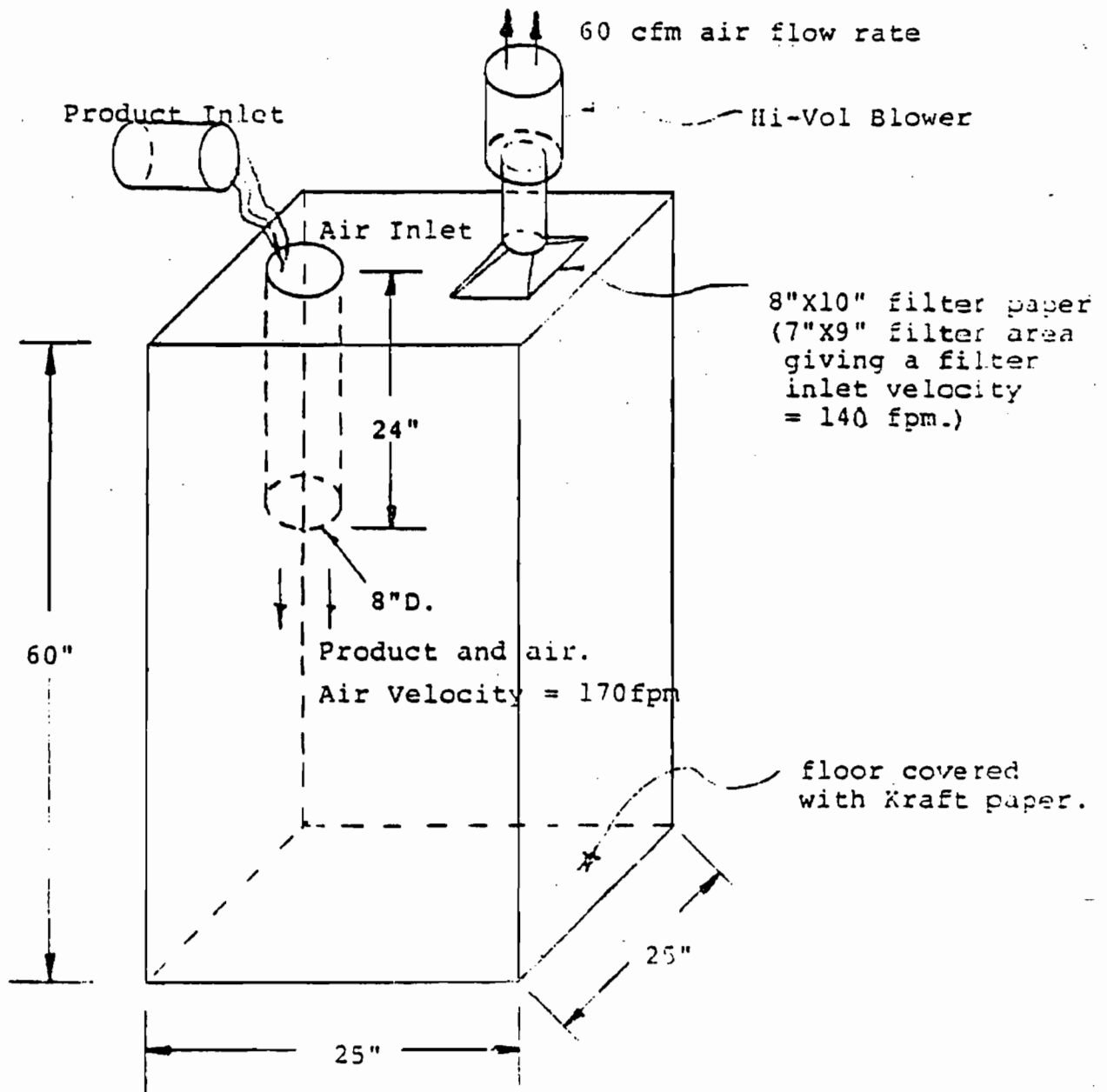
Test results for sulfur prill are 0.0037 pounds dust per ton of product at 2.6% moisture and 0.0098 pounds dust per ton of product at 1.6% moisture. These data are averaged and the emission factor for a 2% moisture sulfur prill is estimated to be 0.0068 pounds per ton. Using this emission factor for 2% moisture prilled sulfur, an estimate of the uncontrolled dust emission rate can be calculated. A water spray control efficiency factor of 50% or a wetting agent control efficiency factor of 90% can then be applied. If the Emission Estimate table prepared by PEDCo is used with the 0.0068 pounds per ton dustiness factor, the following emission rate valves are determined.

Uncontrolled emission rate   10.2 lb/hour

Water control at 50%   5.1 lb/hour

Wetting agent control @ 90%   1.0 lb/hour

The above values are from the table on the following page. On a yearly average basis the respective rates are all reduced by a factor of about 10 to values of 1, 0.5, and 0.1 pounds per ton.

Because of the uncertainty of such estimates, it is likely that the actual emission rate is somewhere between one-half and twice that calculated and may be as little as one-fourth or as much as four times the calculated values for the control conditions given.

Figure 1 - Test Chamber

60 cfm air flow rate

Product Inlet

Hi-Vol Blower

Air Inlet

8"X10" filter paper
(7"X9" filter area
giving a filter
inlet velocity
= 140 fpm.)

24"

8"D.

Product and air.

Air Velocity = 170fpm

60"

floor covered
with Kraft paper.

25"

25"

Emission Estimates

Using PEDCo listed Activities and a 0.0068 #/ton emission factor

Activity	Uncontrolled Emission Factor #/ton	Material Throughput tons/hour	Emission Rate-#/hour		
			Uncontrolled	50% Control	90% Control
Ship Unloading	0.0068	600	4.1	2.05	0.41
Transfer-convey	0.0068	600	4.1	2.05	0.41
Storage(0.0068)					
-onto pile	0.0008	600	0.5	0.25	0.05
-veh. traffic	0.0027	75	0.2	0.1	0.02
-wind erosion	0.0022	75	0.2	0.1	0.02
-loadout	0.0010	75	0.1	0.05	0.01
Transfer-convey	0.0068	75	0.5	0.25	0.05
Truck loadout	0.0068	75	0.5	0.25	0.05
Total			10.2	5.1	1.0

Summary of Wind Tunnel Tests on
Phosphate Rock and Sulfur Prill

by

Dale A. Lundgren

January 26, 1979

Sulphur Prill

% H_2O	% Dust	# Dust/ Ton Product
10.7	0.00014	0.0028
3.5	0.00018	0.0036
2.6	0.00019	0.0037
1.6	0.00049	0.0098
0.1 - initial	0.15	3.0
0.1 - final	0.19	3.8

Phosphate Rock

% H_2O	% Dust	# Dust/ Ton Product
10.6	0.00022	0.0044
3.5	0.00072	0.014
2.2	0.039	0.78
1.3 - new sample	0.045	0.90
1.2 - initial	0.10	2.0
1.2 - final	0.076	1.5
1.6 - new sample	0.077	1.5

Sulphur Development Institute of Canada (SUDIC)
#1702 Canada Trust Building
505 Third Street, S.W.
Calgary, Alberta

May 19, 1982

Mr. R. W. Curtis
Agrico Chemical Company
P.O. Box 3166
Tulsa, OK 74101

Dear Mr. Curtis:

Pursuant to our telephone conversation in March concerning hydrogen sulphide emissions, I would like to confirm the following:

1. Total levels of hydrogen sulphide present as both dissolved hydrogen sulphide and combined hydrogen polysulphide in solid sulphur product from gas plants will generally lie in the 50-250 ppm range depending on the thermal history and age of the product. Most product levels will lie at the lower end of the range (50-100 ppm H_2S).

2. Remelting of this product will release part but not all of this total hydrogen sulphide content. Free dissolved hydrogen sulphide will be released on melting whereas the hydrogen sulphide present as combined hydrogen polysulphide will not be readily emitted. If held in the molten state for long periods, the hydrogen polysulphides will gradually decompose, slowly releasing more hydrogen sulphide. In any event the maximum release of hydrogen sulphide on melting can clearly not exceed the total content and will generally be of lower quantity.

3. The actual concentration of hydrogen sulphide both in process units (e.g., melters) and in the surrounding ambient air will clearly depend on melt rate, tonnage, and the dilution of the released gases.

I will try to find some papers in the literature which will support these statements on my return to Calgary and forward them to you in due course.

Yours sincerely,

Michael Raymont by R. Team

M. E. D. Raymont
Director, Research and Development.
SUDIC

General Background
See especially pp. 24-25

INTERCONVERSION RATES AND EQUILIBRIA IN

THE SULPHUR-HYDROGEN SULPHIDE SYSTEM

W. Schwalm and J.B. Hyne
Fundamental Sulphur Research Group

Almost any sulphur sample, especially sulphur recovered from sour natural gas, is an example of a sulphur-H_2S system. H_2S-free sulphur probably exists only when H_2S is deliberately removed from sulphur, Thus, the behaviour of sulphur can hardly be understood without reference to its H_2S content and for a number of reasons this understanding is crucial.

Because of the toxicity of H_2S, safety is a prime consideration. H_2S is lost from sulphur over a period of time. As will be shown later this loss is slow so build-up of H_2S concentration in the adjoining air space is often not a problem. High H_2S concentrations arise primarily with liquid sulphur in areas with inadequate ventilation. Examples of such situations could include sulphurcrete manufacture, sulphur remelters and liquid sulphur shipment. The last of these has been discussed by Williams et al[1] and by Hyne[2]. In addition, an explosion hazard exists if the H_2S concentration in the air rises above 3.36% or 33,600 ppm[3]. These conditions can occur in localised volumes even with bulk sulphur containing only 10 - 15 ppm of H_2S[4].

ASR's interest in the study of the sulphur-H_2S system originated with the problem of sulphur deposition in sour natural gas collecting systems. This deposition was explained in terms of the formation and decomposition of hydrogen polysulphides or sulphanes, H_2S_x[5]. Sulphanes are also believed to be among the species responsible for the rapid corrosion of steel in the presence of sulphur and water.

It is also well-known that the presence of H_2S can have a dramatic effect on the properties of elemental sulphur. The effect of H_2S on the viscosity of liquid sulphur is particularly marked due to a decrease in the average length of the sulphur chains in the polymeric form. This viscosity modification by the H_2S was investigated by Fanelli in 1943-1946[6,7] and by Rubero in 1964[8]. It was found that 0.3% (3,000 ppm) H_2S increased the temperature of maximum viscosity of sulphur by 100°C and reduced the maximum viscosity by a factor of 1,000. Another property of pure sulphur which is affected by the small quantities of H_2S which can be incorporated is its flexure strength[9]. Saturation with H_2S makes sulphur 50% weaker and even very low concentrations have a marked effect. This, of course, would make sulphur less suitable as a construction material or for paving roads. Fortunately, the effect on sulphur composites is much less dramatic and additives have been identified that virtually eliminate the weakening effect.

Historical Development

In 1949, Fanelli investigated the apparent solubility of H_2S in

sulphur and found that it <u>increased</u> with increasing temperature going through a broad maximum[10]. This behaviour is in contrast to most gases whose solubility in liquids <u>decreases</u> with increasing temperature. From this and the effect of H_2S on sulphur's viscosity he inferred that a chemical reaction must be taking place resulting in the formation of sulphanes. However, the necessary techniques for distinguishing between H_2S and the H_2S_x species were not available. Feher and Winkhaus, in 1957, found H_2S_x species to be thermodynamically unstable with respect to H_2S and sulphur[11]. The solubility of sulphur in gaseous H_2S was investigated by Willand in 1958[12]. He found that more sulphur dissolved at higher temperatures and pressures but the formation of sulphanes in this H_2S rich system was uncertain.

In the mid 1960's two new techniques were used to investigate the sulphur-H_2S system - infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. Discussion of the former will be left to a later section. The NMR spectrum of sulphanes was first published by Schmidbaur and co-workers in 1964[13]. He found a distinct peak for each individual sulphane up to 5 sulphur atoms ($x = 5$ in H_2S_x). Higher sulphanes could not be resolved but formed one broad peak. This new tool allowed Hyne, Muller and Wiewiorowski to study the lower members of the sulphane family[14] and their thermal decomposition was investigated by Hyne and Muller[15,16]. In the course of these studies NMR spectra were run of sulphur in which H_2S had been dissolved and equilibrated. These spectra showed a virtual absence of sulphanes with less than 6 sulphur atoms. A thermodynamic treatment yielded an average chain length of 27 sulphur atoms at 127°C, increasing with rising temperature.
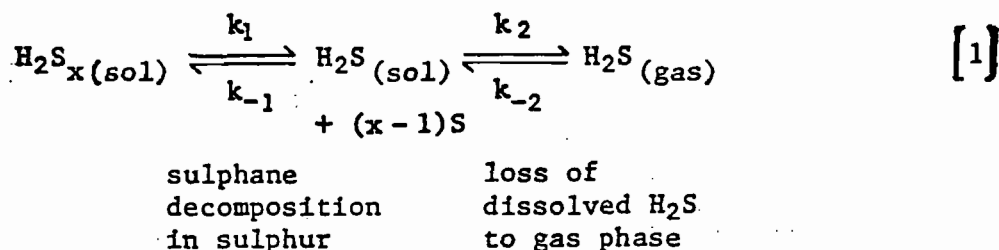
Meyer and his associates investigated the solubility of sulphur in liquid H_2S at elevated pressures in 1969[17,18]. They also found that in the presence of H_2S, the melting point of sulphur is depressed by about 20°C meaning that H_2S must also dissolve in solid sulphur. However, they found no evidence for sulphane formation up to 80°C (176°F). This was confirmed by Parthasarathy at ASR, who found that no sulphanes are formed up to 200°F[19]. Hyne and co-workers also confirmed that sulphane formation is favored by higher temperatures and pressures[20] and proposed a free radical mechanism for their formation[20,21]. A short review of solubility aspects of the sulphur-H_2S system by Wiewiorowski appeared in 1970[22].

The formation of sulphanes, by the reaction of H_2S with liquid sulphur makes the removal of H_2S from sulphur more difficult. H_2S removal was studied by Rennie at ASR using a variety of catalysts to help break down the sulphanes[23]. Patents for removal of H_2S from liquid sulphur obtained in 1974[24] and 1975[25,26] show that this is a continuing concern. Analytical methods for measuring the total H_2S content of sulphur samples must also make allowance for the presence of sulphanes. Both the older method of Tuller[27] and the refinement by ASR[28] involve the use of a catalyst to break down the sulphanes and extended purge times.

The System

Most of the previous work on the sulphur-H_2S system has involved

static or equilibrium situations and little is said about the rates of the various processes. It is for this reason that the study to be described was undertaken. The sulphur-H_2S system can be described by the following set of reactions:

$$H_2S_{x(sol)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2S_{(sol)} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2S_{(gas)} \qquad [1]$$
$$+ (x-1)S$$

sulphane	loss of
decomposition	dissolved H_2S
in sulphur	to gas phase

H_2S_x (sol) represents all sulphanes present and dissolved in the sulphur; $H_2S_{(sol)}$ is the hydrogen monosulphide dissolved in the sulphur and H_2S (gas) is the H_2S present in the gas phase in contact with the sulphur. Examination of this set of reactions shows that the H_2S can be lost from the system to the gas phase only as the monosulphide. The sulphanes must first decompose to reform H_2S which can then be lost. This is a key consideration in any degassing technique for removal of H_2S from sulphur.

The k's in [1] represent the rate constant for the processes in the indicated directions. In addition, when at equilibrium, the system is constrained by the following equilibrium expressions:

$$K_1 = \frac{[H_2S_x]}{[H_2S_{(sol)}]} \qquad [2]$$

$$K_2 = \frac{[H_2S_{(sol)}]}{[H_2S_{(gas)}]} \qquad [3]$$

It should be noted that the concentration of sulphur does not appear in expression [1] since it is present in such large excess that it is essentially unchanged by the formation or decomposition of H_2S_x. Therefore, it has been incorporated into K_1. It should also be noted that at the very low concentrations of H_2S and H_2S_x considered here (ppm level) concentration units can be used instead of the more rigorous thermodynamic activity values in calculating rates and equilibrium constants. An additional equilibrium constant can be defined as:

$$K_3 = \frac{[H_2S_{(sol)}] + [H_2S_x]}{[H_2S_{(gas)}]} \qquad [4]$$

i.e. K_3 is the ratio of total H_2S concentration (both mono and poly-sulphide forms) in the sulphur to the concentration of H_2S in the gas phase.

The rate and equilibrium constants are related because equilibrium exists when the rates of the forward and reverse reactions are equal. For example, for equilibrium between H_2S_x and $H_2S_{(sol)}$

$$k_1\left[H_2S_x\right] = k_{-1}\left[H_2S_{(sol)}\right]$$

$$\frac{k_{-1}}{k_1} = \frac{\left[H_2S_x\right]}{\left[H_2S_{(sol)}\right]} = K_1 \qquad [5]$$

Likewise:

$$K_2 = \frac{k_{-2}}{k_2} \qquad [6]$$

K_3 can be related to the rate constants by making the appropriate substitutions into expresion [4] and rearranging to give:

$$K_3 = \frac{k_{-2}}{k_2}\left(1 + \frac{k_{-1}}{k_1}\right) \qquad [7]$$

Expressions [5], [6] and [7] are useful because if all the constants but one are known for any of the expressions the remaining one can be calculated. If all of the constants are known, the expressions can be used as a check for self-consistency. In this study, the equilibrium constants were first determined. A knowledge of these values is of importance in estimating maximum free H_2S concentrations likely to be found in equilibrium with liquid sulphur in enclosed systems (e.g. rail tank cars). A sulphur sample was allowed to degas (left to right in expression [1]) while the concentrations of H_2S_x and $H_2S_{(sol)}$ were monitored. This allowed k_1 and k_2 to be calculated and expressions [5] and [6] were used to calculate k_{-1} and k_{-2}. Expression [7] was then used to make sure that all values were internally consistent.

The Method

The data required to obtain rate and equilibrium constants were the concentrations of H_2S_x and $H_2S_{(sol)}$ in liquid sulphur. To obtain the K's the concentrations had to be known for equilibrium situations while for obtaining the k's the concentrations had to be followed over a period of time as a sulphur sample with high total H_2S concentration was degassed.

The tool best suited for obtaining these data is infrared

spectroscopy. The use of liquid sulphur as a solvent for IR was first reported by Wiewiorowski and co-workers in 1965[29]. Shortly thereafter, they described the use of IR in determining the hydrocarbon content of sulphur[30]. In another paper they described the use of IR in an investigation of the sulphur-H_2S system including a break down of the "solubility" of H_2S into its components ($H_2S_{(sol)}$ and H_2S_x) over the temperature range from 125 - 182°C[31]. All H_2S_x's appear in one peak and are, therefore, indistinguishable in the infrared. Fig. 1 is based on their data.

In this study, the infrared cell used is similar to that described in reference 29 except that a path length of 3 cm was used. This was achieved by replacing the teflon spacer with another aluminum block 3 cm in thickness, machined to accommodate 2 more heaters. The disassembled cell is seen in Fig. 2. Fig. 3 shows the assembled cell and the temperature controller and Fig. 4 shows the cell mounted in a Beckman IR-20 infrared spectrophotometer which was used for recording the spectra used in this investigation. All data were obtained at 125°C or 257°F.

Determination of Equilibrium Constants

K_1 (the ratio of the concentration of H_2S_x to that of $H_2S_{(sol)}$) was taken from the data of Wiewiorowski and Touro (Fig. 1)[31]. Its value at 125°C is 0.21 meaning that most of the H_2S content of sulphur at this temperature is present as hydrogen monosulphide. Wiewiorowski's data was obtained under an atmosphere of pure H_2S.

K_2 and K_3 were evaluated from an experiment in which sulphur charged with H_2S was placed in a closed IR cell. The spectrum was run numerous times over a period of 1 week at which time the concentrations of H_2S_x and $H_2S_{(sol)}$ had become constant. The concentration of H_2S in the air space was obtained by calculating the decrease in the total H_2S content in the sulphur and dividing by the volume of the air space. The initial total H_2S concentration of the sulphur was 34.5 ppm and the final value was 26.7 ppm, the volume of sulphur in the cell was 29.5 ml and the volume of the space was 3.7 ml. Therefore, the pressure of H_2S in the air space was 52 mm and the concentration was 7.8% or 78,000 ppm. This is well over the lower explosion limit of 3.36% quoted in reference 3. This supports the contention of reference 4 that the lower explosion limit can be reached with sulphur containing as little as 10 - 15 ppm total H_2S, if adequate ventilation of the system is not provided.

If the values for the concentrations in the liquid and gas phases are left expressed in ppm, one obtains a K_3 of 3.4×10^{-4} at Calgary's atmospheric pressure of 660 mm. Converting the data to moles/litre yields a $K_3 = 0.47$. The large numerical difference arises because of the difference in the densities of the gas and liquid phases. The equilibrium concentration of $H_2S_{(sol)}$ in this experiment was 22.6 ppm and, converting again to moles/litre, K_2 is found to be 0.40. Finding K_2 and K_3 to be less than 1 seems intuitively correct since H_2S is a gas at 125° and one would, therefore expect the gas phase to be favored.

FIG. 1

SOLUBILITY OF H2S IN LIQUID SULPHUR

○ Composite curve - true H2S solubility and equilibrium amount of H2Sx

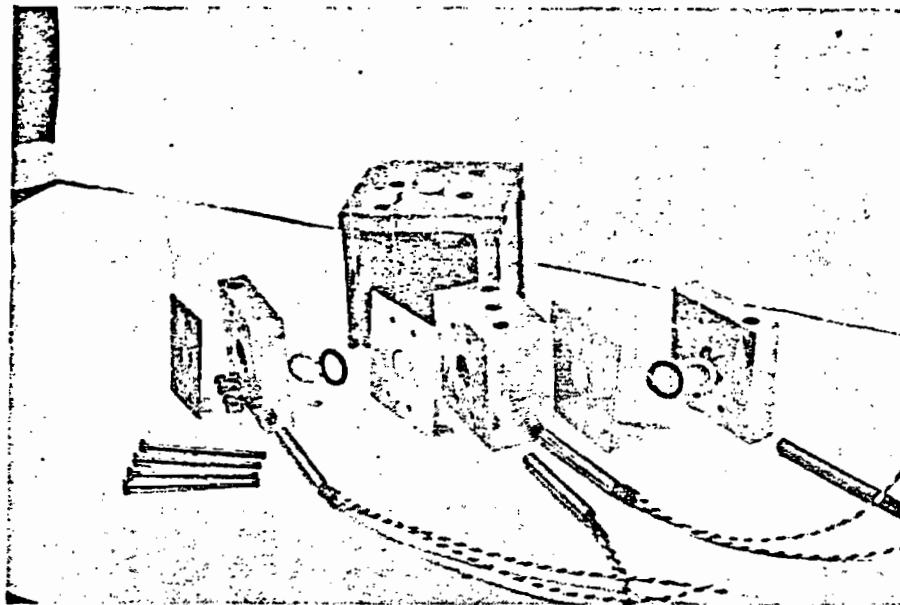△ H2Sx in equilibrium with H2S

X True H2S solubility in SL

18.

Fig. 2
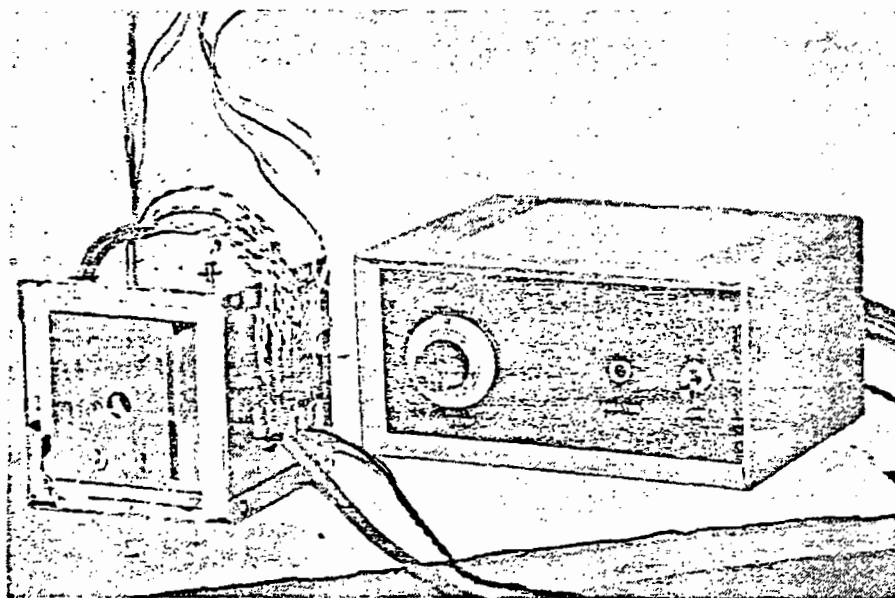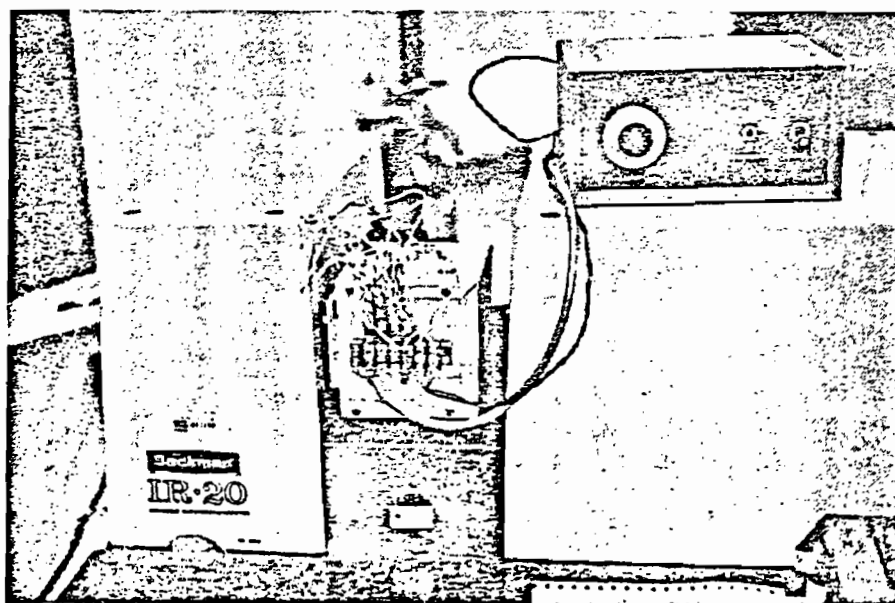

Fig. 3

Fig. 4

Determination of Rate Constants

Rate constants were determined from an experiment in which a
sulphur sample with high H_2S content was placed in an IR cell open to
atmosphere i.e. evolved H_2S was free to escape from the system. The
spectrum was run repeatedly until $H_2S_{(sol)}$ and H_2S_x were no longer

dectectable in the sulphur. The lower limit of detectability (about 1 ppm)
was reached in $4\frac{1}{2}$ days. Fig. 5 shows how the IR spectrum changed as the
H_2S was lost from the sulphur. The H_2S peak is at 2570 cm^{-1} and the H_2S_x
peak at 2498 cm^{-1}. Although the response for H_2S_x is much greater than that
for $H_2S_{(sol)}$ the concentration of $H_2S_{(sol)}$ is actually greater than that of
H_2S_x. This arises because the extinction coefficient for H_2S_x is greater
than that for $H_2S_{(sol)}$, i.e. H_2S_x absorbs infrared radiation more strongly.
Concentrations of both $H_2S_{(sol)}$ and H_2S_x were obtained from spectra such as
those shown in Fig. 5 by application of Beers Law. As mentioned previously,
H_2S_x cannot be lost from sulphur directly - it must first decompose to
produce $H_2S_{(sol)}$. Thus, the rate of decrease of total H_2S concentration
$\left[H_2S_t\right] = \left[H_2S_x\right] + \left[H_2S_{(sol)}\right]$) is directly proportional to the concentration
of $H_2S_{(sol)}$

i.e.
$$\frac{-d\left[H_2S_t\right]}{dt} = k_2 \left[H_2S_{(sol)}\right] \qquad [8]$$

or
$$k_2 = \frac{-d\left[H_2S_t\right]}{dt} \Big/ \left[H_2S_{(sol)}\right] \qquad [9]$$

This holds as long as $\left[H_2S_{(gas)}\right] = 0$ i.e an open system, so that there is no
opposing process where H_2S redissolves in the sulphur. In this experiment
the system was open allowing the H_2S to diffuse away as it was released
from the sulphur and relationhsip [9] was valid. The indicated calculation
was performed a number of times throughout two different runs resulting in
a value which was essentially constant except for a sharp rise near the end
of each run. At this time the concentration of $H_2S_{(sol)}$ became very small
and the rate of decrease of $\left[H_2S_t\right]$ became dependent on the rate of
decomposition of H_2S_x whose concentration was still relatively high (see
Fig. 6). The average value for k_2 obtained from the two runs was 0.035 hr^{-1}.
This is a typical first order rate constant containing no concentration
units. Since K_2 was known, k_{-2} could be calculated from relationship [6]
and was found to be about 0.014 hr^{-1} - another pseudo first order rate
constant.

k_1 and k_{-1} could not be obtained in such a direct manner. Since
formation and decomposition of H_2S_x are taking place at all times, the
observed decrease in the concentration of H_2S_x depends on the difference
between the two rates. However, when the concentration of $H_2S_{(sol)}$

FIG. 5

H_2S H_2S_x

2 ppm
135 HR.

70 ppm
61 HR.

164 ppm
24 HR.

398 ppm
1.4 HR.

IR spectra as a function of time showing decrease in concentration (ppm) of both H_2S (2570 cm^{-1}) and H_2S_x (2498 cm^{-1}).

becomes very small, the rate of re-formation of H_2S_x becomes negligible. We then have:

$$\frac{-d[H_2S_x]}{dt} = k_1[H_2S_x] \qquad [10]$$

or

$$\frac{-d[H_2S_x]}{[H_2S_x]} = k_1 dt \qquad [11]$$

Integration gives:

$$\ln[H_2S_x] = k_1 t + c \qquad [12]$$

The concentration of $[H_2S_x]$ or $[H_2S]$ can be expressed in terms of Beers Law relationship e.g. $\log I_0/I = [H_2S_x]$. Therefore, a log log I_0/I plot for each species as a function of time should yield the linear relationship indicated by equation $[12]$. These plots are shown in Fig. 6. Both the H_2S_x and H_2S plots are good linear relationships during the initial degassing period. This is because the ratio of the concentrations of H_2S_x and $H_2S_{(sol)}$ remains fairly constant and the apparent rate of loss of H_2S_x is due to the difference between the rates of formation and decomposition. However, as the degassing proceeds, $H_2S_{(sol)}$ is depleted faster than H_2S_x since there is no H_2S redissolving. Thus, the net rate of loss of H_2S_x increases as shown by the increase in slope and it is the slope of the steep line at the end which was used to calculate k_1. An average value of 0.065 hr^{-1} was obtained. Equation $[5]$ then yielded a value for $k_{-1} = 0.014$ hr^{-1}.

At first glance it would appear that k_2 could also be obtained from Fig. 6, since the plot for $H_2S_{(sol)}$ is a fairly straight line. However, the change in concentration depends on the balance between the rate of loss of H_2S from the system, the rate of reaction with sulphur to form H_2S_x and the rate of decomposition of H_2S_x. If k_2 is calculated from the slope of the line in Fig. 6 a value of about 0.014 hr^{-1} is obtained, compared with the value of about 0.035 hr^{-1} found as described above.

In summary, the values found for the various constants are:

$k_1 \approx 0.065$ hr^- $k_2 \approx 0.035$ hr^-

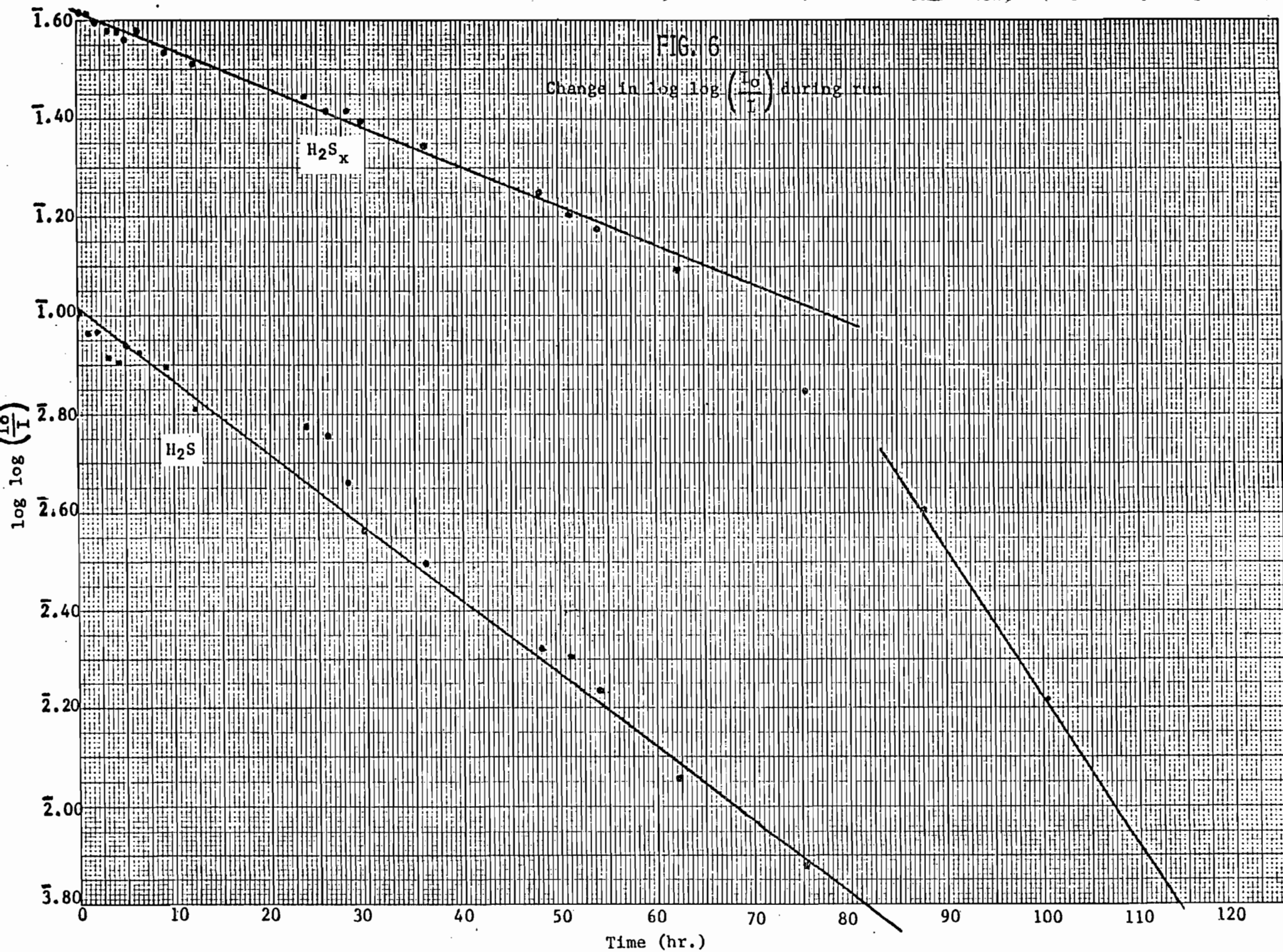$k_{-1} \approx 0.014$ hr^- $k_{-2} \approx 0.014$ hr^-

$K_1 \approx 0.21$ $K_2 \approx 0.40$

$K_3 \approx 0.47$ $K_3 \approx 0.49$ (calc. from eq. $[7]$)

$\approx 3.4 \times 10^{-4} \frac{\text{ppm in liquid}}{\text{ppm in gas}}$

FIG. 6

Change in $\log \log \left(\frac{I_0}{I}\right)$ during run

The use of approximation signs is intended to indicate uncertainty of values quoted. Due to the low concentrations of the species being measured, great accuracy is difficult to achieve. Errors involved in the IR determinations of $\left[H_2S_{(sol)}\right]$ and $\left[H_2S_x\right]$ may be as great as 3%. This makes precise rate constants difficult to obtain. The uncertainty for values for k_1 and k_2 were $\pm$ 15%. K_1, which was taken from the data of Wiewiorowski and Touro is probably accurate to within $\pm$ 5%. However, K_2 and K_3, calculated from their data, are 0.53 and 0.64 respectively, or about 35% greater than our values of 0.40 and 0.47. This difference could be explained if H_2S escaped slowly from the closed cell in these experiments. If so, k_{-2} which was calculated from K_2 would be in error by the same percentage. The fact that the calculated K_3 differs from the experimentally determined value by only 4%, however, shows that the rate and equilibrium constants quoted above are at least self-consistent.

Implications for the Rate of Degassing

This work and other experience point out a number of factors which affect the rate of loss or removal of the total H_2S content of sulphur. One very important factor is temperature. Almost all processes speed up as the temperature is raised and this case is no exception. In a complex system of coupled forward and reverse reactions such as that indicated in equation [1] the effect of temperature on all of the rate constants must be considered before arriving at a conclusion about the effect of temperature on the overall process. Generally speaking, however, both the rate of decomposition of H_2S_x and the rate of loss of H_2S from solution will both increase with temperature. Therefore, provided that the system is open and the released H_2S can escape higher temperatures will favour faster degassing of the sulphur as far as H_2S is concerned. However, at 159°C, the viscosity of sulphur rises sharply as it polymerises. This rise in viscosity slows down the rate of diffusion within the sulphur and, consequently, slows down the rate at which H_2S escapes. A high concentration of H_2S greatly lowers the viscosity of sulphur in this temperature range, allowing a greater rate of loss than would be expected. However, as the concentration of H_2S decreases, the viscosity will increase and the loss of H_2S will become much slower. The time required for sulphur with 100 ppm total H_2S to approach 0 ppm is about 4 days at 125°C but at 160°C this increases to about 10 days.

Purging with an inert gas, such as nitrogen, also speeds the loss of H_2S. Our experience in degassing sulphur samples while using nitrogen sweep indicates that it takes approximately 24 hours to reduce total H_2S content from 100 to 10 ppm. A recent Japanese patent involves removing H_2S from sulphur by blowing countercurrently with waste gas[25].

Since the rate controlling step in H_2S degassing of liquid sulphur is the decomposition of H_2S_x catalysts can greatly reduce degassing times. Tuller's method for determining total H_2S content of sulphur[27] and ASR's refinement[28] involve use of a lead sulphide catalyst and purging with nitrogen to remove all the H_2S from the sulphur. This can be accomplished in about 1 hour even if the sample initially contains 200 ppm

total H_2S. Ammonia and various amines are also effective catalysts for the decomposition of H_2S_x. The objection to use of a catalyst is that another contaminant is added to the sulphur which may be undesirable in itself (e.g. lead). The possibility of using alumina or spent bauxite, has been suggested by Rennie[23]. A recent British patent[26] employs addition of SO_2, along with an amine, to remove H_2S.

Surface area of the liquid sulphur being degassed is another factor. Although a preliminary examination suggested that the effect might be minimal, one would expect faster loss of H_2S if the sulphur is allowed to stand in a very wide, shallow container. Stirring should also help, presumably by increasing the effective surface area by continually bringing fresh sulphur to the surface. This would prevent establishment of a gradient with low H_2S sulphur at the surface and high H_2S sulphur trapped below. This idea has also resulted in a patent involving liquid sulphur being passed over a series of baffles in a vented tower[24]. However, from 1 to 9 days are required. The effect of purging with an inert gas may also be due to an increase in effective surface area with each bubble representing a fresh surface.

The above considerations all deal with liquid sulphur. Solidification of sulphur results in the immediate loss of about 20 to 30% of the total H_2S content, this being almost exclusively H_2S in solution. Melting of solid sulphur also results in the loss of considerable H_2S (20-50%), the amount depending on the thermal history of the solid. Any H_2S_x trapped in the solid sulphur matrix on solidification will slowly decompose in the solid state to yield H_2S which will be released on remelting. The rate of H_2S decomposition in the solid will be temperature dependent. This, of course, is the reason sulphur remelters and sulphurcrete production areas should have good ventilation.

In the solid state, loss of H_2S becomes extremely slow. Loss of 100 ppm total H_2S content would take years at 70°F and would become even slower at lower temperatures. This is not to say that the processes involved stop – they still take place, but at much slower rates. H_2S_x still decomposes and $H_2S_{(sol)}$ still comes out of solution resulting in H_2S gas. The gas, however, becomes trapped in the crystals matrix unless it happens to be at the surface. All of this implies that the longer a solid sulphur sample is stored, the easier it should be to degas, although temperature of storage is also very important[32].

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THE ASR INFRARED LIQUID SULPHUR ANALYZER
DETERMINATION OF H_2S, H_2S_x & HYDROCARBON CONTENT

by
W.J. Schwalm and J.B. Hyne

INTRODUCTION

Over the last several years, Alberta Sulphur Research has gained considerable experience in the analysis of liquid sulphur. By 1975, it had become obvious to us that Tuller's accepted method for determination of the H_2S content of sulphur [1] often gave results which were too low by 20 - 35%. As a result, a modification of this method was adopted and published in ASR's Quarterly Bulletin [2]. However, the slowness of the method, the skill level required and the fact that it does not distinguish between H_2S and H_2S_x make this "wet chemical" method less than ideal for routine analysis.

The pioneering work of Wiewiorowski and his co-workers [3,4] in the infrared analysis of liquid sulphur has been followed up in ASR's research laboratory. Modifications were made in the length of the heated cell and a custom-made temperature control unit was designed and built. The resulting system has proved very satisfactory for H_2S/H_2S_x analysis both in the lab and in the field and has been described in the Quarterly Bulletin [5] as well as at Chalk Talks presented to member companies of ASR.

The article to follow is a written version of the presentation given at the Chalk Talk on June 25, 1980. It represents an update on the system including recent technical improvements and field experience. In addition, the recent extension of the method to the analysis of liquid sulphur for hydrocarbons is described. This makes the ASR Infrared Analyzer even more valuable, especially in view of the increasing amounts of block sulphur (undoubtedly contaminated over the years) being remelted, reformed and shipped to market.

COMPONENTS

The major components of the system are contained in two boxes about the size of small suitcases, weighing 20 to 30 lbs each (see Figure 1). One box contains the infrared spectrometer, the heated sulphur cell, the temperature control unit and a few minor accessories. The second box contains an external recorder.

The infrared spectrometer is a Wilks Miran 1A-CVF Infrared Analyzer, the centre light-colored component in Figure 2. This is a relatively inexpensive instrument which can, with slight modification, accomodate the rather bulky heated cell. An important feature of this particular spectrometer is that absorbance readings can be obtained directly, eliminating the need for conversion of the results to logarithms. The detector is mounted at the opposite end of the cell and its electrical signals are fed back to the spectrometer.

The heated cell has been shown previously [5] and is the small square metallic box on the left side of the spectrometer in Figure 2. Basically, it is an insulated block of aluminum fitted with rod heaters. An internal cavity 4.5 cm in length and 2.5 cm in diameter contains the sulphur sample. A recent improvement consists of incorporation of a siphon system to facilitate unloading. In many cases, the sulphur drains from the cell as soon as the teflon plug is removed from the outlet. Otherwise, application of pressure by means of a rubber bulb is required. Loading is facilitated by use of a small aluminum funnel.

The temperature controller is custom-made and supplies power to the rod heaters in short pulses. The actual temperature of the cell is sensed by a thermocouple. This signal is fed to the controller which modifies the power supplied to the heaters accordingly. The necessity of good temperature control will be outlined in due course. The controller is the dark rectangular object nestled in the right-hand side of the carrying case in Figure 2.

The second box contains a Deluxe Laboratory Chart Recorder, Single Channel Model, from Linear Instruments. As will be seen later, one of the more important features of this recorder is that a number of attenuations of the signal from the spectrometer are available. A portion of the recorder is seen to the left of the opened carrying case in Figure 2.

The last piece of apparatus is a sampling pot, slightly larger than a two-litre container (see Figure 3). The capacity of the pot is only about 50 ml but it has very thick aluminum walls and a layer of insulation. The heat loss is thus very slow and, once heated electrically, this pot is capable of keeping a sulphur sample in the liquid state for 15 - 30 minutes without further heating. Solidification must be prevented if accurate results are to be obtained for the H_2S and the H_2S_x contents of the liquid sulphur samples. The reason for this will be explained later.

It can be seen, from the above description, that the entire system is very portable. It can easily be carried about in a car and set up in a minimal amount of space (about 4 ft x 2 ft). Analyses can be performed anywhere that 115V AC power is available.

OPERATION

The heated cell reaches the set temperature in about 10 minutes. However, the infrared analyzer and the recorder are allowed to warm up for about 30 minutes before running any spectra. Therefore, just over one half hour elapses before the first spectrum is obtained.
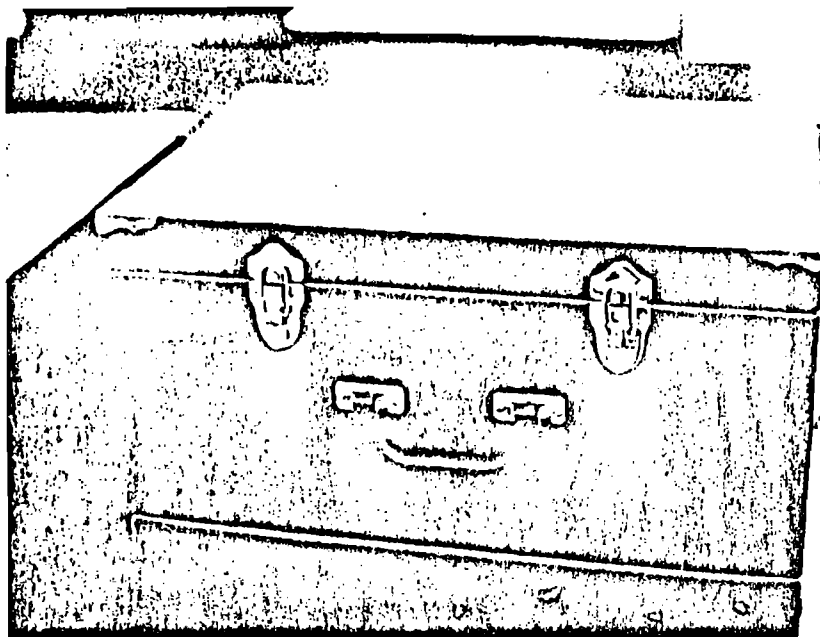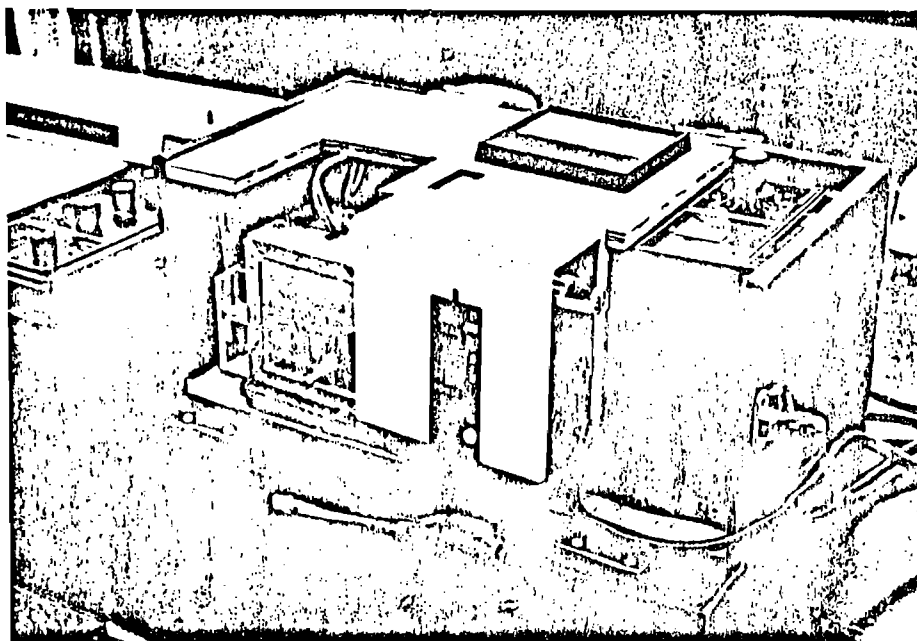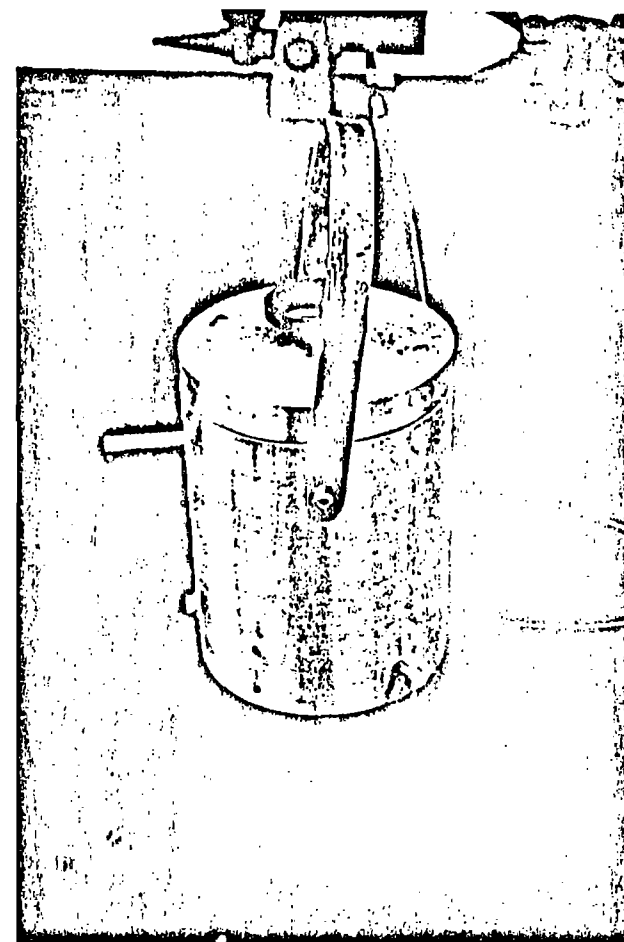
Figure 1

Figure 2

Figure 3

Spectra can now be obtained more quickly than samples can be brought to the instrument from the sampling points in a gas plant. The cell is filled with sulphur from the sampling pot using the aluminum funnel. Appropriate settings are selected for the spectrometer and the recorder and the desired portion of the spectrum is scanned. For H_2S/H_2S_x analysis alone, the region from 3.5 - 4.2 μm (microns) is scanned which takes less than 50 seconds. After unloading the cell using the rubber bulb to force out the last drops of the sample, a new sample can be introduced. The entire procedure takes about 5 minutes per sample.

ANALYSIS FOR H_2S AND H_2S_x

The spectra shown in Figures 4 and 5 were obtained in the field at Alberta sulphur plants. Figure 4 shows the spectra of two samples with very high H_2S/H_2S_x concentrations. In fact, the total H_2S contents of these samples are among the highest ever seen by ASR. Figure 5 shows the spectra of three samples with lower concentrations. Attenuation on the recorder is varied from spectrum to spectrum.

The first four spectra show two peaks each. The peak on the left in each spectrum is at 3.89 microns (2580 cm^{-1}) and is due to H_2S. The peak on the right occurs at 4.00 μm (2498 cm^{-1}) and is due to H_2S_x. This ability to distinguish between the two is one of the great advantages of the infrared method. For a comprehensive discussion of the H_2S-H_2S_x-sulphur system see reference 5.

It may seem rather odd that the peak for H_2S_x is often larger than that for H_2S even though the concentration of the latter is greater. This occurs because the extinction coefficient for H_2S_x is several times greater than for H_2S. In other words, the infrared technique is more sensitive to H_2S_x than to H_2S.

The large size of the H_2S_x peak sometimes makes it rather wide as well as high. This width may affect the separation of the two peaks. In these cases, the H_2S peak becomes a shoulder, rather than a distinct peak but measurement of the H_2S concentration is still possible.

The importance of the attenuation feature of the recorder employed is demonstrated in these spectra. The input factor (I.F.= 2V, 1V or 0.5V) chosen is shown on each spectrum. The readout on the spectrometer is only 0 - 1V. However, the output is 0 - 2.5V and use of the 2V setting on the recorder kept the large H_2S_x peaks of the spectra on Figure 4 on-scale. Had this not been possible, these peaks would have gone off-scale making measurement of the H_2S_x concentrations of the corresponding samples impossible. Only minimum values can be quoted for off-scale peaks.

FIGURE 4

TOTAL – 413 ppm   TOTAL – 405 ppm

H_2S_x 178 H_2S_x 115

I.F. = 2V   I.F.= 2V
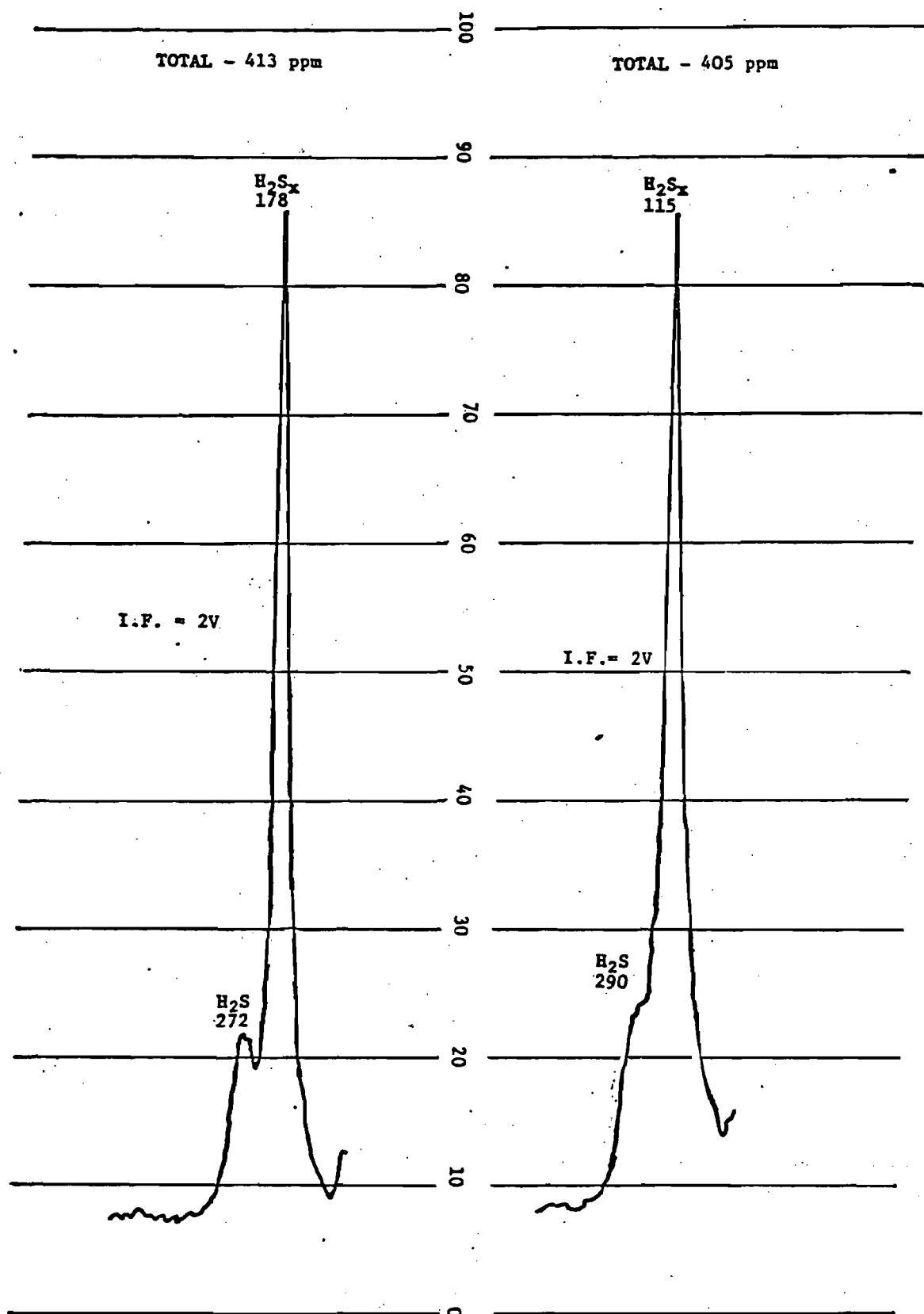
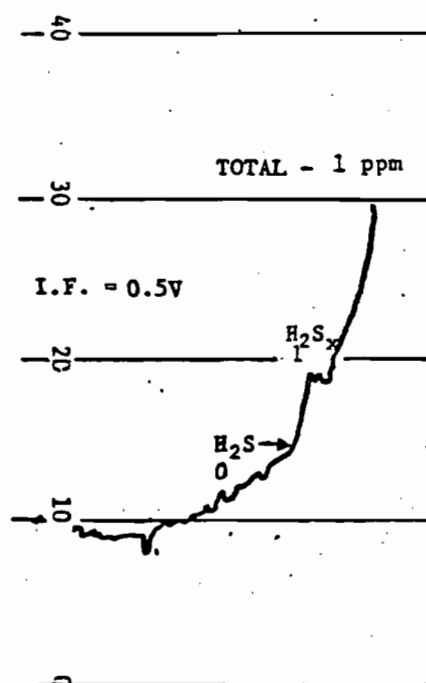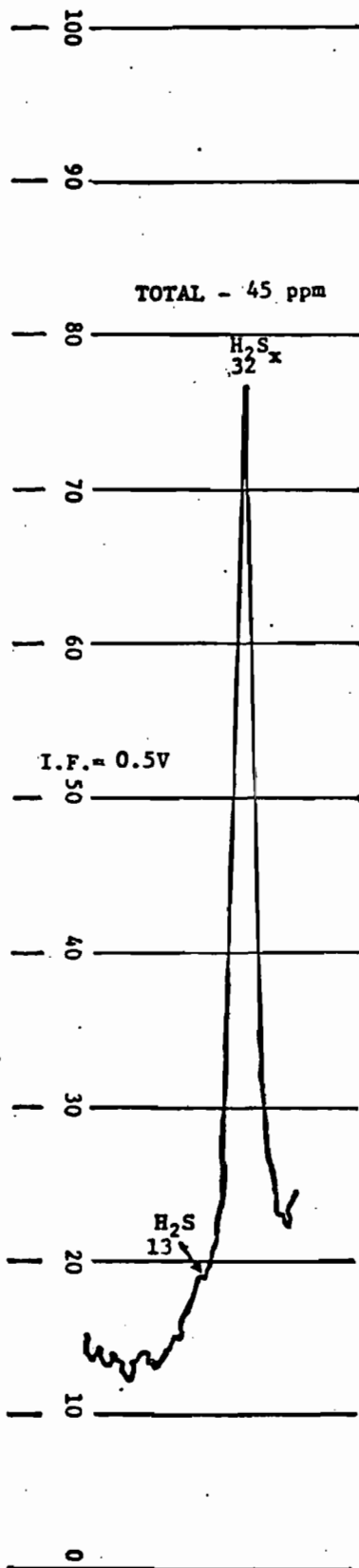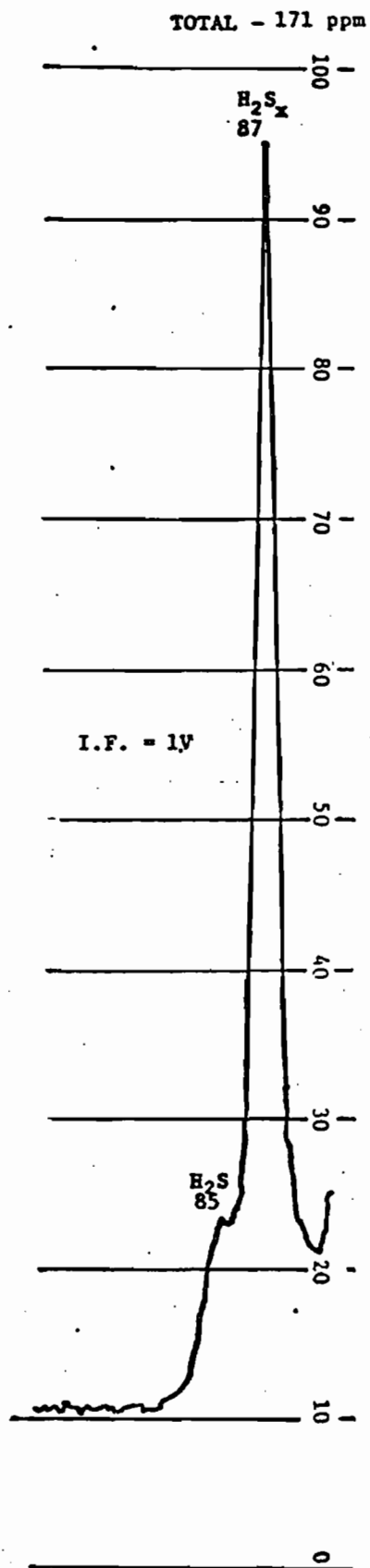H_2S 272 H_2S 290

FIGURE 5

The first spectrum on Figure 5 was run with an input factor of 1V and the last two with 0.5V. By decreasing the attenuation, the peaks are kept as large as possible, thereby increasing the accuracy of the measurements. (Decreasing the input factor below 0.5V usually does not help because electrical noise is also magnified).

The last two spectra on Figure 2 give an idea of the lower limits of detection for H_2S and H_2S_x using the ASR Infrared Analyzer. At 13 ppm, the H_2S peak has almost disappeared, but this is partly due to the width of the H_2S_x peak on this particular spectrum. Normally, one can measure H_2S concentrations down to about 10 ppm. On the last spectrum, the H_2S peak has completely disappeared but the peak due to H_2S_x can still be seen even though it corresponds to only 1 ppm. H_2S_x can be measured down to about 1 ppm in most cases.

Thus we can quote the following values for the range of the ASR Infrared Analyzer, with respect to total H_2S:

Detect to 1 ppm (if in the form of H_2S_x)
Measure quantitatively; 10 - 1300 ppm

This is a very wide range, considering the fact that a constant path length is employed - the entire range can be measured with one cell. Selection of a recorder with a number of attenuation factors has helped to make this wide range possible.

The accuracy of the ASR Infrared Analyzer can be quoted, somewhat conservatively, as:

at 10 ppm - ± 2 ppm (±20%)
at 100 ppm - ± 5 ppm (±5%)
at 1,000 ppm - ± 20 ppm (±2%)

In practice, the accuracy is usually better than indicated. Considering the speed of the method and the low concentrations being measured (100 ppm is only 0.01%), these levels of accuracy are very good. As would be expected, accuracy becomes relatively better at higher concentrations.
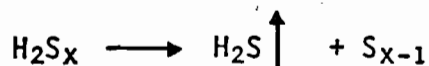
The calculations involved are very simple, which is another advantage of this particular system. As pointed out before, the infrared instrument incorporated in this package can give absorbance values directly, eliminating the need for logarithmic conversions. In addition, absorbance (i.e. peak height) is directly proportional to concentration over the entire concentration range. Therefore, one needs only to multiply peak height by a pre-determined calibration factor. One such factor is obtained for H_2S, and another for H_2S_x, by scanning the infrared spectrum of a liquid sulphur sample saturated with H_2S and H_2S_x. Saturation is achieved by bubbling in H_2S for at least 24 hours under an atmosphere of H_2S.

Figure 6

ACTUAL PLANT ANALYSES (ppm)

Plant 1	H_2S	H_2S_x	TOTAL
1st CONDENSER RUNDOWN	82.6	127	210
2nd CONDENSER RUNDOWN	20	52	72
3rd CONDENSER RUNDOWN	8	11	19
SULPHUR TO SLATER	23	53	76
FRESH SLATE	25	35	60
SULPHUR FROM REMELTER	--	6	6

Plant 2			
W.H.B. RUNDOWN	200	132	332
CONVERTER #1 RUNDOWN	50	57.2	107
CONVERTER #2 RUNDOWN	8	19	27
RUNDOWN PIT	72	69.4	141

with an inert gas, but removal of the H_2S_x requires a catalyst to aid in its decomposition. The sulphur from the rundown pit of Plant 2 (Figure 6) could easily be reduced to about 70 ppm but further degassing, in the absence of a catalyst, could take days. Reference 5 contains a much more complete discussion of the topic of degassing. The ASR Infrared Analyzer is obviously useful for monitoring a degassing process.

The real value of H_2S/H_2S_x analysis in the plant is not so much in the values obtained at a given time but in changes detected by regular monitoring at various points in the plant. Changes in the H_2S and/or H_2S_x levels may be the first indication of changes occurring in the plant. In particular, a change in temperature and/or conversion efficiency should be accompanied by a change in the $H_2S_x:H_2S$ ratio of the sulphur produced. This application is presently being examined.

Figure 7 shows the saturation levels of H_2S and H_2S_x in sulphur as a function of temperature. The true solubility behaviour of free H_2S in sulphur is that of a normal gas-liquid system since there is a slight decrease in solubility with increasing temperature as indicated by the line labelled "H_2S". However, matters are complicated by the reaction of H_2S with sulphur to form H_2S_x. The effect of temperature on this process is twofold.

$$H_2S + S_{x-1} \rightleftharpoons H_2S_x$$

$$\longrightarrow$$
formation

Firstly, H_2S_x formation occurs at a greater rate at higher temperature. Secondly, at higher temperature, equilibrium favors a greater concentration of H_2S_x as shown by the "H_2S_x" curve on Figure 7. An increase in temperature, therefore, favors a higher $H_2S_x:H_2S$ ratio. The fact that this ratio changes with temperature is the most important reason for provision of good temperature control for the cell. It should be noted that Figure 7 is based on data obtained at a normal sea-level atmospheric pressure. The lower pressures encountered at the altitudes of Alberta sulphur plants would result in a lowering of both the "H_2S" and the "H_2S_x" curves but the ratio should remain unchanged.

In view of the above, an increase in the $H_2S_x:H_2S$ ratio at a certain point in a sulphur plant would likely indicate that the temperature has increased or that the H_2S content of the gas stream has increased at that point. It should be pointed out that the data of Figure 7 represent equilibrium situations, whereas samples taken from the various rundowns in a sulphur plant would not have had time to reach equilibrium. Despite this, any increase in temperature

Figure 7

Variation in the "Solubility" of Hydrogen
Sulphide with Temperature

Data Taken from T. K. Wiewiorowski and F. J. Touro,
J. Phys. Chem., 70, 234 (1966)

should still result in an increase in the H_2S_x:H_2S ratio (i.e. any change would be in the direction indicated by the equilibrium data).

The analyses of samples from Plant 2 (Figure 6) can be used to illustrate one further point regarding sulphur plant monitoring. If the rundown pit contains only fresh sulphur which has not had a chance to equilibrate and degas, analysis of the various rundowns being collected and of the sulphur in the pit may make possible an estimation (or confirmation) of the amounts of sulphur coming from these various sources. If all points are sampled at about the same time, the weighted averages of both the H_2S and H_2S_x contents of the various sulphur sources should be close to the H_2S and H_2S_x concentrations of the sulphur in the rundown pit.

HYDROCARBON CONTENT

Thus far the discussion has dealt exclusively with H_2S and H_2S_x determinations. However, with no modifications whatsoever, the hydrocarbon content of liquid sulphur can also be determined using techniques previously described by Wiewiorowski and co-workers.

This information is important for two basic reasons. Sulphur, to meet export specifications, must contain no more than 250 ppm of hydrocarbons. Figure 8 shows the spectrum of a sulphur sample containing 242 ppm of an aliphatic hydrocarbon mixture. This spectrum was run using the 5V input factor of the recorder which is the least sensitive setting for this recorder. The fact that the recorder had to be attenuated so much shows that the extinction coefficient for hydrocarbons is even larger than that for H_2S. However, even with the long path length of the heated sulphur cell, the peak height was only 2.3 absorbance units. Thus, the upper specification limit for hydrocarbons is just within the maximum range of the instrument (0 - 2.5 volts which corresponds to 0 - 2.5 absorbancs units).

The second major reason for analyzing sulphur hydrocarbon content is the reaction between liquid sulphur and hydrocarbons:

$$-(CH_2-CH_2)- + S \xrightarrow[\text{eg. remelting}]{\text{heat}} H_2S + -\overset{|}{\underset{\underset{S_y}{\overset{|}{\underset{|}{S}}}}{C}} - C - S - S_x - S - \overset{|}{C} - \overset{|}{C} -$$

hydrocarbon   "carsul polymer"

FIGURE 8

EXPORT SPECIFICATION

MAXIMUM HYDROCARBON CONTENT = 250 ppm

HYDROCARBON CONTENT OF THIS SAMPLE = 242 ppm

Although the reaction has been illustrated for an aliphatic hydrocarbon, aromatic hydrocarbons also react. In the early stages of the reaction, only a few of the hydrogen atoms are replaced by sulphur chains. However, as the reaction continues, more hydrogens are replaced until a high molecular weight polymer consisting largely of carbon and sulphur atoms is formed. This "carsul" is a typical polymer in having high viscosity and it can cause problems in handling and forming sulphur. Of course, the higher the concentration of hydrocarbons at the start, the more "carsul" can be formed. The reaction is a fairly slow one and can be minimized by keeping the temperature of the liquid sulphur as low as possible and keeping the sulphur in the liquid state for as short a time as possible. Removal of dissolved hydrocarbons from sulphur, unfortunately, is very difficult, requiring boiling it over magnesium oxide for many hours [6] or contacting it with sulphuric acid [7].

The hydrogen removed from the hydrocarbon combines with sulphur to produce H_2S and H_2S_x. This slow production of H_2S can influence analyses for H_2S and H_2S_x, especially if the sulphur is in an enclosed space (such as a rail car) where significant loss of H_2S to atmosphere cannot take place. Since the atomic weight of sulphur is 32 and that of carbon is only 12, conversion of 100 ppm of aliphatic hydrocarbon to carsul and H_2S could give rise to a theoretical increase of over 250 ppm in total H_2S content. Aromatic hydrocarbons should cause less problems than aliphatics, partly because the reaction should be slower and partly because aromatics contain proportionately less hydrogen which would mean a lower production of H_2S.

An additional problem caused by the reaction of hydrocarbons with sulphur is the resulting discoloration of the sulphur. The color of the sulphur becomes brown and, under extreme conditions, a black color may result. In fact, this color change can be used for a qualitative evaluation of the hydrocarbon content of sulphur. If a sulphur sample containing hydrocarbon is heated to 210°C for two hours the color of the solid on resolidification gives a rough idea of the hydrocarbon content. However, the length of time required and the non-quantitative nature of the results obtained make this method very unsatisfactory.

Four oxidation and heat-treatment methods are available [8] for determination of the hydrocarbon content of sulphur. Unfortunately, all share the disadvantage of lengthy procedures requiring considerable operator skill.

ANALYSIS FOR HYDROCARBON, H_2S AND H_2S_x

The ASR Infrared Analyzer can be used, without modification, to obtain hydrocarbon concentrations as well as H_2S/H_2S_x contents of liquid sulphur samples. Only one very minor change in procedure is

required - the spectrum is run from 3.0 to 4.2 μm to obtain both hydrocarbon and H_2S/H_2S_x analyses whereas for H_2S/H_2S_x alone the narrower range from 3.5 to 4.2 μm is scanned. This adds less than one minute to the time required.

Figure 9 shows the spectrum of a sulphur sample over the wider range. It is obvious that the response of the instrument to aliphatic hydrocarbons is much stronger than even the response to H_2S_x. The extinction coefficient for aromatic hydrocarbons is about the same as for H_2S_x. Because of the differences in response factors and because the hydrocarbon and H_2S/H_2S_x contents are normally independent of each other, it will often prove desirable to change attenuations between the aliphatic hydrocarbon peak and the H_2S peak. One half of the spectrum may require higher attenuation (a higher input factor) to keep the peak(s) on-scale whereas lower attenuation is desirable for the other half of the spectrum for greater accuracy.

The shoulder on the side of the aliphatic hydrocarbons peak is typical - all aliphatics show two peaks in this region, a strong peak at about 3.4 μm and a somewhat weaker peak at about 3.5 μm. Only the larger of the two peaks is used in calibrations and in the determination of concentrations. Usually, only one peak at about 3.25 μm is seen for aromatic hydrocarbons.

There is a major difference between the calculations for H_2S/H_2S_x content and those for aliphatic hydrocarbon content. The response of an infrared instrument to aliphatic hydrocarbons is not related to concentration in a linear manner as it is for H_2S and H_2S_x. Therefore a single calibration factor cannot be determined for aliphatics content. A calibration curve, such as that shown in Figure 10 must be used. The curve is obtained by plotting the absorbances of several samples of known hydrocarbon content. This curve will then give the hydrocarbon concentration of an unknown sample once its absorbance has been determined (provided that its concentration is within the range of concentrations covered by the calibration curve).

If the identities of the hydrocarbons in the sulphur to be analyzed are known, these should be used in the calibration. Most sulphur samples, unfortunately, contain complex mixtures of hydrocarbons. Thus, it is preferrable to use a typical aliphatic hydrocarbon (or a mixture of aliphatics) to calibrate the instrument for aliphatic hydrocarbons and an aromatic hydrocarbon (or a mixture) to calibrate for aromatics. We have found Nujol (a complex mixture of high molecular weight aliphatics commonly used in infrared work) to be satisfactory for calibration in the aliphatic region although Tuller [9] has recommended decahydronaphthalene. He recommends naphthalene for the aromatic region.

FIGURE 9

H$_2$S AND HYDROCARBON CONTENT

ALIPHATIC
HYDROCARBONS
25 ppm

I.F. =1V

TOTAL H$_2$S
19 ppm

H$_2$S$_x$
9 ppm

AROMATIC
HYDROCARBONS
3 ppm

H$_2$S
10 ppm

3.30 3.45 3.52   3.89 4.00

wavelengths in μm

Figure 10

HYDROCARBON CONTENT CALIBRATION CURVE

HYDROCARBON CONTENT (ppm)

...

and the H_2S/H_2S_x ratios at various points in a gas plant could provide useful information on the performance of the relevant components of the plant. H_2S is also known to affect the physical properties of sulphur, especially the strength of the solid [10] and the viscosity of the liquid [11, 13].

2) With no modifications to the equipment and without a major increase in analysis time, hydrocarbon levels can also be determined. The export specification for sulphur is a maximum of 250 ppm of hydrocarbon. The reaction between hydrocarbons and sulphur to form the "carsul" polymer plus more H_2S makes knowledge of the hydrocarbon level of sulphur still more desirable. As more block sulphur is remelted, after several years of exposure to possible contamination, a fast and accurate determination of its hydrocarbon content will become more and more valuable.

Calibrations must be done from time to time as the instrumental response can change. The method is not absolute and reference to one or more standards is, therefore, required. Measurement of very low levels of H_2S is not possible due to the low extinction coefficient of H_2S in the infrared. These levels, however, are of little concern at this time.

The advantages to use of the ASR Infrared Analyzer easily outweigh the disadvantages mentioned above. This package is a compact, highly portable system ideal for routine analyses of liquid sulphur for H_2S, and H_2S_x and both aromatic and aliphatic hydrocarbon concentrations. Results are obtained quickly and easily and a high degree of accuracy is the norm.

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The Removal of H_2S "dissolved" in Liquid Sulphur

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Introduction

Elemental sulphur produced by the Claus Process from sour natural gas always contains some dissolved hydrogen sulphide. The hot, liquid sulphur stream is in contact with a gaseous phase containing hydrogen sulphide resulting in dissolution of the hydrogen sulphide in the sulphur. This in itself would not be a serious problem if the dissolution was the only absorption process. However the hydrogen sulphide also combines chemically with the sulphur to form hydrogen polysulphides.

$$S_x + H_2S \rightleftharpoons H_2S_{x+1}$$

The problems associated with hydrogen polysulphides in the production of sour gas wells have long been recognised (1), and the above equilibrium reaction has been extensively studied (2, 3, 4). If hydrogen sulphide was merely dissolved in the sulphur, it could be readily stripped from the sulphur by an inert gas stream, such as nitrogen or even air. Also on first sight one would expect, as hydrogen sulphide is removed from the sulphur in an inert gas stream, the above equilibrium would be driven to the right, resulting in the breakdown of hydrogen polysulphides with the subsequent release of more hydrogen sulphide. This is in fact true, as has been demonstrated by Wiewiorowski (3) but the rate of the reaction is not instantaneous and extremely long purge times would be required. This explains why hydrogen sulphide release is not a serious problem at the plant in the area of the liquid sulphur storage pits, although an odour of H_2S is generally obvious in this area. Where sulphur is transported as a liquid in tank cars however, sufficient hydrogen sulphide may have been degassed by the time the shipment reaches its destination to present a definite hazard to personnel involved in the unloading operations if the prescribed safety procedures are not observed. There are potentially increasing markets for liquid sulphur, but it is probable that both customers and governmental agencies will regulate the allowed amount of hydrogen sulphide in the head space of liquid sulphur tank cars. It is therefore important to do something about the problem if these markets are to be taken advantage of and to ensure the retention of present markets for liquid elemental sulphur. The industry is aware of these problems and has been successful in some instances in removing the hydrogen sulphide from the liquid sulphur during the loading operation. For example one such method is to carry out a Claus reaction in liquid sulphur (5). Nitrogen containing compounds such as amines are known to catalyse the reaction between hydrogen sulphide and sulphur dioxide in liquid sulphur.

$$2H_2S + SO_2 \underset{S_1, \text{ amine}}{\overset{110° - 160°C}{\rightleftharpoons}} 3S + 2H_2O$$

The removal of all the hydrogen sulphide from elemental sulphur produced by the Claus Process is likely to become more important as new uses are found for sulphur. In particular, it would obviously be undesirable to have seepage of hydrogen sulphide from such materials as sulphur concretes and ashphalts. The decomposition of the hydrogen polysulphides would be very slow in the solid state and the hydrogen sulphide released would be largely trapped in the solid matrix and released slowly to the atmosphere. Also it would be advantageous to remove the hydrogen sulphide from the sulphur prior to the slating operation as hydrogen sulphide is known to reduce the strength of elemental sulphur (6).

The purpose of this research project is to develop a cheap, efficient method for the removal of hydrogen sulphide from liquid sulphur as it is produced at the plant. As was mentioned earlier one method used at the present time is to add an organic base to the sulphur to promote decomposition of the hydrogen polysulphides and also to act as a catalyst for reaction between the liberated hydrogen sulphide and sulphur dioxide which is added to the system. This procedure does not remove all the hydrogen sulphide and adds another contaminant, namely the organic base which can adversely effect strength of solid sulphur (7). The approach used in the work reported here is to replace the organic base with an inert basic material which will not dissolve in or chemically react with the sulphur.

Experimental Results

In any examination of the efficiency of various techniques for the removal of H_2S from liquid sulphur it is essential that an effective and reliable analytical technique be available for determining the H_2S content before and after treatment.

Molten sulphur at 140°C is saturated with hydrogen sulphide. A sample of this sulphur (100 - 200 g) is then analysed for hydrogen sulphide content by the procedure outlined below which is based on a published method (8). A sample of this sulphur (∿250 g) is also added to a heated vessel (160°C) containing 40 g of the catalyst to be tested. (Approximate depth of catalyst bed 1" and height of sulphur column 4"). The sulphur is allowed to stand over the catalyst with occasional agitation for 10 minutes. The sulphur (∿200 g) is then transferred to a heated (140°C) pre-weighed purge vessel containing 2 g of lead sulphide to catalyse the release of the remaining hydrogen sulphide. The system is purged 2 hours with nitrogen, the off gases being passed through two traps containing 100 mls of 3% zinc acetate solution in each trap.

After 2 hours the absorption flasks are removed from the system and the contents transferred to a 500 ml Erlenmeyer flask. The flask is then cooled in an icebath to below 10°C. Formaldehyde solution (5 mls) and 10% acetic acid (20 mls) are added to prevent any sulphur dioxide present consuming iodine. Maintaining the temperature below 10°C, 0.1N standard iodine is pipetted into the solution until a deep iodine colour persists after allowing the solution to stand for 5 minutes. (Usually 20 mls of 0.1N iodine is sufficient). Maintaining the temperature below 10°C, the solution is titrated with a standard thio-sulphate solution (0.1N) using a starch solution as indicator.

A blank determination is carried out on the reagents.

Calculations

$$\% \ H_2S = \frac{1.7N}{W} \ \frac{(\nu_B V_D - \nu_D)}{V_B}$$

Where

W = Wt. of sulphur sample in grams
V_D = ml. of standard iodine solution used in the determination
ν_D = ml. of standard sodium thiosulphate used in determination
V_B = mls. of standard iodine used in the blank
ν_B = mls. of standard sodium thiosulphate solution used in blank
N = normality of standard sodium thiosulphate solution

Results

Table I

Catalyst	BLANK (ppm $H_2S \pm 2$)	SAMPLE (ppm $H_2S \pm 2$)	% REDUCTION
Limestone	85	65	23.5
PbS[a]	108	56	48
Soda Glass	40	46	–
Soda Glass (acid washed)	84	71	–
Kaiser Alumina (KA-201)	117	37	68.4
Spent Bauxite[b] (2nd Bed)	101	34	66.3
Spent Bauxite[c] (1st Bed)	94	86	–
Spent Bauxite[c] (1st Bed)	101	99	–
Spent Bauxite[c] (2nd Bed)	75	49	34.5
Fire Brick[d]	87	79	–

a - prepared using Kaiser Alumina KA-201 as a support
b - the catalyst was not dried prior to use
c - catalyst predried for 2 hours at 140°C before use
d - high alumina - 90%

Each of the several catalysts for H_2S release were examined first measuring the H_2S content of a sample of the H_2S loaded sulphur (BLANK) and then determining the residual H_2S in the remainder of the sample after treatment with catalyst - (SAMPLE). The results in Table I are therefore relative and demonstrate the degree of removal of H_2S achieved (% REDUCTION).

The results shown in Table I indicate that the catalysts Kaiser Alumina (KA-201) and spent bauxite (2nd Bed) merit further investigation. In the case of the lead sulphide catalyst, it was necessary to coat the sulphide on a support to prevent contamination of the sulphur. The support used in this case was Kaiser Alumina KA-201 and as better results were obtained with uncoated KA-201 (Table I) it would be pointless to continue experimenting with this particular system.

The experiments using spent bauxite (2nd catalyst bed) showed an improvement in the ability to promote the removal of hydrogen sulphide when the catalyst was not predried. This is probably due to a combination of the purging action of the stream and a catalysed Claus reaction. The spent bauxite catalyst from the 2nd Bed is obviously superior to that from the 1st Bed which operates under heavier loads and consequently may be more deactivated (sulphated) than the 2nd Bed (i.e. less basic sites).

The results obtained with the high alumina (90%) fire brick are interesting in that very little surface area active alumina (KA-201) promoted a substantial hydrogen sulphide release. This could in part be due to the vast differences in surface areas but may be due to the alumina in the fire brick being a different modification to that in the KA-201.

The system being used in the laboratory is a static system in that the sulphur, saturated with hydrogen sulphide stands over the catalyst for a short time prior to being analysed for hydrogen sulphide. This is an inefficient method of contacting the sulphur and catalyst and could be improved by allowing the sulphur to pass down a heated column packed with the catalyst. A further improvement should be achieved if an inert gas is used to purge the system.

- 23 -

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METHODS FOR ANALYSIS OF H$_2$S IN SULPHUR

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Introduction

For various reasons a knowledge of the amount of hydrogen sulphide in sulphur is often needed. Since H$_2$S is a very toxic gas, safety aspects must be considered. The release of H$_2$S from solid sulphur is slow, so this seldom becomes a problem in open spaces. However, in confined areas, especially if the sulphur is remelted, dangerously high concentrations of H$_2$S in the air can arise (e.g. head spaces of railway tank cars (1)). In addition, the presence of even 10 ppm of H$_2$S can substantially reduce the strength of elemental sulphur (2) or of sulphur composites. This is currently an active area of research by workers in the sulphurcrete field. This strength reduction aggravates an already serious dusting problem and, of course, released H$_2$S is itself a pollutant.

It is now well established that H$_2$S does not simply dissolve in sulphur, but also reacts to form hydrogen polysulphides or sulphanes (H$_2$S$_x$) (3,4,5). This complicates analysis because one must decompose the polysulphides in order to remove all of the H$_2$S (6). Thus, methods such as the use of lead acetate tape are susceptible to errors, since they only detect the free H$_2$S. One approach is to look at the H$_2$S and H$_2$S$_x$ directly by an in situ technique such as the IR method recently developed by Alberta Sulphur Research Ltd. The other approach is to remove the H$_2$S and H$_2$S$_x$ from the sulphur and analyze chemically to obtain a total H$_2$S value. This is the basis of the "wet chemical" techniques also employed by ASR.

Search for an Accurate Method

Until the summer of 1974 ASR employed the method described by Tuller (7). This method involved bubbling nitrogen through liquid sulphur to purge out the free H$_2$S and that arising from the H$_2$S$_x$. The nitrogen stream was passed through two scrubbing towers containing zinc acetate solution which removed the H$_2$S by forming the insoluble zinc sulphide, ZnS. This was then treated with acetic acid to liberate the H$_2$S and a known excess of iodine was added, giving rise to the reaction:

$$H_2S + I_2 \rightarrow S \downarrow + 2H^+ + 2I^-$$

Finally, the remaining iodine was titrated with thiosulphate and from this, the amount of H$_2$S in the sample was calculated.

Although this is a widely accepted method, results were frequently obtained which were too low by 20 - 35%. It was suspected that the problem arose from the loss of H_2S on reliberation from the ZnS. Small bubbles were sometimes observed at this stage, indicating that some of the H_2S was escaping before reacting with the iodine. In addition, the solutions involved are subject to bacterial degradation so that their concentrations can change over a period of time.

A literature search for a more reliable method was then launched. One method which seemed to show promise involved the formation of methylene blue on the reaction of the zinc sulphide, formed as in the above method, with p-aminodimethylaniline in the presence of acid and ferric chloride. The amount of H_2S present in the sample is calculated from the absorbance of the solution at 670 nm. in the red end of the visible spectrum (8,9). This method is widely used for the determination of small quantities of H_2S in gas streams. Unfortunately, this method is very sensitive to slight variations in conditions such as small quantities of impurities and the dielectric constant of the solution. Since this method is designed for very small amounts of H_2S, analysis of sulphur samples from gas plants would require considerable dilution of solutions, introducing another source of error. In addition, many standards would have been required for calibration of the method. For these reasons, it was decided not to proceed in adapting this method for our H_2S analyses.

The literature search also produced a method (10) using silver nitrate, $AgNO_3$, as the absorbent for H_2S, forming silver sulphide, Ag_2S, which is exceedingly insoluble in water. The Ag_2S is then filtered off and washed thoroughly and the filtrate is titrated with ammonium thiocyanate using ferric ion as the indicator. This is a standard method for the determination of silver ion (11,12). From the difference between the amount of silver in the solution before and after purging the sample, the amount of H_2S in the sample can be calculated. The reactions involved are:

$$H_2S + 2Ag^+ \rightarrow Ag_2S\downarrow + 2H^+$$

$$Ag^+ + SCN^- \rightarrow AgSCN\downarrow$$

$$Fe^{3+} + SCN^- \rightarrow (FeSCN)^{2+}$$

(deep red brown)

The thiocyanate is standarized by titrating with $AgNO_3$ which is standardized against a sodium chloride solution whose concentration is accurately known, using chromate ion as the indicator:

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

$$2Ag^+ + CrO_4{}^{2-} \rightarrow Ag_2CrO_4\downarrow$$

(red)

This method was tested for accuracy by analyzing a known weight of H_2S dissolved in water with the following results:

Actual Weight of H_2S	From Analysis	Error	Corresponding ppm
0.01660 g.	0.01652 g.	-0.48%	83
0.01659 g.	0.01656 g.	-0.18%	83
0.04532 g.	0.04607 g.	+1.65%	227
0.04523 g.	0.04581 g.	+1.28%	226

This method appears to be a very significant improvement over that involving the iodine-thiosulphate titration. We believe that we can analyze to a precision of ±1 ppm up to at least the 100 ppm level, although the uncertainty rises at higher H_2S contents. $AgNO_3$ seems to remove H_2S from the purge stream more efficiently than does zinc acetate. Up to concentrations of 100 ppm of H_2S, no Ag_2S appears in the second scrubbing tower, meaning that the first tower removes all the H_2S.

In the past year, this method has been used to analyze a wide variety of sulphur samples, generated both in our laboratories and supplied by outside sources. Some typical results are given below:

lab degassed sulphur	0.1 ppm
lab produced H_2S - containing sulphur	12 - 274 ppm
sulphur from Claus 1st condenser	336 - 494 ppm
sulphur from Claus 2nd condenser	38 - 73 ppm
sulphur from Claus 3rd condenser	12 ppm
liquid sulphur storage pit	108 - 190 ppm
gas plant degassed sulphur	61 - 240 ppm
bulk sulphur stockpile	92 - 132 ppm

Experimental Details for Silver Nitrate Method

Solutions: -

$AgNO_3$ - approximately 0.05M solution made by dissolving 32g. of solid $AgNO_3$ in 4 ℓ. of distilled water. 2 ml. of conc. HNO_3 added to prevent formation of silver oxide.

NH$_4$SCN - approximately 0.21M solution made by dissolving 62 g. of
solid NH$_4$SCN in 4 ℓ. of distilled water.

NaCl - approximately 0.086M solution made by drying 5 g. of solid
NaCl at 110°C for 1 hr., weighing accurately and dissolving
in enough distilled water to make exactly one liter of solution.
Molarity calculated to 4 significant digits.

Fe^{3+} - approximately 1M solution made by dissolving 482 g. of ferric
alum [FeNH$_4$(SO$_4$)$_2$ · 12 H$_2$O] in the minimum amount of distilled
water, filtering the resulting solution and making it up to
one liter with concentrated nitric acid.

CrO$_4{}^{2-}$ - approximately 0.1M solution made by dissolving 2 g. of
potassium chromate (K$_2$CrO$_4$) in 100 ml. of distilled water.

Standardizations: -

AgNO$_3$ - 20.0 ml. of NaCl solution of accurately known molarity,
30 ml. of distilled water, 2 ml. of CrO$_4{}^{2-}$ solution and
0.5 g. of solid calcium carbonate (CaCO$_3$) are placed in
a 200 ml. Erlenmeyer flask. The solution is titrated with
the AgNO$_3$ solution being standardized until the red precipitate
of silver chromate (Ag$_2$CrO$_4$) can be detected. About 36 ml.
is required. Under these conditions one overshoots the true
end point by up to 0.25 ml., so an indicator blank must be
subtracted. The blank is determined by titrating a solution
containing 80 ml. of distilled water, 2 ml. of CrO$_4{}^{2-}$ solution
and 0.5 g. of solid CaCO$_3$ (i.e. no NaCl).

NH$_4$SCN - 100.0 ml. of the standardized AgNO$_3$ solution, 250 ml. of
distilled water and 20 ml. of Fe^{3+} solution in a 500 ml.
Erlenmeyer flask are titrated with NH$_4$SCN solution until
the first lasting tinge of red-brown colour appears. The
solution must be stirred or shaken well just prior to the
end point to dispel the non-permanent colour which appears
before the end point is actually reached. In this case no
indicator blank need be subtracted. About 23 ml. is required.

Analysis Procedure: -

Solid samples - 2 g. of PbS and 200.0 g. of sulphur are weighed into
a 500 ml. round bottom flask with a 45/50 ground glass joint.
This is fitted with an open-ended glass tube reaching to the
bottom and provision is made for gases to exit from the top.
A slow stream of nitrogen gas is passed through the sample
and through two scrubbing towers each containing 100.0 ml.
of AgNO$_3$ solution by means of open-ended glass tubes reaching
close to the bottom of the towers. The sulphur sample is

heated to 125 – 130°C and purged at this temperature for
2 hrs. after melting is complete. The Ag_2S is then filtered
off and the scrubbing towers and the solid on the filter paper
are washed repeatedly with distilled water (total of at least
100 ml.). To the filtrate is added 20 ml. of Fe^{3+} solution
and the resulting solution is titrated with standardized NH_4SCN
solution until the first lasting tinge of red-brown colour appears.

Liquid samples – analysis flask and inlet tube and PbS are weighed and
warmed to 125° – 130°. The inlet tube is removed, sample is
poured in and the inlet tube is replaced. Nitrogen purge is
carried out for 2 hrs. The analysis flask, PbS, sample and
inlet tube are weighed to determine weight of sulphur by
difference. The remaining $AgNO_3$ in the scrubbing towers is
filtered and titrated as above.

Calculation –

$$\text{ppm } H_2S = \frac{V(Ag^+) \times C(Ag^+) - V(SCN^-) \times C(SCN^-)}{2,000} \times \frac{34.1 \times 10^6}{Ws}$$

where $V(i)$ and $C(i)$ are the volumes and concentrations,
respectively, of solutions containing species i and Ws is
the weight of the sulphur sample.

Cleanup – the scrubbing towers and glassware used for filtrations and
titrations present no problem (soap and water). The sulphur
in the round bottom flask is poured out as thoroughly as possible.
The flask, with its film of solid sulphur, is allowed to stand
until the next day or longer, if possible, to allow the sulphur
to age (13). Chloroform is run over the sulphur film which can
then be easily scraped off.

Precautions to be Taken

The major source of error arises from the adsorption of Ag^+ ions
on the surface of the Ag_2S precipitate (14). This tends to make the H_2S
levels calculated too high and becomes more serious at higher H_2S levels
because there are more, and larger, particles of Ag_2S present. As shown
before, our analyses of known samples of H_2S in water were about 0.2 to
0.5% low at the 80 ppm level but about 1.5% high at the 230 ppm level.
One must, therefore, wash the precipitate thoroughly after filtering.
Thorough washing of the scrubbing towers is also essential to ensure that
all of the unconsumed Ag^+ is transfered into the titration flask. Any
lost Ag^+ will again give high values for the H_2S determination.

Another difficulty is the standardization of the AgNO$_3$. Chromate ion in solution tends to mask the colour of the red Ag$_2$CrO$_4$ precipitate, so the end point is not a sharp one. This difficulty, however, is alleviated by the determination of an indicator blank. Provided that one is consistent in observing the colour change, the error should be greatly diminished. It has been our experience that differences in the calculated molarities are in the fourth significant digit, making the errors in the determined H$_2$S levels less than the errors due to the Ag$^+$ ion adsorption.

It is important that the titrations of silver solutions with thiocyanate be very accurate, both in the standardizations and in H$_2$S determinations. This is because of the indirect nature of the method resulting in a calculation based on the difference between two terms. In cases where the H$_2$S level is low, this difference will be small and any errors in volumes or concentrations will be magnified. The volumes of Ag$^+$ and SCN$^-$ must, of course, be accurately known. Titrations can be consistently made within 0.03 ml. of SCN$^-$ solution or ±0.5 ppm of H$_2$S in a 200 g. sample. One advantage of an indirect titration is that overshooting the end point is no problem. One simply adds more AgNO$_3$, continues the titration and inserts the appropriate volumes into the equation.

Finally there is one difficulty common to all methods for analysis of H$_2$S levels in solid sulphur - avoiding loss of H$_2$S on sample preparation. Some of the H$_2$S will be present in the gas phase within the interstices of the solid and this will be lost from each new surface produced in reducing the sulphur to a suitable size for introduction into the analysis vessel. The losses will be especially serious with old samples where 30% of the H$_2$S may be present as the gas. For this reason, a wide mouthed round bottom flask is used and one must work quickly in weighing the sulphur and start the gas purge as soon as possible. The loss of H$_2$S becomes more rapid with higher H$_2$S content. This is partially compensated for by the fact that at high concentrations one tends to get results which err on the high side due to Ag$^+$ ion adsorption on the Ag$_2$S precipitate. Liquid sulphur samples are best analyzed without allowing them to solidify. 20% of the H$_2$S present may be lost on solidification and up to 30% on remelting (15). It is important, therefore, that solid samples be melted in the analysis vessel.

Applications

Although the procedures outlined above have been designed for the analysis of H$_2$S levels in sulphur, they could be readily adapted to any system from which H$_2$S could be liberated and purged. Such a system could be the determination of sulphide (or hydrosulphide) which would release H$_2$S on reaction with acid:

$$S^{2-} \ + \ 2H^+ \ \rightarrow \ 2H_2S\uparrow$$

This might include analysis of the sulphide content of ores. The procedure could also be modified by adding $AgNO_3$ directly to sulphide solutions to give the Ag_2S precipitate in situ. This would eliminate the necessity of purging out the H_2S which would be difficult or impossible if the concentration of sulphide were very low (e.g. waste water sulphide determinations).

The lower limit of measurement using solutions of the concentrations recommended above is $\sim$ 1 ppm of H_2S in 200 g. sample, i.e. 0.0002 g. of H_2S. We have worked with samples containing up to 500 ppm H_2S. The only limitations to working at higher levels could be those mentioned previously - loss of H_2S on sample preparation and adsorption of Ag^+. The latter could be alleviated by reducing the sample size and the former by modification of the apparatus to accommodate large samples without breakup.

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E. Fuels

Type (Be Specific)	Consumption*		Maximum Heat Input (MMBTU/hr)
	avg/hr	max./hr	

*Units Natural Gas, MMCF/hr; Fuel Oils, barrels/hr; Coal, lbs/hr

Fuel Analysis:

Percent Sulfur: _____ Percent Ash: _____

Density: _____ lbs/gal   Typical Percent Nitrogen: _____

Heat Capacity: _____ BTU/lb   _____ BTU/gal

Other Fuel Contaminants (which may cause air pollution): _____

_____

F. If applicable, indicate the percent of fuel used for space heating. Annual Average _____ Maximum _____

G. Indicate liquid or solid wastes generated and method of disposal.

_____

_____

_____

H. Emission Stack Geometry and Flow Characteristics (Provide data for each stack):

Stack Height: _____50_____ ft.   Stack Diameter: _____2.5_____ ft.

Gas Flow Rate: _____12,300_____ ACFM   Gas Exit Temperature: _____105_____ °F.

Water Vapor Content: __Saturated (150°F)__ %   Velocity: _____41.66_____ FPS

SECTION IV: INCINERATOR INFORMATION

Type of Waste	Type O (Plastics)	Type I (Rubbish)	Type II (Refuse)	Type III (Garbage)	Type IV (Pathological)	Type V (Liq & Gas By-prod.)	Type VI (Solid By-prod.)
Lbs/hr Incinerated							

Description of Waste _____

Total Weight Incinerated (lbs/hr) _____ Design Capacity (lbs/hr) _____

Approximate Number of Hours of Operation per day _____ days/week _____

Manufacturer _____

Date Constructed _____ Model No. _____

April 1, 1982

Agrico
P. O. Box 3166
Tulsa, OK 74101

ATTENTION: Mr. William Banner

Gentlemen:

We have completed the design for the H_2S scrubber as requested. The design is based on 900 tons per day from each of the two sulfur melting pits. The pits are 12' x 60' in size. The scrubber is described as follows:

1. Scrubber tower, 5'-6"Ø x 30' high packed with ceramic raschig rings. Reservoir at bottom to collect caustic solution for recirculation to top of scrubber. Single fan taking suction on top of scrubber and discharging air through stack. Inlets to scrubber from each covered melting pit.

2. Air flow through scrubber - 125 cfm.

3. Water vapor content - air at discharge saturated at $150^{\circ}F$.

4. Stack dimensions - 30" x 50' high.

5. Exit velocity - 2500 ft/min. at $105^{\circ}F$.

We are enclosing a schematic of the above described unit. The lime to be added will be at a rate of 1 lb. per hour. The material will be dry and can be dispensed with augar or star valve. The quantities required are small and we see no possibility of reaching the 25 tons per year allowable to atmosphere.

We wish to thank you for allowing us to help you further in this phase of your work.

Very truly yours,
BARNARD AND BURK ENGINEERS &
CONSTRUCTORS, INC.

H. W. Allen
Project Manager

HWA/gw

SECTION III: AIR POLLUTION SOURCES & CONTROL DEVICES (Other than Incinerators)

A. Raw Materials and Chemicals Used in your Process, if applicable:

| Description | Contaminants | | Utilization Rate - lbs/hr | Relate to Flow Diagram |
	Type	% Wt		
Prilled Sulfur	Dust	(.05 or less)	168,000	6-A
	H_2S	(.025 or less)		6-A

B. Process Rate, if applicable: (See Section V, Item 1)

1. Total Process Input Rate (lbs/hr): _____168,000_____

2. Product Weight (lbs/hr): _____167,998.86_____
   Maximum Lb./Hr. Basis = 1800 L Ton/Day ÷ 24

C. Airborne Contaminants Emitted: Actual T/Yr. Basis = 600,000 L Ton/Yr.

| Name of Contaminant | Emission[1] | | Allowed Emission[2] Rate per Ch. 17-2, F.A.C. | Allowable[3] Emission lbs/hr | Potential Emission[4] | | Relate to Flow Diagram |
	Maximum lbs/hr	Actual T/yr			lbs/hr	T/yr	
Particulate	1.14	4.57	17-2.610 (3)		1.14	4.57	6-A,B
H_2S	1.9	8.40	N/A	N/A	42	1680	6-C,D

D. Control Devices: (See Section V, Item 4)

Name and Type (Model & Serial No.)	Contaminant	Efficiency	Range of Particles[5] Size Collected (in microns)	Basis for Efficiency (Sec. V, It[5]
Wet Scrubber	H_2S	95%	N/A	See Supple-
				ments 2 & 3

[1]See Section V, Item 2.

[2]Reference applicable emission standards and units (e.g., Section 17-2.05(6) Table II, E. (1), F.A.C. — 0.1 pounds per million BTU heat input)

[3]Calculated from operating rate and applicable standard

[4]Emission, if source operated without control (See Section V, Item 3)

[5]If Applicable

E. Fuels

| Type (Be Specific) | Consumption* | | Maximum Heat Input (MMBTU/hr) |
	avg/hr	max./hr	

*Units Natural Gas, MMCF/hr; Fuel Oils, barrels/hr; Coal, lbs/hr

Fuel Analysis:

Percent Sulfur: _____ Percent Ash: _____

Density: _____ lbs/gal Typical Percent Nitrogen: _____

Heat Capacity: _____ BTU/lb _____ BTU/gal

Other Fuel Contaminants (which may cause air pollution): _____

F. If applicable, indicate the percent of fuel used for space heating.   Annual Average _____ Maximum _____

G. Indicate liquid or solid wastes generated and method of disposal.

_____

_____

_____

H. Emission Stack Geometry and Flow Characteristics (Provide data for each stack):

Stack Height: ____50____ ft. Stack Diameter: ____2.5____ ft.

Gas Flow Rate: ____12,300____ ACFM Gas Exit Temperature: ____105____ °F.

Water Vapor Content: ____Saturated (150°F)____ % Velocity: ____41.66____ FPS

SECTION IV: INCINERATOR INFORMATION

Type of Waste	Type O (Plastics)	Type I (Rubbish)	Type II (Refuse)	Type III (Garbage)	Type IV (Pathological)	Type V (Liq & Gas By-prod.)	Type VI (Solid By-prod.)
Lbs/hr Incinerated							

Description of Waste _____

Total Weight Incinerated (lbs/hr) _____ Design Capacity (lbs/hr) _____

Approximate Number of Hours of Operation per day _____ days/week _____

Manufacturer _____

Date Constructed _____ Model No. _____

ATTACHMENT   4

November 22, 1982

Fri, Feb 18, 5pm.

DER

NOV 29 1982

BAQM

Mr. C. H. Fancy, P.E.
Deputy Bureau Chief
Bureau of Air Quality Management
Department of Environmental Regulation
Towers Office Building
Blair Stone Road
Tallahassee, FL 32301

Dear Mr. Fancy:

Re: Air Pollution Source Construction Application -
     South Pierce Chemical Works, AC53-55780

This is to advise you that Agrico agrees to a 90 day extension
from this date to continue your review of referenced permit
application.

Very truly yours,

H. W. Long, Jr.
Manager
Environmental Control

HWL/jm

cc: Mr. B. L. Latham
     Mr. L. Lahman

ATTACHMENT   5

February 8, 1983
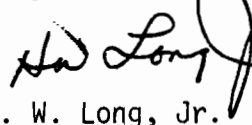
Mr. Steve Smallwood
Department of Environmental Regulation
2600 Blair Stone Road
Tallahassee, FL 32301

Dear Mr. Smallwood:

Enclosed are test data on emission factors for various
prilled sulfur samples. These tests were conducted by
Dr. Dale Lundgren of the University of Florida.

If you have any questions concerning these tests please
contact either Dr. Lundgren or me.

Very truly yours,

H. W. Long, Jr.
Manager
Environmental Control

HWL/jm
Enclosure

cc: Mr. D. R. Morrow
     Dr. D. Lundgren

Emission Factor Determination for Prilled Sulfur

by

Dale A. Lundgren, Ph.D., P.E.

February 1, 1983

During January 1979 this author conducted a limited number of tests to determine an "emission factor" for wet formed sulfur prill. An emission factor was needed to estimate the dust emission rate for a proposed prilled sulfur unloading facility. Prilled sulfur emission factors did not exist in the literature, including EPA reports; therefore, an appropriate measurement was needed.

A dust emission factor measurement procedure was developed and tests run on both phosphate rock and prilled sulfur at various moisture contents. A test chamber (or wind tunnel) was specially built and operated to measure the suspended particulate matter generated by the tested product. Total suspended particulate matter (TSP) is the term used by EPA to describe the airborne particles regulated by the national ambient air quality standards and collected by the prescribed colletion method called the "High Volume Method".

This same test chamber design was again used in 1980 to perform a study of the effect of various dust suppression additives on five (5) granular products. The five products tested were: monammonium phosphate (MAP), diammonium phosphate (DAP), granular triple superphosphate (GTSP), urea, and dry phosphate rock. Phosphate rock was again included as a "control material" because emission factor values have been published for it in EPA documents. In total, several hundred tests were run on the five products to determine the effectiveness of various amounts of various dust suppression additives. Ageing test and tumble test were also run on each product. The reproduceability and usefulness of this measurement technique was clearly demonstrated.

Even though the 1980 test series clearly demonstrated the measurement technique usefulness, additional data on prilled sulfur dustiness, or emission factor, was desired. Therefore, a thorough test program was planned to obtain a large number of emission factor measurements using prilled sulfur with a known history.

Eighty (80) emission factor measurements were made using the prilled sulfur described in the following section (Sulfur Samples). Replica samples were tested and retested, tumble test were conducted, sulfur samples were aged both indoors and outdoors and tested over a two month time period, drop test at both 5 feet and 10 feet were conducted, and a total

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of about sixty (60) moisture measurements were made. Both a Sulphur Development Institute of Canada (SUDIC) method and a standard ASTM type method of moisture determination were used and compared. Two different batches of wet formed sulfur prill and one dry formed Polish prill were tested in the "as received" state and at other moisture levels. Results of the January 1979 tests (February 28, 1979 report) were verified and the importance of product moisture on controlling product dustiness was clearly demonstrated.

Summary of Test Results

Every sulfur emission factor test and the results obtained are listed in the appended table. Samples of the wet prilled sulfur obtained from Coastal Sulphur are numbered sample #1, 2, 3, etc. Samples of the wet prilled sulfur obtained from P.V. Commodity Systems are numbered sample #P-1, P-2, etc. Samples of the dry formed Polish prill obtained from Gulf are numbered sample #G-1, G-2, etc.

In reading across the appended data table the column headings are 1) Test date, 2) Filter #, which is also the test number, 3) Weight gain by the filter as a result of sulfur dust collected during the test, 4) conversion to an emission factor expressed as pounds of dust per ton of product (#/Ton), 5) product moisture content, 6) sulfur test sample number, as described in the paragraph above and in next section, 7) a brief description of the test and 8) a note on how many times that product sample had been tested or dropped (i.e. 3rd drop means the third time that sample of sulfur had been tested or dropped).

A total of 14 test on product samples #1, #2, #3, #4 (filter tests #1 through #14), with an "as received" moisture content of about 4.2%, produce an average dust emission factor of about 0.008 pounds of dust per ton of product (#/Ton). A second shipment of material, again a wet formed prill but from a different source, had four "as received" samples tested (samples #P-1, P-2, P-3 & P-4, filter test #37 through #40). Product moisture was about 4.4% and the dust emission factor averaged 0.008 #/Tons. Four additional samples (P-10, P-11, P-12 and P-13) had an average dust emission factor of 0.007 #/Ton on the standard 5 foot drop test and 0.016 #/Ton on a 10 foot drop test.

Some of the test results are shown plotted in the attached Figures. Of particular importance is filter test #35 and #36 which show that the two samples, aged outdoors for 4 weeks, had a dust emission factor of only 0.006 #/Ton after a fairly heavy rain raised their moisture content to about 4.9%. One week earlier the samples had dried in the sun to a moisture of 0.4% and had a measured dust emission factor of 0.10 #/Ton. After 6 weeks outdoors the moisture dropped to 0.25% and the dust emission factor increased to 0.16 #/Ton.

Indoor aged samples dried to a moisture content of less than 0.1% and had a dust emission factor of about 0.4 #/Ton. Four samples of prill were saturated with water (moisture content of about 6.5%) and produced dust emission factors of only 0.004 #/Ton. Two of these samples (G-1 and G-2) were the dry formed Polish prill. Except for sulfur samples P-1, P-2, G-1 and G-2 referred to above, none of the samples were sprayed with water or artificially wet in any way. Samples #5 and #6 were exposed to the natural weather outdoors and were wet by the natural rain fall.

In summary, if all 22 tests with product moisture 3% or higher are averaged, the dust emission factor is 0.007 #/Ton. The average emission rate for the four tests reported in the 1979 report was 0.005 #/Ton for product moistures of 1.6, 2.6, 3.5 and 10.7% - an average of about 4.6%. The 1979 report used an estimated emission factor of 0.0068 #/Ton. This agreement is remarkably close considering the nature of this test.

As stated in the final paragraph of my February 28, 1979 report, and restated again for emphasis, emission factor measurement are, at best, only good estimates. They are not intended to be of $\pm10\%$ accuracy. Because of product variability and environmental conditions the actual field emission rates will vary widely. It is, therefore, necessary to use some meaningful, reproduceable test to determine a product dust generation rate (not a potential for dust generation but an actual dust generation). The measurement technique used in this study provides the type of dust measurment needed and allows direct comparison of the relative dustiness of dry sulfur prill (0.4 #/Ton) with that of "as received" wet sulfur prill (<0.01 #/Ton).

To avoid the pretence of unjustified emission factor accuracy, one could use an emission factor estimate of 0.01 #/Ton, for transfer operations involving a material drop of less than 10 feet, when handling wet formed sulfur prill having a moisture content of more than 3%.

The tumble tests and multiple drop tests clearly show that only the product moisture content relates to product dust generation. Although measures of various sieve fractions of a product may be of interest and value for other purposes, it cannot directly correlate with product dust generation and is therefore a misleading product property measurement to use for that purpose.

Settleable dust is a term used, in general, to describe everything but suspended dust. It therefore includes spillage, poor operation and poor housekeeping. Settleable dust control requires good plant operation and good housekeeping in the same way the proper operation of an air pollution control device requires good maintenance. Good

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housekeeping cannot be obtained by imposing a product specification. Proper maintenance and good housekeeping must be a basic requirement of an operating permit and should not be neglected by thinking a product specification will work in its place.

Sulfur Samples

On November 9, 1982, Dale Lundgren received delivery of three (3) containers of prilled sulfur from Ryder Truck Lines, Inc. (Freight Bill No. 271-869438). These containers (total weight of 184 pounds) were sealed with tape and numbered railroad door locks. Tape and seals were in place and neither containers nor seals had been damaged or tampered with.

On November 12th, these three containers were opened and the sulfur product was found to be stored in plastic bags. Each container had the sulfur sealed in an inner bag which was then sealed in a second outer bag. The product was noticably wet. A total of 17 test samples, of five (5) kilogram weight each (+5 grams), were prepared using an Ohaus beam balance. These samples were numbered #1 through #17. Each sample was then stored in a marked, double lined, sealed plastic bag in the original shipping containers. There were no noticeable fines remaining in the original plastic bags after the above test samples had been weighed out. A small amount of sulfur was left over.

These containers of prilled sulfur were obtained at Coastal Sulphur's facility on Jasinto Port Blvd. by H.W. Long in the presence of Hal Scott and, by Transfer of Custody, given to Mary Buyer of Ryder Truck Lines on November 2, 1982 for delivery to Dale Lundgren, Gainesville, Florida.

On December 21, 1982, Dale Lundgren received four (4) boxes of wet prilled sulfur collected at the P.V. Commodity Systems facility at Strachan, Alberta, Canada. These boxes, marked PVC 1, PVC 2, PVC 3, and PVC 4, were collected by Harold Long, and witnessed by Hal Scott, at 1 PM on December 1, 1982. In addition to the above, Dale Lundgren received four (4) boxes of Polish Prilled Sulfur collected by Harold Long, and witnessed by Hal Scott, at the Gulf Facility at Strachan, Alberta, Canada, at 3 PM on December 1, 1982. These boxes were marked Gulf 1, Gulf 2, Gulf 3, and Gulf 4. Each box weighed approximately 50 pounds, for a total shipment weight of 400 pounds.

All eight (8) boxes were obtained via Transfer of Custody from Hal Scott to R.G. Shaw of P.V. Commodity Systems to Bruce McGinnis of Canadian Freightways to Dale Lundgren of Gainesville, Florida. The boxes were cardboard and each contained sulfur prill sealed in plastic bags. The P.V. Commodity wet prilled sulfur was noticably wet and the Gulf Polish prilled sulfur was very dry.

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Five kilogram samples of each box of product were prepared, as described above, and used for testing the "as received" material. These samples were numbered P-1 through P-4 for the P.V. Commodity prill, and G-1 through G-4 for the Gulf Facilities prill. Four additional test samples of the P.V. Commodity prill marked P-10 through P-13 were also used for testing. All samples were stored in marked, sealed, double lined plastic bags between preparation and testing.

Moisture Tests

Most moisture tests were run using the SUDIC procedure of drying at 75°C. A drying time of 24 hours produced a stable weight. Several sulfur samples were also dried at 100°C for periods of 1, 2 and 4 hours and compared to the 75°C, 24 hour drying. Data shown in the appended table for test #37 through #40 are replica test on wet sulfur prill and test #41 through #44 are replica test on dry Polish prill. Average moisture results, by the two moisture measurement methods, for the wet and dry formed prill are, respectively, 4.38% vs 4.45% and 0.04% vs 0.03%. Other comparison test also produced comparable results. It must be concluded that the two techniques of moisture determination are approximately equal.

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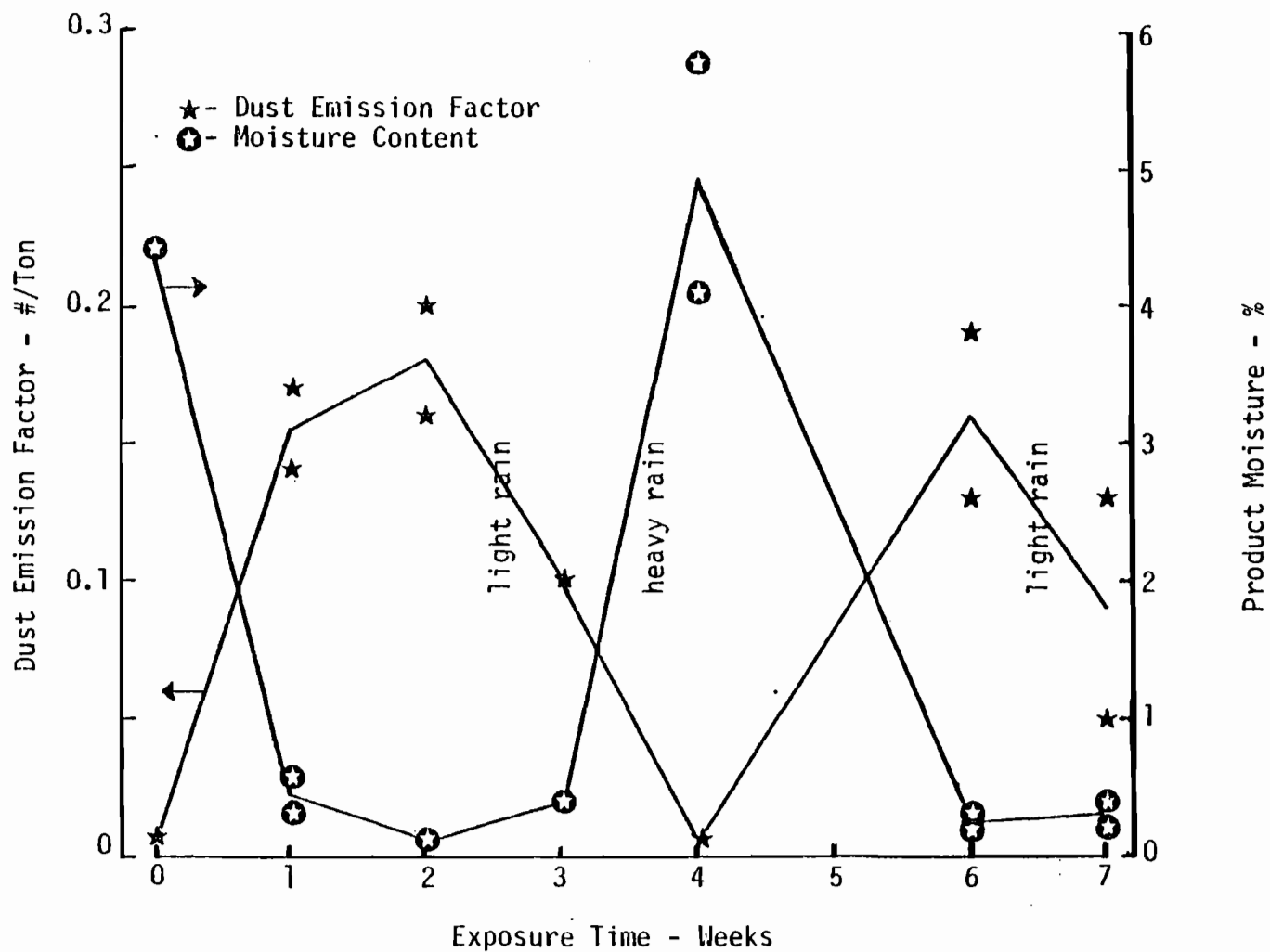
Figure 1 Dust Emission Factor vs Product Moisture Content
For Wet Formed Sulfur Prill Exposed Outdoors
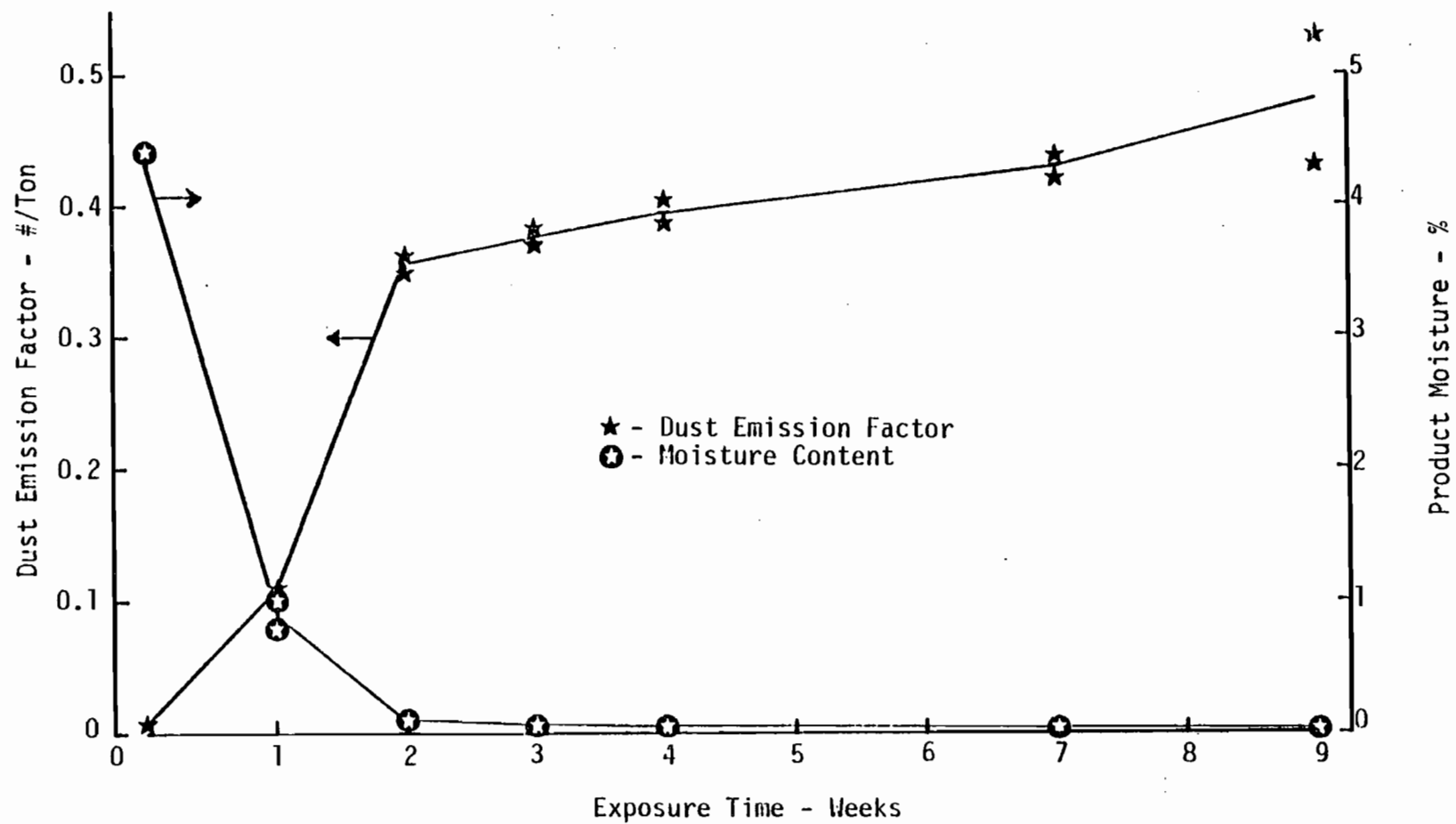
Figure 2   Dust Emission Factor vs Product Moisture Content
For Wet Formed Sulfur Prill Exposed Indoors
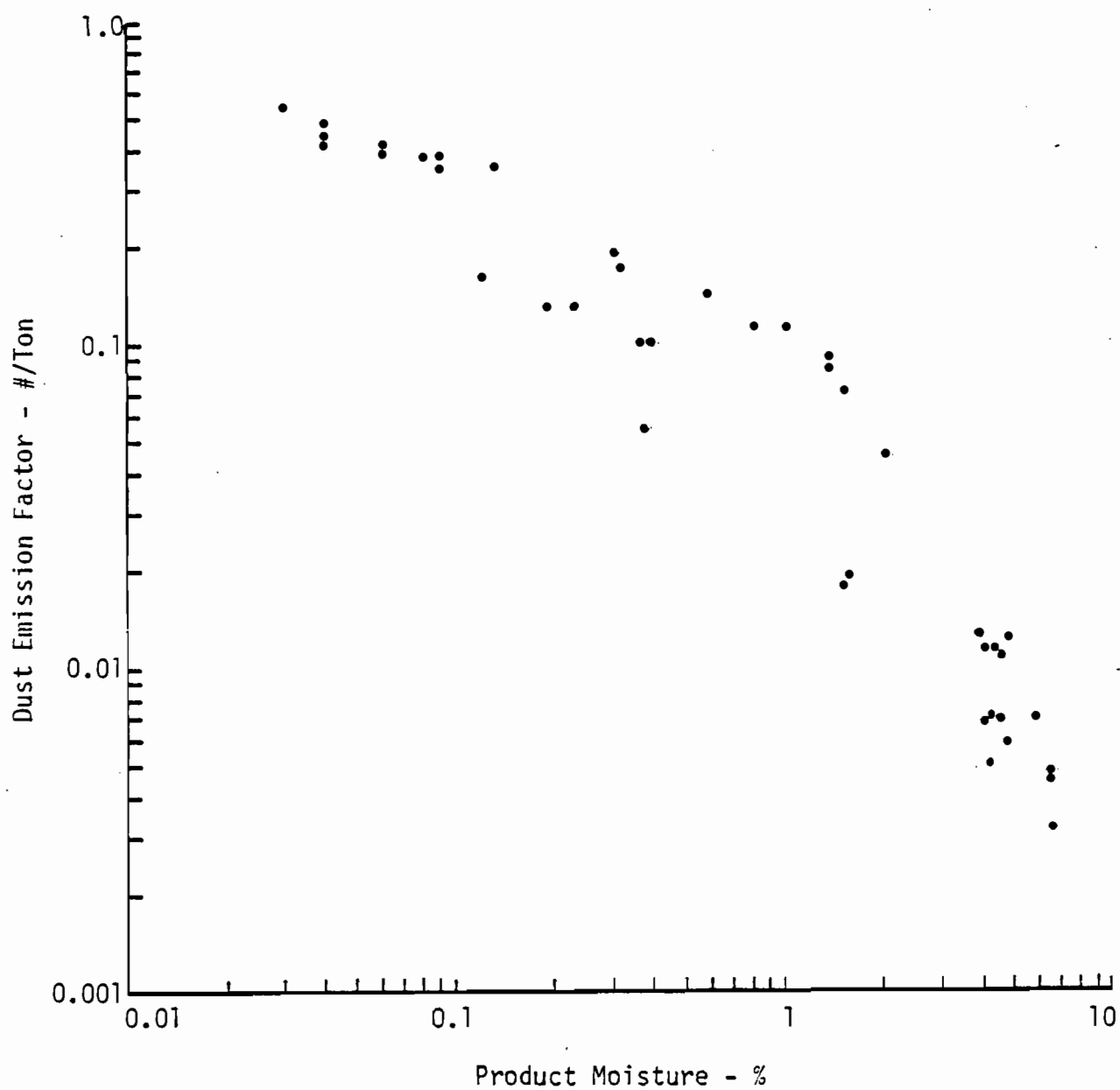
Figure 3   Dust Emission Factor vs Product
Moisture for Sulfur Prill

∞

Table 1 - Summary of Test Data

Test Date	Filter #	Dust Concentration mg	Dust Concentration #/Ton	Moisture-%	Sample-#	Test Description	Test
11-17-82	1	31.0	0.0124	3.8	1	"as received"	1st drop
"	2	18.4	0.0074	–	1	"	2nd drop
"	3	13.7	0.0055	–	1	"	3rd drop
"	4	27.9	0.0112	4.0	2	"	1st drop
"	5	18.3	0.0073	–	2	"	2nd drop
"	6	13.3	0.0053	–	2	"	3rd drop
11-19-82	7	30.8	0.0123	4.7	3	"	1st drop
"	8	10.1	0.0040	–	3	10 tumbles	2nd drop
"	9	60.0	0.0240	–	3	20 tumbles	3rd drop
"	10	8.9	0.0036	–	3	40 tumbles	4th drop
"	11	27.9	0.0112	4.4	4	"as received"	1st drop
"	12	8.9	0.0036	–	4	10 tumbles	2nd drop
"	13	7.5	0.0030	–	4	20 tumbles	3rd drop
"	14	6.0	0.0024	–	4	40 tumbles	4th drop
11-24-82	15	275.0	0.11	0.80	7	aged 1 wk indoors	1st drop
"	16	276.2	0.11	1.01	8	aged 1 wk indoors	1st drop
11-26-82	17	432.6	0.17	0.31	5	aged 1 wk outdoors	1st drop
"	18	342.7	0.14	0.57	6	aged 1 wk outdoors	1st drop
12-1-82	19	877.5	0.35	0.13	7	aged 2 wk indoors	2nd drop
"	20	888.2	0.35	0.09	8	aged 2 wk indoors	2nd drop
12-3-82	21	411.8	0.16	0.12	5	aged 2 wk outdoors	2nd drop
"	22	493.2	0.20	0.36	6	aged 2 wk outdoors	2nd drop
12-8-82	23	927.9	0.37	0.09	7	aged 3 wk indoors	3rd drop
"	24	961.6	0.38	0.08	8	aged 3 wk indoors	3rd drop
"	25	56.3	0.02	2.27	9	heated 24hr @75°C	1st drop
"	26	61.1	0.02	1.53	10	"	1st drop
12-10-82	27	252.3	0.10	0.36	5	aged 3 wk outdoors	3rd drop
"	28	252.1	0.10	0.39	6	"	3rd drop
12-16-82	29	985.9	0.39	0.06	7	aged 4 wk indoors	4th drop
"	30	1013.2	0.40	0.06	8	"	4th drop
"	31	86.6	0.03	2.20	11	heated 2hr @95°C	1st drop
"	32	47.3	0.02	2.13	11	"	2nd drop
"	33	72.2	0.03	1.66	12	"	1st drop
"	34	42.3	0.02	2.38	12	"	2nd drop
12-17-82	35	12.2	0.005	4.08	5	aged 4 wk outdoors	4th drop
"	36	17.7	0.007	5.76	6	"	4th drop
12-29-82	37	27.6	0.0110	4.31/5.19	P-1	"as received" PVC	1st drop
"	38	17.1	0.0068	3.95/4.04	P-2	"	1st drop
"	39	14.7	0.0059	4.89/4.48	P-3	"	1st drop

6

A-

Test Date	Filter #	Dust Concentration mg	Dust Concentration #/Ton	Moisture-%	Sample-#	Test Description	Test
"	40	17.4	0.0070	4.35/4.10	P-4	"	1st drop
"	41	104.9	0.042	0.05/0.03	G-1	"as received"GULF	1st drop
"	42	106.3	0.043	0.03/0.03	G-2	"	1st drop
"	43	102.2	0.041	0.06/0.04	G-3	"	1st drop
"	44	95.1	0.038	0.04/0.03	G-4	"	1st drop
12-31-82	45	475.1	0.190	0.30	5	aged 6 wk outdoors	5th drop
"	46	321.1	0.128	0.19	6	"	5th drop
"	47	152.4	0.061	0.05	G-1	aged 2 days indoors	2nd drop
"	48	148.4	0.059	0.07	G-2	"	2nd drop
"	49	152.8	0.061	0.09	G-3	"	2nd drop
"	50	158.2	0.063	0.08	G-4	"	2nd drop
1-3-83	51	203.9	0.082	1.34	P-1	aged 5 days indoors	2nd drop
"	52	174.7	0.070	1.47	P-2	"	2nd drop
"	53	110.9	0.044	1.95	P-3	"	2nd drop
"	54	219.3	0.088	1.34	P-4	"	2nd drop
"	55	1042.6	0.42	0.04	7	aged 7 wk indoors	5th drop
"	56	1110.8	0.44	0.04	8	"	5th drop
"	57	1197.0	0.48	–	8	", retested	6th drop
"	58	1261.7	0.50	–	8	", retested	7th drop
1-5-83	59	46.2	0.018	1.48	P-1	sprayed w/water	2nd drop
"	60	46.8	0.019	1.55	P-2	"	2nd drop
"	61	58.5	0.023	1.5	G-1	"	2nd drop
"	62	69.9	0.028	1.5	G-2	"	2nd drop
1-6-83	63	321.1	0.128	0.23	6	aged 7 wk outdoors	6th drop
"	64	134.7	0.054	0.37	5	"	6th drop
1-9-83	65	6.9	0.0028	6.67	G-1	saturated w/H_2O	3rd drop
"	66	11.2	0.0045	6.35	G-2	"	6th drop
"	67	7.9	0.0032	6.5	P-1	"	6th drop
"	68	9.3	0.0037	6.5	P-2	"	6th drop
1-13-83	69	26.7	0.011	4.5	P-10	std. 5' drop test	1st drop
"	70	17.6	0.007	4.5	P-11	"	1st drop
"	71	1065.9	0.43	0.04	7	" (aged 9 wks) indoors	6th drop
"	72	1320.7	0.53	0.03	8	" (aged 9 wks) indoors	8th drop
"	73	42.6	0.017	4.5	P-10	10' drop test	2nd drop
"	74	32.6	0.013	4.5	P-11	"	2nd drop
"	75	43.6	0.017	4.5	P-12	"	1st drop
"	76	39.5	0.016	4.5	P-13	"	1st drop
"	77	2531.3	1.01	0.04	7	" (aged 9 wks) indoors	7th drop
"	78	3039.9	1.22	0.04	8	" (aged 9 wks) indoors	9th drop
"	79	12.9	0.005	4.5	P-12	std. 5' drop test	2nd drop
"	80	13.1	0.005	4.5	P-13	"	2nd drop

Appendix on

History of Fugitive Dust Measurement

by

Dale A. Lundgren, Ph.D., P.E.

February 1, 1983

History of Fugitive Dust Measurement

To enable the reader to better understand the present
lack of knowledge and technology in the fugitive dust
suppression area the following material has been prepared.
It provides both a historic background and a better
understanding of how research and regulations in the fugitive
dust area have proceeded.

1. Federal Air Pollution Regulations

    In 1967 the Air Quality Act was passed by the U.S.
Congress. In 1970 this act was amended (Public Law 91-604,
Dec. 31, 1970) to provide for the federal government setting
national ambient air quality standards and also setting
national emission standards for "new" stationary sources and
for hazardous air pollutants (both for existing and new
plants). National ambient air quality standards are
contained in 40 CFR 50. New stationary source performance
standards are contained in 40 CFR 60 and hazardous air
pollutant standards in 40 CFR 61. Old stationary sources,
those in existence before an effective date, are covered by
state standards. In each of the above cases, the industry is
allowed to discharge a specified quantity of pollutant
through a duct or stack. In each case where an industrial
emission standard exists, a test method is specified and
special instructions or measurement conditions identified.
These test procedures could be considered as routine.

    Industrial emissions are regulated in order to control or
maintain the ambient air quality. However, only the ducted
industrial emissions have specific regulations. Other
industrial emissions together with natural emissions are
usually grouped into a fugitive catagory. This fugitive
catagory is not specifically regulated, even though it may
cause a major degradation of ambient air quality. (Control
of air pollution from new motor vehicles, a third major area,
has been covered by federal regulations which started with
the 1965 Amended Clean Air Act.)

    There is no universally accepted definition for the
general "fugitive" air pollution catagory. In the EPA
document titled "Technical Guidance for Control of Industrial
Process Fugitive Particulate Emissions" (EPA - 450/3-77-010,
March 1977), "fugitive dust" is defined as particle emissions
from wind and/or man's activity such as from unpaved roads,
construction sites and tilling of land, and "fugitive
emissions" is defined as particles generated by industrial
activities which escape to the atmosphere through non ducted
sources, such as vents, doors, windows, etc. These are not
totally useful definitions. An additional catagory, which
includes some of both of the above, is called "Industrial
Process Fugitive Particulate Emissions" (IPFPE) and is
defined as - "Particulate matter which escapes from a defined
process flow stream due to leakage, material
changing/handling, inadequate operational control, lack of
reasonably available control technology, transfer or
storage". Because IPFPE are not emitted from a stack, they
cannot be easily measured by conventional techniques. These
emissions and their impact on air quality are extremely
difficult to quantitate and to regulate. During the initial
development of ambient air standards and industrial emission
standards, the fugitive emissions were believed to be minor.

Initial effort was directed toward control of emissions which could be readily quantified.

With the installation of air pollution control devices on ducted stationary sources, together with the fact that the pollutants are generally discharged significantly above ground level, causing dilution before the pollutant reaches a ground level receptor, the relative impact of fugitive emissions has become more important. Even though measurement of fugitive emissions is difficult, estimates made do indicate that fugitive emissions comprise a significant portion of the nationwide particulate emissions problem.

2. Ambient Standards for Particulate Matter

The national primary ambient air quality standards for particulate matter are:
   a)   75 ug/m^3 - annual geometric mean'
   b)   260 ug/m^3 - maximum 24-hour concentration
        not to be exceeded more than once per year.

The secondary standards state levels of 60 and 150 ug/m^3. Primary standards define levels intended to protect the public health. Secondary standards define levels for protection of public welfare.

The reference method for determination of particulate matter, also refered to as suspended particulates or total suspended particulate matter (TSP), is called the "High Volume Method". This method is a unique air sampling device and, therefore, there is not an "equivalent method".

Because the ambient air quality standard is specifically based upon use of the high volume air sampler, it is important to understand its collection characteristics and limitations. An exact upper limit of the particle size collected is unknown. Operational and design requirements described in 40 CFR 50, Appendix B (July 1, 1981) state that particles less than 100 um are collected. A laboratory calibration report by Wedding, McFarland and Cermak (ES&T 11:387, 1977) show an inlet classification at about 15 or 20 um diameter (the particle size at which unit collection efficiency is 50%). Results of a field study published by Lundgren and Paulus (JAPCA 25:1227, 1975) indicates the high volume sampler collects particles up to about 60 um diameter. This 60 um value is also refered to in several unpublished EPA reports.

The impact an industrial source of dust has on the ambient air quality standards for particulate matter must be determined by using a high volume sampler because this is the basis of the standard. In addition, the particles produced must be of a size that can be collected by the EPA reference

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"high volume method". This would correspond to particles less than a size somewhere between 20 and 100 um diameter.

The 1977 Clean Air Act Amendmends require EPA to review the scientific basis for the existing national ambient air quality standards (NAAQS) for particulate matter. (The NAAQS were promulgated in 1971). As a result of that requirement, EPA has prepared a review and is planning to propose a new standard based on particulate matter of a carefully defined upper size (often refered to as inhalable particles). EPA also intends to propose a new reference method for measuring particulate matter. This new standard and measurement method is based on the mass concentration of particulate matter less than 10 um aerodynamic diameter, in the ambient air and sampled over a 24-hour time period. A notation of PM-10 is presently being used to note this new measured quantity which is described as that portion of the total suspended particulate matter that is of a size likely to be deposited in the thoracic region of the human respiratory tract.

Because this PM-10 is only a part of the present NAAQS for particulate matter, it is expected that a lower standard will be proposed (less than the 75 ug/m^3). A very significant effect of a new regulation of this concept is that fugitive dust, from either industry or nature, would have a greatly reduced effect on the standard. Wind blown dust (on a mass concentration basis) is predominantly greater than 10 um diameter. A major object of the new regulation would be to measure the aerosol which would effect health rather than that which would only be considered a nuisance. A secondary standard could include aerosol in the nuisance category as it is not a health related standard. An article titled "Size Considerations for Establishing a Standard for Inhalable Particles" by Miller et. al. (JAPCA 29:610, 1979) presents and discusses the topic and particle deposition in the respiratory tract.

3. Fugitive Particulate Emission Sources

A list of the important industrial process fugitive particulate emission sources would certainly include transfer and conveying, loading and unloading, storage piles and roads. These major sources and their control are briefly discussed below.

Transfer and Conveying
Solids in bulk (or granular) form are often transferred or conveyed using belt, screw, bucket, vibrating, drag, continuous flow and/or pneumatic conveyors. Of these types the belt conveyor has the most universal application and probably the longest life. Bulk materials can be conveyed for miles, at high speed (1000 fpm), and at high volume (5000 tons per hour). A belt is selected to be compatable with the

material being transfered. High product moisture can cause
material sticking and poor material discharge. When the
material transfer direction must change it is normal to use
more than one conveyor. Loading, transfer and discharge are
the major points of particulate emissions. Occasionally,
emissions from the belt conveyer itself can be significant.

Wetting of the bulk product is probably the most
effective means for reducing fugitive emissions. However,
not all bulk materials can be wetted and wet material may
stick to the belt causing discharge problems.

Fugitive emission rates for the transfer and conveying of
bulk material is highly variable and not well known.
Emission rates vary with the type of conveyor, the
transferred material, meteorological conditions, etc.
Published transfer and conveying emission factors are so
variable (0.04 to 0.96 lb/ton for coal for example) and of
such low reliability that they are of questionable value.
Control by wet suppression is known to be effective but the
optimum point of application and application rate are
unknown. This is true because no standard or generally
accepted method for testing a dust suppression agent exists.
Dust suppression has evolved into an art of unknown
effectiveness. This is probably difficult to accept or
believe in an era of space age science and technology.

Loading and Unloading
The transfer of material between a storage facility and a
truck, ship, barge or rail car is included in the general
loading and unloading catagory. The mechanical agitation of
material and the dissipation upon impact of kinetic energy
possessed by the material causes the generation of fugitive
emissions. Air displacement and air turbulence caused by the
product movement carries the generated pollutant away from
the source. However, the moving air is not the major factor
in creating the fine particulate matter, or fugitive aerosol.

Emission rates for loading/unloading operations vary with
product type and moisture content, method of
loading/unloading, meteorological conditions, the vehicle
being used and/or dust control technique being used. Very
few experimental measurements have been made of these
fugitive emission factors. Available emission factor data is
therefore limited and of fairly poor reliability. Dust
control procedures again include use of wet suppression
agents. Design of the enclosure and constrants on the
loading/unloading operation are probably of greatest
importance.

Storage Piles

Large tonnages of bulk materials are most often stored in open or partially enclosed storage piles if the bulk material is not affected by precipitation. Storage may be for a short time with high turnover or may be for a long time to provide emergency supply or to meet cyclical demand.

Belt conveyors are most often used to transfer material to the storge pile. A dust problem may arise as material is loaded onto the pile, as material is moved or removed from the pile, or as a result of wind erosion from the pile itself. In the previously referenced technical guidance document (EPA-450/3-77-010), the four major emission producing activities and their approximate relative contribution for open storage of crushed rock were given as follows:

Loading onto piles	12%
Equipment and vehicle movement in storage area	40%
Wind erosion	33%
Loadout from piles	15%

These approximate values depend on storage pile activity, pile configuration, method of loading and unloading, wind, precipitation, etc.

Emissions from a storage pile would be the same chemically as the pile material. The referenced report states that only material less than 100 um diameter becomes airborne. Typical particle size distribution data for the dust emissions were given as follows:

    30%   by weight less than 3 um
    53%   by weight less than 30 um

Many techniques are available for controlling or reducing fugitive dust emissions. These include enclosing the storage, wind screens or partial enclosure of storage piles, telescoping chutes to minimize free fall of material onto the storage pile and use of dust suppression materials such as water, foam and chemicals (water plus a wetting agent, oils, or various chemical mixtures).

Dust suppression agents are sprayed onto the bulk project during processing, at transfer points, at discharge to storage, on storage and/or at load out. In the referenced technical guidance document (EPA-450/3-77-010) the following dust control efficiency values were given for storage piles using various spray techniques (watering, chemical wetting agents or foam):

Emission point	Spray technique	Efficiency
Loading onto pile	chemical wetting agents or foam	80% to 90%
Movement of pile	chemical wetting agents watering	90% 50%
Wind erosion	chemical wetting agents or foam	90%
Loadout	water spraying	50%

It was stated that "Wetting agents or foam which are sprayed onto the material during processing or at transfer points retain their effectiveness in subsequent storage operations. Wetting agents retain surface moisture for extended periods, thereby preventing dusting".

Roads

Roads are an important source of fugitive emissions. Traffic movement causes mechanical breakdown of material. Vehicles and air movement causes the fine material to become airborne. The emission factor for unpaved roads is a direct function of vehicle speed. Particle size data for the emissions indicate that 60% to 70% of the material is less than 30 um diameter. Oiling, regular watering and good housekeeping all help reduce unpaved road fugitive emissions. Acutal emission rate values are not readily available however.

4. Fugitive Emission Rates

In order to estimate the amount of pollutant released into the atmosphere from an industrial operation, EPA has developed a technique using emission factors. An emission factor is defined as the rate at which a pollutant is released into the atmosphere as a result of an industrial activity, divided by the level of that activity. To the extent possible these emission factors are based upon actual measurements. Emission rates for other materials (those for which measurements are not available) can only be estimated by comparative judgement with the known or measured rates. The chemical characteristics of the fugitive material is assumed to have the same chemical characteristics as the material being transfered. The physical or size characteristics of fugitive particles are generally less than 100 um diameter.

5. Measurement of Fugitive Emissions

There are six generally accepted methods for measurement of fugitive emissions. Three of these are described in the following EPA published documents:

1) Technical Manual for Measurement of Fugitive Emissions: Upwind/Downwind Sampling Method for Industrial Emissions, EPA-600/2-76-089a, April 1976.

2) Technical Manual for Measurement of Fugitive Emissions: Roof Monitor Sampling Method for Industrial Fugitive Emissions, EPA-600/2-76-089b, May 1976.

3) Technical Manual for Measurement of Fugitive Emissions: Quasi-Stack Sampling Method for Industrial Fugitive Emissions, EPA-600/2-76-089c, May 1976.

Upwind/Downwind Sampling
    The upwind/downwind sampling method involves the measurement of pollutant level in the atmosphere both before (upwind) and after (downwind) the pollutant source. Using sampling equipment suitable for the pollutant of interest, a background or baseline pollutant concentration is determined. Within the cloud of pollutant being emitted by the source, downwind measurements are made (using the same or similaar sampling equipment). Differences in pollutant concentration, wind speed, and pollutant cloud crossectional area are then used to calculate source emission rate and/or emission factor. Measurement of particulate matter is usually best satisfied by using high volume filtration type samplers.

    Downwind sampling must be carefully designed to ensure that representative samples are obtained. Wind speed and direction must be monitored to assure proper placement of the samplers and a correct emission rate calculation. The tested site topography should be flat and free of obstructions. Ideally, the sampled pollutant cloud would be of known physical size and homogeneous.

    Calculation of emission rates normally involve standard diffusion equations, which take into account variables of meterorology and topography, to produce concentration distributions of the pollutant within the generated cloud. These calculations are designed to determine pollutant source strength.

Roof Monitor Sampling
    Roof monitor sampling can be used to measure fugitive emissions coming from enclosures with openings such as roof vents, doors and windows. Samples are taken at the opening to determine the pollutant concentration and air flow rate.

This method would be suitable for measuring an indoor source where the pollutant is emitted into the atmosphere at low velocity through a large opening.

Calculation of emission rate is a simple product of the measured concentration times the measured exhaust flow rate (velocity times opening area). Utilization of this method requires that the source be enclosed in a structure with a limited number of openings of measurable size and flow rate. Meteorological measurement are not required.

Quasi-Stack Sampling

In the quasi-stack sampling method, the process is temporarily enclosed and the fugitive emissions drawn off through a hood and duct work. Air flow rate and pollutant concentration are measured using standard stack sampling equipment or other suitable techniques.

This approach is restricted to emission sources which can be isolated and physically enclosed. The enclosure and air flow should not interfere with the process and should not alter the characteristics of the generated pollutant. Because the source must be effectively enclosed, it is usually restricted to smaller or single sources. A storage pile would not be a candidate source. A conveyor belt transfer point could be tested using the quasi-stack sampling method.

In one EPA report it is stated that this is the most accurate sampling technique for fugitive emission measurement.

Exposure Profiling

A fourth method developed under EPA contract by Midwest Research Institute (MRI) is called exposure profiling. This technique employs a single tower with multiple sampling heads, to obtain a vertical dust concentration profile. Several simultaneous multipoint isokinetic samples are obtained. The tower is usually about 5 meters high and is located about 5 meters downwind of the source. An upwind monitor would determine background dust concentration. It is also possible to modify this technique and use balloon-suspended samplers.

Wind speed and direction must be determined and recorded. Sampler inlets must be directed into the wind and the sampling velocity adjusted to obtain an isokinetic sample. Source emission rate is calculated using the measured concentration values. MRI believes this technique is more accurate than the upwind-downwind measurement method.

Wind Tunnel Method

Dust emissions generated by wind over an exposed area or storage can be measured by the wind tunnel method. A portable device, consisting of an inlet, test section and diffuser, is placed over the surface of interest. The floor of the wind tunnel is open. Air flow rate is adjusted and measured by means of a pitot tube. An isokinetic sample of the gas stream, located after the test section, is used to determine dust concentration. Tests conducted at various wind speeds can be used to determine the relative surface emission rates.

Tracer Method

The tracer method involves the release of a known amount of tracer at the fugitive emission source. Downwind from the source, both the tracer and the dust from the source are measured. From a sample ratio, the dust emission rate is calculated. This technique is simple in theory but very difficult to conduct in the field. The tracer, normally a gas, does not always act, or settle, the same as the dust. Also, it is very difficult to release a tracer to match the release of the actual pollutant or dust cloud.

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ATTACHMENT   6

Emission Factor Determination for Prilled Sulfur

Addition #1

by

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February 28, 1983

Several additional tests were conducted to determine:
1) dust background concentration,
2) dust generation from drops onto an angle plate,
3) dust generation from material dropped onto material,
4) amount of material collected on sides of dust chamber,
5) and sieve size-distribution of product.

Test Procedure: The standard test procedure is as follows. A calibrated high-volume air sampler is first fitted with a pre-weighed 8" x 10" glass fiber filter. It is then set in place in a gasketed opening at the top of a 5 foot test chamber. The blower is turned on and flow rate recorded. Average flow rate is 65 cfm. A pre-weighed, 5 kilogram (11 pounds) sample of product is then discharged into the center of a 8-inch diameter vertical air inlet duct. The downward air velocity through the duct is about 180 fpm (approx. 2 MPH). The product sample is gradually and uniformly dumped into the duct at a rate of about 5 kilograms per minute, and allowed to free fall onto a cement slab (covered with Kraft paper or a plastic sheet for ease of product recovery). Generated dust is carried by the air stream to the high-volume air sampler filter and collected. Product dumping requires one minute. The chamber air flow is continued for one additional minute (total of 2 minutes) to flush out any remaining airborne dust. This provides a total of > 6 air changes in the chamber, 3 of which are after the product has been dumped. Final air flow rate is recorded and the filter removed for final weighing and dust emission rate determination.

Test results for the topics listed are as follows:
1) Background Concentration. No corrections were made for background dust concentration. Measurements of actual background in the test chamber are shown in test #81, 82, 83, 93 and 111. The average filter weight gain was ~0.5 mg which converts to a 0.0002 #/Ton correction factor. This value should be subtracted from the dust emission factor determinations but was not because it is negligable.

2) Effect of Surface Angle on Dust Emission Rate. Dust generation rates for drops onto an angle plate of $0°$, $15°$, $30°$ and $45°$ show no significant difference. Average dust emission factor was about 0.005 #/Ton for a wet product moisture content of about 3.5%. This data (test #84 through 100) is plotted in the attached Figure 4.

3) Effect of Product Sample Size on Dust Emission Rate. Dust generation rate measurements were made by drop test of material on top of material. First, a 5 Kg sample was dropped in the standard manner and the dust generation rate measured. Then a second 5 Kg sample was dropped on top of the first sample and the dust rate for this second 5 Kg sample measured. This was repeated for a third, fourth and fifth sample. This 25 Kg sample was then split into 5 samples of 5 Kg each and the test repeated. Dust generation rate again averaged about 0.005 #/Ton with no significant difference in the data (no effect of product coating the chamber bottom). An effect was expected but was not measured. Data for tests 101 through 110 is shown plotted in the attached Figure 5.

4) Analysis of Dust Deposited on Chamber Walls. After the above described 25 tests were completed the dust chamber was very carefully cleaned to determine the amount and size distribution of material on the chamber sides. The sides were very thoroughly cleaned and all dust either filtered or recovered as settleable dust. The total filtered fraction is shown as test 112, as equivalent of 0.0012 #/Ton. The remaining or total settleable dust was then collected and a sieve size distribution performed. A total of 2.8 grams or 0.045 #/Ton was recovered. The size distribution of the dry dust is as follows (the dust must be dry to sieve):

Sieve # U.S. Standard	Particle size µm	Quantity grams
40	> 420	0.415
60	> 250	0.820
80	> 177	0.442
100	> 149	0.296
120	> 125	0.152
140	> 105	0.164
200	> 77	0.397
<200	< 77	0.119
	Total	2.805

5) Sieve Size Analysis of Product. Questions have been asked about the percent fines in the product as determined by a standard sieve analysis. As previously stated, wet product cannot be sieved. The product excess moisture bonds the fines to the course material and prevents size fractionation. A 100 gram sample of wet (3.5% moisture) material was placed above a 40 mesh (420 µm opening) sieve. None of the fines (less than 0.001%) passed through the sieve.

A 100 gram samples of this same material was dried to <0.1% moisture and a second sieve analysis run. Measured distribution was as follows:

Sieve # U.S. Standard	Particle size μm	Quantity grams
40	> 420	98.825
60	> 250	2.427
80	> 177	0.833
100	> 149	0.517
120	> 125	0.303
140	> 105	0.299
200	> 77	0.734
<200	< 77	0.910

If this dry material is rewet the fines again fail to pass through the 420 μm opening sieve.

All tests conducted during 1982-1983 (up to Feb. 28, 1983) on wet prilled sulfur have been included in this above report or the report dated Feb. 1, 1983. No further tests are planned as of this date. All the data obtained on wet prilled sulfur has been plotted on semi-log paper as dust emission factor (log scale) vs product moisture (linear scale), in Figure 6 attached.

Table 1A – Summary of Additional Test Data

Filter #	Dust Concentration #/Ton	Moisture-%	Sample #	Test Description	Test
81	0.0002	---	----	dust background test	---
82	0.0001	---	----	"	---
83	0.0003	---	----	"	---
84	0.0073	3.4	P-20	"as received"	1st drop
85	0.0087	3.5	P-21	"	1st drop
86	0.0076	3.8	P-22	"	1st drop
87	0.0059	---	"	drop on 15° plate	2nd drop
88	0.0048	---	"	drop on 30° plate	3rd drop
89	0.0046	---	"	drop on 45° plate	4th drop
90	0.0032	3.9	"	drop on 0° plate	5th drop
91	0.0051	3.5	P-21	drop on 15° plate	2nd drop
92	0.0005	---	----	high dust background test	---
93	0.0001	---	----	normal background test	---
94	0.0041	---	P-21	drop on 30° plate	3rd drop
95	0.0046	---	"	drop on 45° plate	4th drop
96	0.0027	3.3	"	drop on 0° plate	5th drop
97	0.0043	---	P-20	drop on 15° plate	2nd drop
98	0.0038	---	"	drop on 30° plate	3rd drop
99	0.0042	---	"	drop on 45° plate	4th drop
100	0.0027	2.5	"	drop on 0° plate	5th drop
101	0.0071	4.8	P-23	standard drop	1st drop
102	0.0065	"	P-24	drop on top of above	1st drop
103	0.0053	"	P-25	"	1st drop
104	0.0046	"	P-26	"	1st drop
105	0.0050	"	P-27	"	1st drop
106	0.0035	"	P-23X	standard drop	2nd drop
107	0.0041	"	P-24X	drop on top of above	2nd drop
108	0.0045	"	P-25X	"	2nd drop
109	0.0046	"	P-26X	"	2nd drop
110	0.0038	"	P-27X	"	2nd drop

after above 25 drop tests the test chamber was cleaned out

Filter #	Dust Concentration #/Ton	Moisture-%	Sample #	Test Description	Test
111	0.0002	---	----	dust background test	
112	0.0291	---	----	sweeping of chamber sides onto filter	

(0.0291 - 25 = 0.0012)
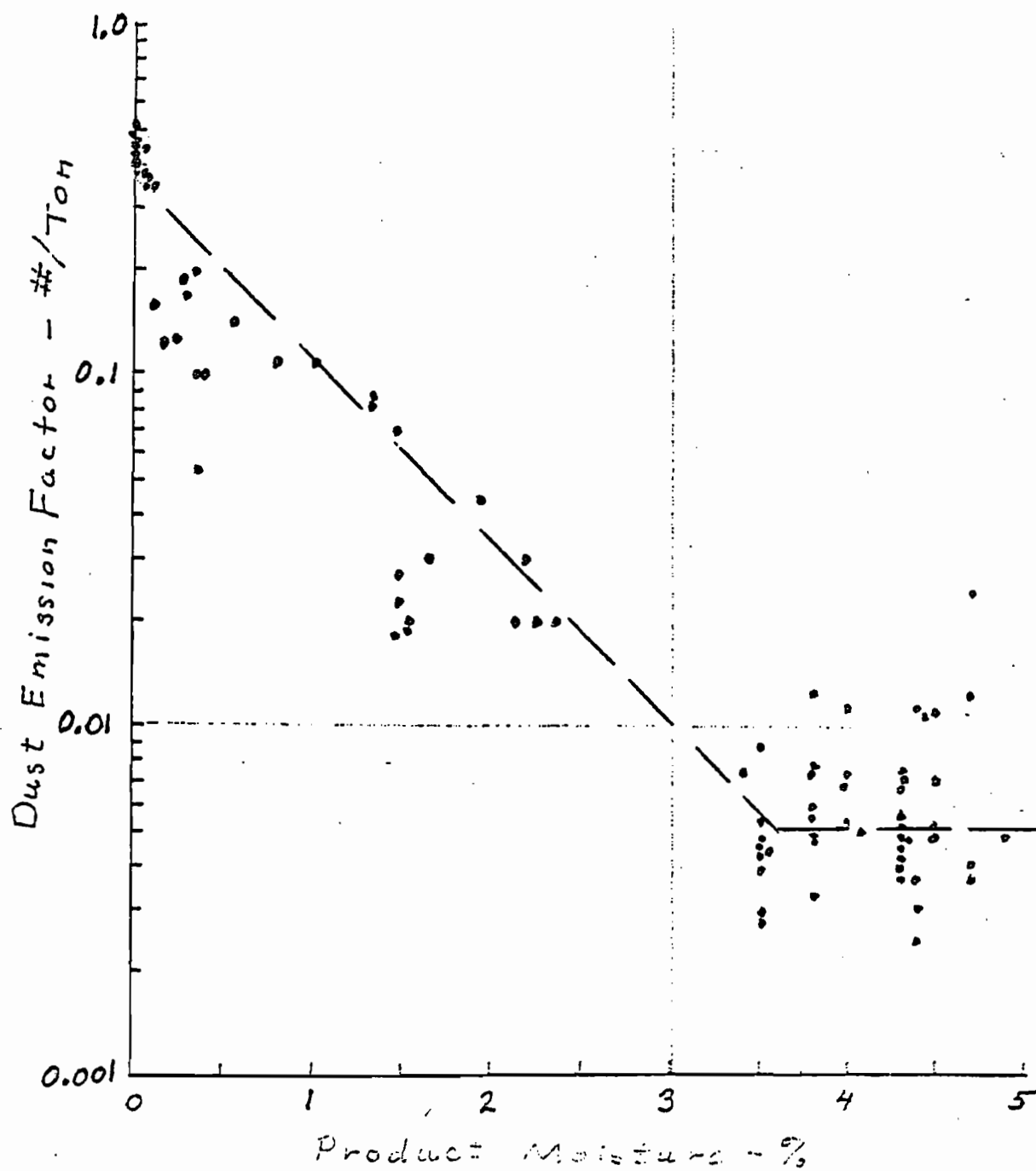
Figure 6. Dust Emission Factor vs Product Moisture for Wet Sulfur Prill

Figure 5
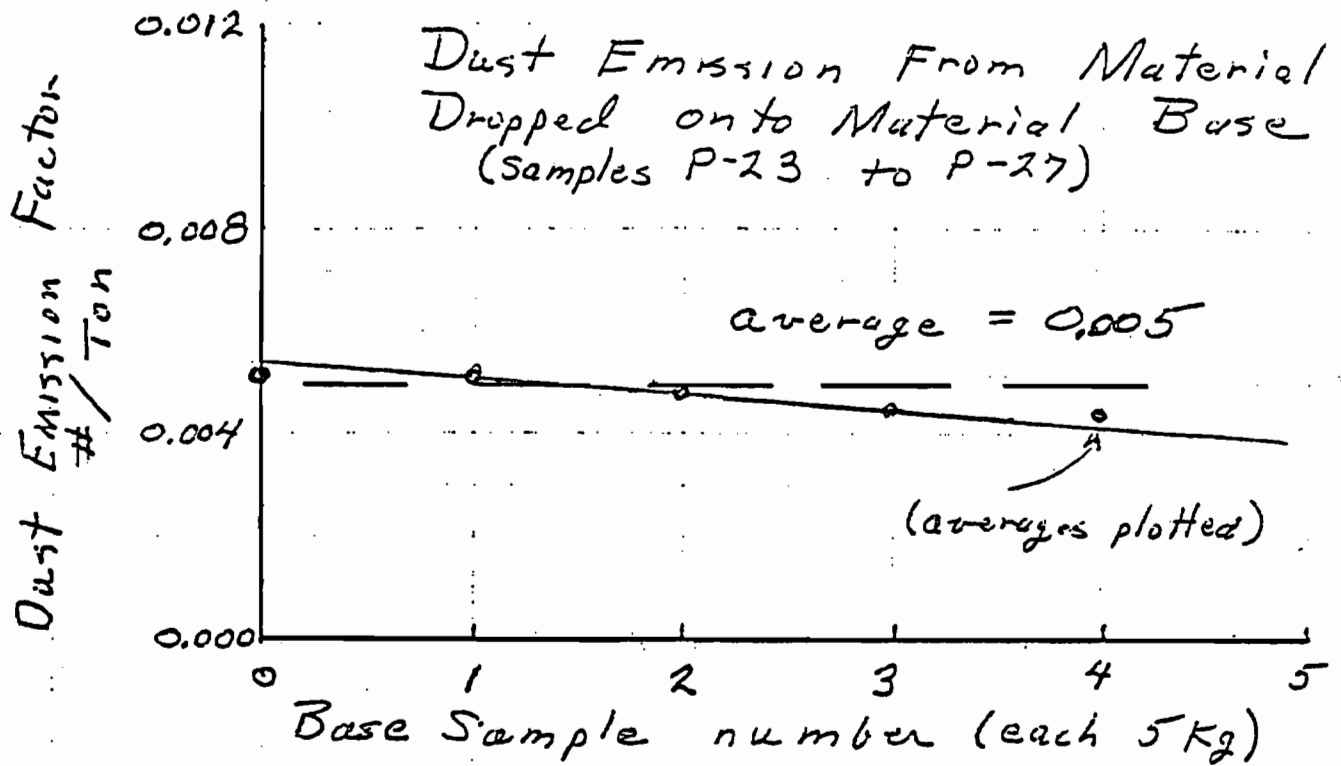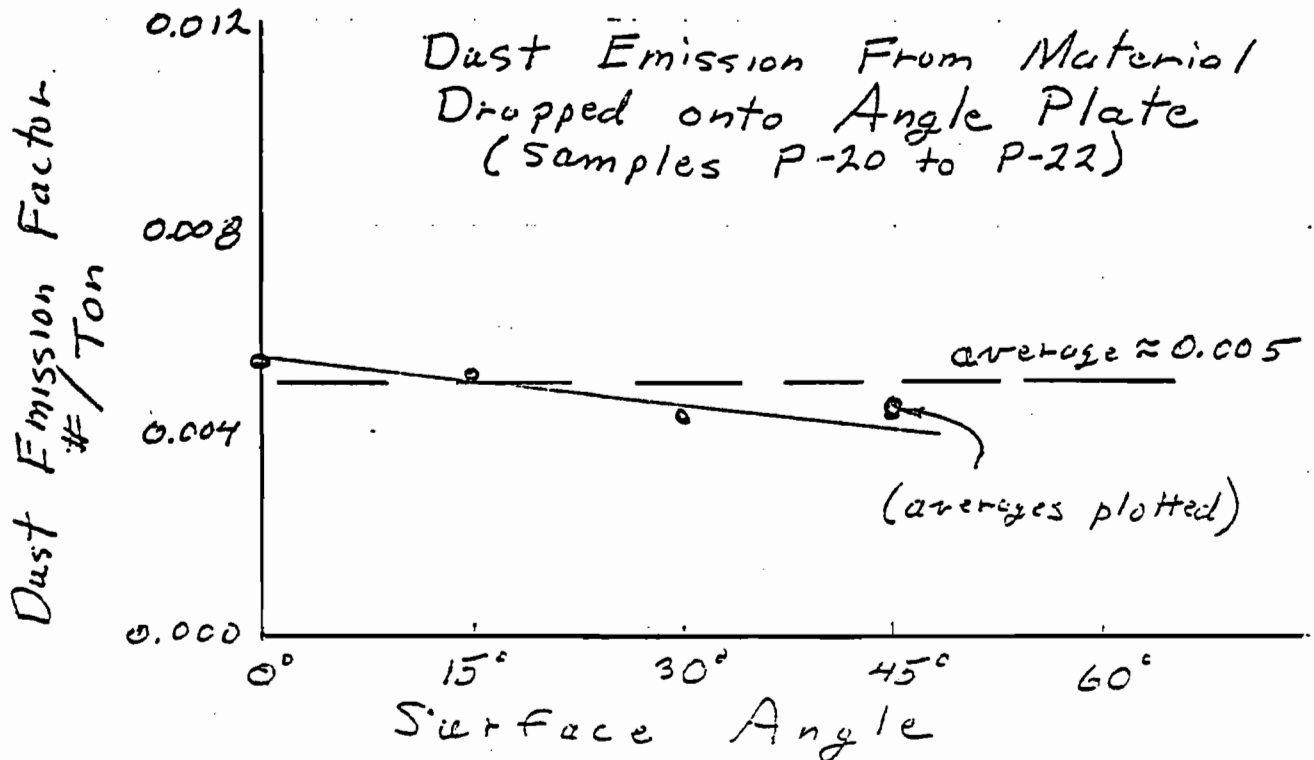
Dust Emission From Material
Dropped onto Material Base
(samples P-23 to P-27)

average = 0.005

(averages plotted)

Base Sample number (each 5 Kg)

Figure 4.

Dust Emission From Material
Dropped onto Angle Plate
(samples P-20 to P-22)

average ≈ 0.005

(averages plotted)

Surface Angle

ATTACHMENT   7

DEPARTMENT OF ENVIRONMENTAL REGULATION

TWIN TOWERS OFFICE BUILDING
2600 BLAIR STONE ROAD
TALLAHASSEE, FLORIDA 32301-8241

BOB GRAHAM
GOVERNOR

VICTORIA J. TSCHINKEL
SECRETARY

March 17, 1983

Dr. Dale A. Lundgren
Professor of Air Pollution Engineering
Environmental Engineering Department
University of Florida
410 Black Hall
Gainesville, Florida 32611

Dear Dr. Lundgren:

RE: Prilled Sulfur Handling Emission Factor
Agrico, So. Pierce, Permit Application

On Tuesday afternoon March 1, 1983, you, Matt Livingood, Hal Scott, John Svec, and I met in my office in Tallahassee to discuss the emission factor development work you have been doing for Agrico Chemical Company in connection with their 1982 permit application to construct a prill sulfur unloading facility at South Pierce in Polk County.

As a result of that meeting, I believe a misunderstanding has existed between us concerning the specific information I thought I had requested at our January meeting. It is my hope that this letter in combination with the results of our discussion on March 1, will serve to remedy any remaining misunderstanding concerning the specific type of information which I believe the department needs in order to resolve the sulfur handling particulate emission factor question to the extent that it applies to the South Pierce application.

REQUESTED INFORMATION

I'll begin by listing for you the specific information I thought I requested at our January meeting. And, I'll explain my rationale concerning each request in each case where in may not be self-evident.

(1) I asked for a detailed decription of how you conducted your particulate drop test to quantify the prill sulfur emission factor, so the department or any other interested person could

reproduce your results if it were to become necessary or desirable to do so. An analysis of your apparatus was performed by Mr. Douglas Anderson of Texasgulf Chemical Company (copy attached). It indicates only particles under 29 micron could be captured by the filter. Your analysis of this paper is needed to justify the emission rate results obtained by your apparatus.

(2) I asked you to conduct a test using a 10 foot drop in addition to your normal 5 foot drop to test Meisen's theory (as I understand it) that the amount of particulate generated would be a linear function of the freefall height, providing the particles had not reached terminal velocity.

(3) I asked you to conduct a few special drops on an angle plate. Miesen's theory seems to suggest that a 10 foot drop onto a 45 degree angle plate would produce the same amount of emission as a 5 foot drop onto a flat plate. I wasn't sure that prill sulfur pellets would behave that way, because it seemed that the assumption had to be that the particles would behave in an elastic way. Determining whether this was true or not would have application to freefall into the side of a bin or an angled shoot.

(4) I asked that several samples be repeatedly dropped at least 10 or 15 times to determine the progressive attrition of particles; that is, to determine if the amount of dust generated on each drop, would approximately increase, decrease, or remain the same after successive drops. I felt this was necessary to more realistically assess the total effect of prills passing through a number of drops transfer points in an actual live conveying and handling system.

(5) I asked that there be a determination of the wettability of the prill sulfur sample and that such data be developed to allow an assessment of how quickly a wetted prill sulfur sample would dry out. I asked for this because it appears that the department is being asked to rely on the ability of prill sulfur to be wetted and to be kept in a moist state during storage and handling as the principle means of preventing excessive sulfur dust emissions from occurring.

(6) I asked that you repeat your standard test at least 30 times so enough data would be generated to make an assessment of the statistical variability and validity of the results.

(7) I asked that prior to and after each of these experimental drops that a standard sieve analysis be conducted to determine the fraction of the sample that was less than approximately 300 microns (a 50 mesh screen); the fraction that was below approximately 60 to 70 microns (a 200 mesh screen) and one or two cuts within that range (60-300 micron).

The purpose of the sieve analysis prior to each drop was to determine what fraction of fines existed prior to the drop, so a determination could be made as to how much fine particulate was generated as a result of the drop, as opposed to that fraction which already existing in the sample. The purpose of the sieve analysis after your standard test was to determine what fraction of fines remained with the sample deposited on the bottom of the chamber as opposed to the amount of fines collected by the high volume air sampler.

I had asked for the minus 60/70 micron cut (which I refer to as silt or suspended fines, for convenience) because that fraction approximately corresponds to what would be collected in the outside air by a high-volume air sampler.

I asked for the determination of the larger particle size increment ranges (up to approximately 300 microns) because those size ranges represents particles that have the potential for settling out in the immediate area of a facility if, in fact, they become airborn as a result of the materials handling operations being conducted. I refer to particles in this larger size range as course fines or settleable particulate.

(8) For the series of standard test that you were going to run, I had ask that the tests be run at various moisture contents so a determination could be made of the effect that various moisture contents would have on the apparent emission factor. It was my intent that the sieve analysis requested also be conducted at various moisture contents, specifically the ones for which you were running the standard tests.

(9) I also asked that you show that what was collected on the Hi-vol filter in your chamber represents essentially all of the dust that in fact became airborn as result of the drop.

EVALUATION OF INFORMATION SUBMITTED

Based on the written information you have provided me to date, and the information provided during our March 1 conversation the following is my current understanding of what can and can not be concluded from the results you have obtained to date.

Bone-dry Prill Emission Factors

First, the Fletcher wet prill samples you have tested have contained approximately one percent silt fines as received, prior to any drop test, (based on determining the silt content by first drying the samples to less than one-tenth percent moisture and performing a sieve analysis with a standard 200 mesh screen, approximately 77 microns). If all of these silt fines were to become airborn as a result of handling this material, through truck unloading or other types of drop transfer operations, the appropriate emission factor would be approximately 20 pounds per ton of material handled. When such a bone-dry sample is dropped in your drop-test chamber, the indicated actual emission rate is approximately 0.2 to 0.4 pounds per ton per a five foot drop. Based on a ten foot drop test$ which you have conducted, you would expect that the indicated emission rate from a 10 foot drop would be approximately twice that much. Therefore in using the emission factor derived from your drop-test chamber, it is appropriate and in fact necessary to take into account the freefall height involved in the drop transfer operation for which the emission factor is being applied.

Dropping a sample on an angle plate doesn't appear to give significantly less emission than dropping a sample on a flat plate. I would appreciate having your views on why this is so.

If I understood your discussion properly on March 1, you think that if the twenty pound per ton bone-dry sample were to be redropped, that prior to the second drop the total silt fines content would probably increase from approximately 20 pounds per ton to 21 or 22 pounds per ton. And that if you continue to redrop the same sample, that upon each five foot redrop, you would get an increase in the total silt fines content of the sample of approximately 5 to 10 percent. However, the amount of silt fines actually released into or entrained in the ambient air as a result of each drop, would remain approximately constant at around 0.2 to 0.4 pounds per ton; or approximately no more than 2% of the total silt fines content of the sample would be

discharged to the open air as a result of the impact associated with each five foot drop.

One of the questions raised about this result is whether such a sample, during freefall in a 5 to 10 mph wind, would still only release approximately 2% of the total silt fines content during each five foot drop or whether it is more likely that an additional amount of silt fines would be stripped from the falling column of particles due to wind entrainment. Do you think this is likely? If so, how can the effect of wind entrainment be quantified? If you don't think wind stripping is an important factor in determining the actual total amount of particulate released per drop, why not?

To conclude my discussion of the bone-dry emission factors, it seems that if the undropped sample contains 1% silt fines by weight, it is likely that it also contains at least 1% settleable fines, (that is particles in the range of approximately 75 to 250 or 300 microns). In fact, I would think that if the silt fines content is 1%, it is not unlikely that the settleable fines portion could be 2 or 3 percent.

For PSD applicability determination purposes, and for purposes of modeling with respect to the particulate ambient air quality standard, we would be concerned with the silt fines content (or more specifically the silt fines emission rate).

For purposes of other env_ronmental impacts associated with the project we would also be concerned with the potential for the emission of settleable fines because it is this fraction that can result in sulfur dust deposition within the immediate vicinity of the plant.

Many of the concerns expressed about handling prill sulfur and sulfur in other solid forms, have their origin in the possibility of increased acidification of soil due to excessive deposition of sulfur particles in the vicinity of the sulfur dust generating operation. Without a way of reasonably quantifying the potential of a project for emitting particles in the settleable size range it is not possible to make an assessment of the potential adverse environmental effects that might be associated with the project. That is one of the reasons that I felt that the sieve analysis data was an important factor in the determination the department has been asked to make.

For example, if the South Pierce facility is to handle 600,000 tons per year of prill sulfur, and if 2% of that constitutes settleable fines, the potential exist for a emission of 12,000 tons per year of settleable particulate. If that all fell out within a three kilometer radius of the plant, there would be an average deposition rate of approximately 320 kilograms per hectare per month which would indeed be excessive. The Canadians apparently feel that a sulfate deposition rate of above 20-30 kilograms per hectare per month is unacceptable. I don't think the proposed project would result in deposition rates of that magnitude. But the point of the illustration is, that in the limiting case, there appears to be a basis for real concern about the potential adverse affects of such a project, if we can't adequately quantify the actual emissions, and if we cannot determine what emission controls would be adequate to prevent such emission rates of settleable particulate from occurring.

If only 1/50th of the potential were actual emitted for each five foot drop and the South Pierce operation were equivalent to five such drops then the average deposition rate would be more like 3% kilogram per hectare. If 3% kilograms of pure sulfur is equivalent to 8% of sulfate, then on average the deposition rate would still be unacceptable.

If keeping the prill moist would further reduce the actual emission by another 1/50th there probably would not then be a problem.

Why should the department believe that the actual emissions from moist prill would be only 1/500th or so of the settleable particulate fines content of the dry prill? And, if that is approximately true, what assurance does the department have that the prill will, in fact, be keep in an appropriately moist state?

Moist Prill Emission Factor

That leads to a discussion of the effect of moisture content on the actual emission rates that would result from handling various kinds of prilled or pelletized sulfur. I felt and still feel that the before and after standard sieve analysis at various moisture contents is one good way in which the effect of moisture content could be demonstrated on both the apparent silt and settleable fines content of the samples. I think such

information is needed, in combination with the information on the amount of silt fines generated per a five drop, in order to adequately evaluate all potential environmental effects of handling prill sulfur at various moisture contents.

During our meeting on March 1, you presented us with a demonstration of the effect of moisture content on the apparent fines content of a prill sulfur sample. With small standard sieves you demonstrated that a bone-dry sample would pass through the smaller sieves. Upon adding enough moisture to the sample to represent at least three to five percent moisture content you then attempted to resieve the material and demonstrated that only an inperceptible amount of material would even pass through the coarser screen, which illustrated that the moisture tended to bind the smaller particles to the larger particles, effectively reducing the apparent silt and settleable fines content. That is what I was asking you to quantify with the before and after sieve analysis at various moisture contents. If you feel, for technical reasons, that cannot adequately be done, then I would like for us to discuss the point further to see what alternative there is for providing objective quantifiable information on the point. What I would like to know is this: if you progressively increase the moisture content of a sample of undropped prill, and another sample that has been repeatedly dropped 10 to 20 times, (beginning at a tenth percent moisture and increasing the moisture content to 0.5%, 1% 1.5%, 2%,; 3% moisture) what progressive effect does that increase in moisture content have on the apparent fraction of silt fines and settleable fines in the sample and the amount the silt fines generated and caught by the Hi-volume air sampler in your standard drop test chamber?

In the demonstration you gave, and in the discussion presented with it, you seemed to think that by moistening the sample that had been redropped many times, you effectively reduce the fines content to a point where its actual emissions on handling would not be significantly different than the moistened undropped sample. If that is the case, it is important to have some kind of quantative demonstration of that fact.

It is important to know whether it is necessary to keep the sample at 3% moisture, 2% or is 1% adequate. It is important to know whether the "percent moisture versus the airborn fines generation rate" is or is not approximately the same for different types of prills that might be used at the South Pierce facility. In conflict with the air quality consideration, it is

indicated in R. A. Joyce's paper "Improvement in Export Sulphur Facility" (page attached) that each one percent increase in moisture content requires an additional twenty percent increase in energy consumption during melting. This conflict has to be balanced for operation of the facility. Information provided in your February 8, 1983 submittal indicates the sulfur pile would dry to essentially bone-dry, without a heavy rain. Therefore, the methodology and frequency for a spray system is necessary to provide assurance that the moisture content of the sulfur would be maintained.

Conclusion

The practical implications of this information involves questions such as: if the prill needs to be maintained at or above 2% moisture, is it necessary to have water sprays or other means to keep it at such levels in order to prevent unacceptable emissions of either silt fines or settleable fines? If such controls are needed, they probably could be designed into the project. But at this point it is not clear to the department whether such precautions are needed or not. If maintaining a certain moisture content is the important part of an acceptable control plan, how do we readily determine moisture content in the field, and what assurance do we have that the moisture content will be kept at or above an appropriate level? If there is a significant fraction of settleable fines that needs to be prevented from being emitted into the air through the use of water sprays or other means, how will this collected material be confined and prevented from affecting surface or ground water, surrounding land, or vegetation?

In summary, with the exception of the sieve analysis data, you have provided the department with essentially all of the other information requested.

The department is faced with a situation where it looks like you are dealing with a material whose moisture content in the field could vary significantly if means are not taken to prevent the material from drying out. The material will be dropped through more than a 5 foot distance, and more than once, possibly at some times under windy conditions. The emission factor developed by your chamber appears to be for an individual 5 foot drop in still air. Some of your results seem to support the assertion that the material can be readily wetted; and by keeping it wet at 2 to 3% moisture the actual emission rates

resulting from handling the material are significantly reduced from the bone-dry situation.

Basically what I am asking you is how to properly apply the emission factors developed from your drop test along with other relevant information to establish that: (1) the emissions of the silt fines fraction at South Pierce will not result in any violation of the particulate ambient air quality standard or PSD increments; and (2) that the realistic potential emissions of settleable fines resulting from the operation of the facility will ,not result in sulfur dust deposition rates around the facility that in any significant way would have adverse effects on soils, vegetation, surface or groundwater quality or other environmental values. If you feel such conclusions can be drawn from the information you have already presented, please outline for me how such a conclusion can be reached. If not, let's agree on what additional information is needed, so we can preceed to resolve this question as soon as possible.

To bring this matter to a conclusion so that a permit may be issued, I would suggest that the following things are done after you discuss with Agrico who would have responsibility for completing them.

(1) Please advise me if it appears that I have an understanding of your work that you have completed and a comprehension of the results. If not, please correct any misunderstandings.

(2) Please provide any answers for each specific question that has been raised in this letter. Please provide us with the sieve analysis data unless the data is unpractical or unnecessary. Please explain to us how we will be able to reach a reasonable decision if this data is unnecessary.
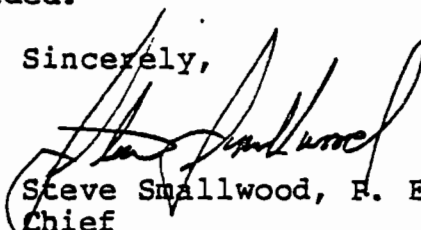
(3) After a reasonable time has expired to evaluate this request, we are prepared to meet to discuss any technical issues with you and Agrico.

John Svec and ~~myself~~ I enjoyed our conversation with you on March 1, 1983. It was very interesting and informative. In this letter, I have attempted to described the information needed to

Dr. Dale A. Lundgren
March 17, 1983
Page Ten

properly recommend the approval of the permit.   Basically, I am
asking you and Agrico to provide us with the information we feel
is needed to reach a sound decision on this matter or to explain
to us why this information is not needed.

Sincerely,

Steve Smallwood, P. E.
Chief
Bureau of Air Quality
Management

SS/ks

cc: M. Livingood
      H. Scott
      H. Long
      L. Lahman
      D. Thompson
      E. de la Parte
      J. Svec
      C. Fancy
      B. Thomas

SUMMARY AND CRITIQUE OF LUNDGREN'S DETERMINATION OF EMISSION FACTORS FOR FUGITIVE EMISSION SOURCES

By Douglas H. Anderson, Texasgulf Chemicals Co.

Dr. Dale A. Lundgren, University of Florida, used a test apparatus consisting of a 2 foot square, 5 foot high box with the test product dropped in through an 8 inch duct terminating 3 feet above the bottom to model the fugitive emissions from handling sulphur prill and phosphate rock. A high volume sampler drew air into the box through the duct and then out through a standard 8 X 10 inch glass fiber filter. Two series of tests were run, one using prilled sulphur and one using phosphate rock. Phosphate rock was used to get an indication of how the dust created in the test apparatus compared with published data. Phosphate rock had the most reliable estimate of emissions of several different materials listed in two referenced EPA documents.

The product (sulphur prill or phosphate rock) was dropped

into the test chamber through the 8 inch duct and allowed
to fall to the bottom of the test chamber. The fall was
approximately 5 feet. If the product attained the same
velocity as the incoming air (172 ft/min or 2 miles/hr) it
would be the equivalent of an additional drop of 0.13 feet
in a vacuum; thus, the additional energy that could be added
by the air stream is neglibible. The 2 mile/hour or less
air stream does not seem great enough to simulate wind in
actual practice except possibly where the fall is in an
enclosed area. The downward air stream is supposed to blow
the generated dust into the air space where the particles
less than 60 uM (60 microns or micro-meters) in diameter are
supposed to be carried to the filter.

Roger Gay, Texasgulf Chemicals Co., and I did some calcula-
tions to determine the terminal falling velocities of several
different sizes and types of particles to determine their
capture characteristics. Because of their velocities none
of the particles were in the "Stokes' law" range but were
either in the "intermediate" range or between the "Stokes'
law" range and the "intermediate" range (see "Transport
Phenomena", by R. Byron Bird, Stewart and Lightfoot, pages
190-194). The basic data for predicting flow in these
higher ranges is not as accurate as that for the "Stokes'
law" range so the results are approximate. Another source

of error is that the equation assumes the particles are
perfect spheres whereas in actual practice they rarely
are. The density of sulphur is 129 lb/cu ft ("Facts
About Sulphur", Texasgulf Sulphur Co.) and the density
of phosphate rock was assumed to be 206 lb/cu ft based
upon some rough laboratory work.

If it is assumed that the downward flowing inlet air
stream occupies a negligible area when it is descending
and that when it hits the bottom of the test chamber it
is directed upward and distributed uniformly across the
cross sectional area the calculations show that the largest
unit density particle (1 gm/cc or 62.4 lb/cu ft) that can
be carried to the filter is 41 uM. The calculations show
that the largest transportable sulphur particle is 29 uM
and the largest phosphate rock particle is 25 uM (see
Table 1. Velocities of Various Particles). The average
upward air flow in the test chamber was 14 ft/min and the
flow needed to carry a 100 uM unit density particle upward
is 58 ft/min. The air flow inside the box is more complex
than that assumed and some localized areas will have air
flow rates greater than the calculated average and others
less but it is difficult to predict the air flow pattern.

It is possible for a 100 uM unit density particle in the test chamber to be captured by the filter paper but it must be entrained in a localized air flow pattern with a velocity of at least 58 ft/min. CFR 40, Part 50, Appendix B, indicates that a high volume particulate sampler should collect particles (assume unit density) 100uM in size or smaller. Dimension measurements made on a standard high volume sampler in our laboratory indicate a 94 to 131 uM particle can be captured, depending on the inlet flow rate which can vary between 40 and 60 cu ft/min. The equivalent size range for sulphur particles is 63 to 83 uM and for phosphate rock particles is 49 to 63 uM. Since one of the purposes of the test chamber was to simulate the characteristics of a high volume sampler it seems that the air flow in the chamber should have been sufficient to transport 100 uM particles to the filter. It appears that with the air flow in the chamber there may have been a large number of particles that could not reach the filter because the air flow was too low. The air flow at the face of the filter was sufficient to capture a 109 uM sulphur particle if it could be transported to the vicinity of the filter.

The source, size, method of manufacture, age, fines content,
shipping history and other pertinent data were not given for
the sulphur prill, nor were similar data given for the phos-
phate rock. ·This information would be helpful in evaluating
the performance of a real system.

I have found it difficult from the write up to determine
the history of the handling and treatment of the products
during the tests. On page 3 it is stated, "a total of
eight tests were run on dry phosphate rock (duplicate tests
on four samples)." I do not know how to interpret this
statement; was each sample tested twice at each different
moisture level or is there another meaning? The summary
table lists seven tests and it is difficult for me to re-
late this to the history of the product under evaluation.

The emission estimate table also raises several questions.
The same emission factor determined by the test (0.0068
lb/ton) was used for each activity. Apparently "storage"
was assigned an emission rate of 0.0068 because the sum of
the activities listed under it add up to 0.0067 and the
difference could be in rounding off. I do not know how he
arrived at the "storage" breakdown; maybe the method is in

TABLE 1. TERMINAL VELOCITIES OF VARIOUS PARTICLES

TERMINAL VELOCITY, ft/min @ DIAMETER	49 @ 60 uM 98 @ 100 uM	73 @ 60 uM 137 @ 100 uM	26 @ 60 uM 58 @ 100 uM
LARGEST TRANSPORTABLE PARTICLE IN TEST CHAMBER	29 uM	25 uM	41 uM
LARGEST PARTICLE TRANSPORTED NEAR FILTER IN TEST CHAMBER	109 uM	81 uM	170 uM
LARGEST PARTICLE TRANSPORTED INTO A STANDARD HI VOL SAMPLER	63 uM to 83 uM	49 uM to 63 uM	94 uM to 131 uM

NOTES: uM = micrometer or micron
AVERAGE VERTICAL AIR FLOW IN CHAMBER = 14 ft/min
AIR FLOW INTO A HIGH VOLUME SAMPLER = 52.6 ft/min AT 40 cu ft/min
= 79.0 ft/min AT 60 cu ft/min

"Technical Guidance for Control of Industrial Process Fugi-
tive Particulate Emissions" which we do not have. Why should
each major activity have the same emission rate? Most of
the rest of the material in the table is inapplicable because
it was probably for their Big Bend terminal.

In the test on dry phosphate rock an average emission rate
of 1.5 lb/ton was obtained and apparently it was compared
with the 2 lb/ton factor in AP-42 in the "transfer and storage"
category of phosphate rock processing and a conclusion was
drawn that the method was reasonably satisfactory. In the
emission estimates table the AP-42 "open storage piles"
category emission factor of 40 lb/ton or 20 times that for
"transfer and storage" was apparently neglected. Based on
this it seems that open storage of sulphur prills may have
emissions greater than 0.0068 lb/ton, though an increase of
20 times may not be applicable.

This test partially evaluates the dusting characteristics
for the falling of small amounts of product but does not
evaluate dusting from the fall of large amounts or particle
break up caused by the rubbing together of product during
other transfer operations or during shipping. Neither does

it evaluate the break up caused by the pressure of high
stacks of product. The test may be valuable for comparing
similar products such as different prills or different
moisture contents of the same product when they drop.

When one considers the large sums of money and the poten-
tial environmental problems that are at stake it seems
reasonable that this test should be further authenticated.

this dustiness, the terminals have installed water sprays at various locations throughout the handling system. In addition, PCT has utilized dust collection and wet scrubbers at the rotary dumpers for several years. The use of large quantities of water for dust control has proved effective in reducing dust emissions. Unfortunately, the use of water has several adverse side effects which can be summarized as follows:

1. Sulphur laden water used in dust control cannot be disposed of directly to the ocean and must, therefore, be collected and treated in sumps or settling ponds. This treatment is costly in terms of ongoing maintenance and ultimately creates a contaminated sulphur disposal problem when the dust is settled out of the water effluent.

2. Water tends to reduce the effectiveness of belt cleaning devices and leads to generally messy site conditons. Here again there is an ongoing maintenance problem.

3. Water containing elemental sulphur will acidify over time and thereby lead to corrosion of terminal facilities such as conveyor support structures, mobile equipment and rail-car dumpers.

4. In most cases, the water added at the terminals must ultimately be boiled off by the user prior to remelting the sulphur itself. Boiling off the water results in higher than necessary energy costs for the end user. As a rule of thumb, each 1% increase in moisture content results in a 20% increase in energy consumption during melting.

Faced with these sorts of water related problems, there has been an ongoing effort by the industry and the terminals to reduce terminal water addition. Progress has been slow to date, because of conditions which exist at the terminals. The following is a brief summary of some of the steps which have or will be taken to reduce terminal moisture addition.

1. Pneumatic water sprays have been installed at the Vancouver Wharves rotary dumper. These sprays when operated regularly should reduce the water addition at this location from 20 pounds per tonne to less than 1 pound per tonne. The rotary dumper at both terminals is recognized today as a main source of terminal water addition.

2. New conventional fine spray nozzles are being installed at both terminals which add much less water than the coarse nozzles now in use. These nozzles are being installed at transfer points which cannot be served by the pneumatic system being installed at the Vancouver Wharves dumper.

3. Paddle switches are being installed on conveyors and shiploaders which will automatically stop sprays when product is not being handled. Heretofore, spraying frequently continued even when belts were stopped due to hold changes, coffeebreaks, and the like.

4. New, more effective belt scrapers and brushes are being tested at both terminals. These new scrapers combined with reduced moisture addition should lead to less site clean-up requirements particularly around transfer points.

5. It is possible that a full scale foaming system will be installed at PCT in the near future. This system incorporates an organic foam which suppresses dust emissions not only at the point of application but also at other transfer

ATTACHMENT   8

Bill

July 5, 1983

Mr. Steve Smallwood
Department of Environmental Regulation
2600 Blair Stone Road, Twin Towers
 Office Building
Tallahassee, Florida

DER

JUL 07 1983

BAQM

Re: Agrico's South Pierce Air Construction
     Permit Application; AC 53-55780

Dear Steve:

Enclosed please find Dr. Lundgren's response to your
letter of March 17, 1983. We apologize for having taken so long
to respond, but Dr. Lundgren needed the time to re-examine all
outstanding information in order to address your concerns. How-
ever, before reviewing Dr. Lundgren's letter, it would be helpful
to examine your letter in light of this particular project.

The proposed South Pierce sulphur facility will receive
prill sulphur by either rail or truck, ▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓ 1
▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓ it in 900   ccc,c
long ton per day melters. This facility will have ▓▓▓▓▓▓▓▓▓▓ 24hrs
▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓▓. Any emissions from the dumping
hopper will be controlled by a mist spray system and any emissions
from the storage hopper will be controlled by a wet scrubber in
the head house.

There will be no open stock piles of prill sulphur at this
facility. The material will be unloaded and melted as soon as
it arrives. Furthermore, the sulphur will ▓▓▓▓▓▓▓▓▓▓▓▓▓▓ if it
is ▓▓▓▓▓▓▓ ??

In your March 17, 1983 letter, we believe DER lost sight
of these particulars. For example, you voice concerns about the
effect of wind erosion on open stock piles and the re-wettability
of the material. Although these would be legitimate concerns
in permitting a Big Bend-type project or in a rule inquiry, they
are completely inapplicable to the facility at issue. Here, the
prill sulphur will not be exposed to the wind and the material will
not have an opportunity to dry out before being melted.

de la PARTE AND GILBERT, P. A.

We are confident that when viewed in the context of this particular project, Dr. Lundgren's letter constitutes a full and complete response to your concerns. Additionally, when coupled with new information previously submitted by Agrico, it constitutes reasonable assurances that the facility will meet all applicable standards. Consequently, we request that the Department reconsider its previous decision and issue a letter of intent to grant Agrico's permit application.

Sincerely,

de la PARTE & GILBERT, P.A.

Edward P. de la Parte, Jr.

EPD1P/mew
cc: Don Morrow

ATTACHMENT   9

September 22, 1983

Mr. Edward T. Huck
Bureau of Air Quality Management
Department of Environmental Regulation
2600 Blair Stone Road
Tallahassee, FL   32301

Dear Mr. Huck:
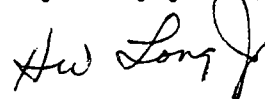
Re   SPCW Sulfur Permit - Application No. AC 53-55780

This letter and attachments are in response to several
questions you had on the referenced permit application,
during meetings with Agrico and DER personnel on
August 23-24, 1983 in Tallahassee.

The questions were given verbally during our meetings and
we have attempted, with help from notes taken, to respond
to each question you posed.

The attached materials are in response to the questions.
Please advise me if you may require further clarification.

Very truly yours,

H. W. Long, Jr.
Manager
Environmental Control

HWL/jm
Attachments

cc: Mr. D. R. Morrow
     Mr. D. H. Lynch
     Mr. B. Trusty
     Mr. L. Lahman
     Edward P. de la Parte, Jr., Esq.

Moisture Content of Prill Received At SPCW

Wet prill sulfur received at SPCW will not be unloaded if the moisture content is less than 3%. This moisture content will be determined by the following procedure:

Truck:

The upper three (3) feet of the prill will be randomly thieved, samples composited, and percent moisture determined by microwave oven procedure. Percent moisture could be determined within 10 minutes. If percent moisture is determined to be below 3%, water will be added to the entire load with a metered, movable spray system. The net weight of the prill would be known and water addition would be made on a weight basis to adjust moisture percent to 3 minimum before unloading to system. Sampling frequency may be adjusted by mutual agreement of Agrico and DER representatives after first hand observations are made on moisture consistency, and threshold moisture contents relative to particulate emission.

Rail:

Percent moisture determination and required adjustment would follow the above truck procedure, except for the unit train the first and last car would be sampled.

Quality assurance and unloading determination will be assigned to the Area Manager - Sulfuric Acid or his designated representative.

Control of Prill Shipments and Personnel:

Agrico would have control of any truck shipments from Big Bend Terminal. Once other rail or outside truck shipments are received at SPCW, Agrico will have full control of the product and all personnel involved in any prill activity. All records, data and reports on prill activity would be maintained in a special file. This file would be housed at a specific location designated by the Area Manager - Sulfuric Acid.

Dump Hopper Shed - Wind Tunnel Effects:

Most high winds in Florida are created by rainstorms and are normally of short duration. However, to minimize any windage effect on the unloading operation; Agrico will install a wind anemometer that will sound an alarm at a wind speed of 35 MPH. Prill unloading operations will be terminated until the wind has subsided to below the 35 MPH velocity. The closest non-Agrico owned property is approximately 400 feet west of the unloading shed and 90 degrees off the north-south opening configuration. This area is a phosphate clay settling area owned by W. R. Grace, a mining company and is not accessible to the public. The nearest public property is State Road 630, one and three-quarter miles south of SPCW. The nearest residence is approximately three and one-half miles southeast of SPCW. We are providing you with a property ownership map of the SPCW area and an aerial map (1983) of the same area.

Emission Testing:

All emission tests for initial permit compliance will be conducted by the Agrico Environmental Department, witnessed by a DER observer. This department has certified visual observers and trained stack sampling personnel.

Particulate Emission Projection:

From data contained in the permit application and a report by Dr. Dale Lundgren on February 28, 1983 (figure 6), we have prepared a chart of emission projections for various conditions:

Is Waste Heat Steam Available for Sulfur Melting?

From page 47 of Freeport Sulfur Handbook, the enthalpy of molten sulfur at 125° C (257° F) is 61.97 Btu/lb., and of solid sulfur at 25° C (77° F) is 7.53 Btu/lb. Thus, the heat required is 61.97 - 7.53 = 54.44 Btu/lb., or 121,946 Btu/L.ton. At 4.0% moisture, moisture content = 2,240 x 0.04 = 89.6 lb/L.ton. The enthalpy of atmospheric steam is 1150.5 Btu/lb., and water at 25° C (77° F) is 44.4 Btu/lb. Hence, heat required for water removal is (1150.5 - 44.4) Btu/lb. x 89.6 lb./L.ton = 99,107 Btu/L.ton. Thus, total heat required is 121,946 + 99,107 = 221,053 Btu/ton of wet prilled sulfur. If 95 psia (80.3 psig) saturated steam is used, the available heat from the steam is 891.5 Btu/lb. Thus, steam requirement per ton of sulfur melted would be 221,053 Btu/L.ton divided by 891.5 Btu/lb. or 248.0 pounds of steam per ton of sulfur. At the requested rate of 75 LTPH of sulfur, total steam required is 75 x 248.0 = 18,600 pounds per hour. Each of the two SPCW sulfuric acid plants are rated at 200,000 lb./hr. of steam production. These

plants typically enjoy about 95% individual annual onstream factors, so the chances of both plants being down on an unscheduled basis is very slim. However, SPCW does have a permitted standby start-up boiler with a rated steam generation capacity of 120,000 lb./hr., and is typically put into operation if both sulfuric acid plants are down. There would be no net emission increase.

In summary, we have sufficient excess steam required for melting the maximum rate of sulfur at the maximum moisture content. This is less than nine percent of the normal steam generation from a single sulfuric plant. If both sulfuric plants are shut down inadvertently, a package boiler is started to supply steam to keep sulfur molten, and can also supply melting steam, if required.

Cleanup and Good Housekeeping Procedures:

The system is designed to minimize the possibility of spillage of wet prilled sulfur. Agrico recognizes, however, that equipment failure and/or human error could possibly cause an occasional spill. During initial operation, the area superintendent or his designate will survey the entire area for fugitive wet prilled sulfur on a daily basis. After some experience is gained, the survey frequency will be adjusted to more closely match probable frequency of need for housekeeping activity. If a significant spill occurs, such as perhaps a break in the conveyor belt, the sulfur will be reclaimed into a Bobcat or front-end loader with brooms and shovels and returned to the dumping pit. The area beneath the conveyor will be paved to facilitate easy pick-up of the sulfur without contamination. Any sulfur that becomes contaminated with soil, grease, oil, etc., will be handled in the

same manner as spilled molten sulfur is handled in the existing operation.

Corrosion and Erosion Considerations:

Agrico is very familiar with the necessity of designing to resist both corrosive and erosive attack for a wide range of chemical and mechanical conditions. A wide array of stainless steels, rubber, acid-proof and carbon brick, and polymeric materials are in use at our SPCW facility. Our approach to handling wet prilled sulfur will be to avoid contact of the wet prill with bare carbon steel. The receiving pit and surge hopper will be fabricated of carbon steel for necessary strength and lined or coated with materials which have been proved to be resistant to attack by wet prilled sulfur. See J. F. Babbitt paper, Attachment U, submitted to the Department on June 2, 1982. The conveyor belt will be of rubber construction with a stainless steel belt wiper. The screw conveyors will feature aluminum screws running in stainless steel troughs. The melter will be of a proven design and will be provided with a generous free board allowance to prevent foamover during surges of high moisture feed.

Structural steel within the general area of the sulfur system but not exposed to normal contact with the sulfur will be protected with a three-coat epoxy paint system. This is standard practice at SPCW, as is demonstrated by the attached field painting specification which was utilized on a recent expansion project at that facility.

Big Bend permit application is for 300,000 LTPY and SPCW application
is for 600,000 LTPY. Explain this discrepancy and if possible, state
where additional 300,000 LTPY will come from.

The existing sulfuric acid plants at SPCW are currently consuming
sulfur well below the 300,000 LTPY rate due to economics. When operating
at nameplate design conditions, they would consume approximately 375,000
LTPY. Thus, the Big Bend permit would supply about 80% of full rate
requirements, allowing Agrico to take advantage of good spot prices
on molten sulfur for the remaining 20% of maximum current need.

The SPCW permit application requests permission to bring in up to
600,000 LTPY to allow for implementation of long range corporate plans
to expand SPCW through the addition of a third sulfuric acid plant. In
addition, the 1,800 LTPD receiving rate of wet prill sulfur will permit
SPCW to utilize existing molten storage capacity to handle surges in
receipts of prilled sulfur that are higher than daily consumption rates,
without exceeding permitted unloading and melting rates.

The source of the additional 300,000 LTPY cannot be firmly defined
at this time due to the variability between FOB Tampa molten sulfur prices
and FOB Vancouver wet prilled prices. Agrico is willing to commit,
however, that the additional sulfur shipments would originate outside
the State of Florida and that this sulfur would not be handled in the
State of Florida prior to unloading at SPCW. Agrico would expect to
withdraw this commitment if additional wet prilled sulfur receiving
permits are granted in the future by the Department of Environmental
Regulation, such that Agrico had an opportunity to obtain sulfur through
such a facility.

Final disposition of the spent caustic soda solution from the
hydrogen sulfide scrubber to which the melters are vented.

Evolved hydrogen sulfide reacts with caustic soda to form NaSH.
At the maximum predicted rate of hydrogen sulfide evolution, the scrubber
will absorb 42 lb./hr. of hydrogen sulfide, or 1.235 moles per hour. The
hydrogen sulfide will react with caustic soda (NaOH) on 1:1 mole basis,
so that 1.235 moles/hr. of caustic soda is required. Since NaOH has a
molecular weight of 40 lb./mole, 49.4 lb./hr. NaOH will be reacted.
Since the caustic soda is to be supplied as a 25% aqueous solution, feed
(and blowdown) volume will be 49.4/0.25 = 197.6 lb./hr. At 10 lb./gal.
makeup will be 20 gal./hr., or 480 gal./D. This solution will be
collected and reacted batchwise in 450-500 gallon batches in apparatus
similar to the attached sketch. The overall reaction in the batch reactor
is as follows:

$$2 \; NaSH + SO_2 + H_2SO_4 \longrightarrow 3 \; S \downarrow + 2 \; H_2O + Na_2SO_4$$
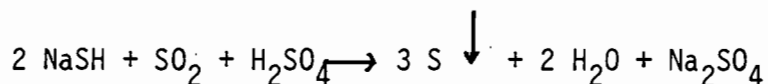
Sulfur dioxide will be sparged into the reactor from a scale-
mounted cylinder. Since the scrubber will be designed for 95% hydrogen
sulfide scrubbing efficiency, maximum daily hydrogen sulfide recovered
in the scrubber as NaSH will be 1.235 moles per hour x 0.95 (efficiency)
x 24 hours per day or 28.16 moles per day. Since two moles of NaSH react
with one mole each of sulfur dioxide and sulfuric acid, 14.08 moles of
each of these reactants will be required per batch. The sulfur dioxide
required per batch will therefore be 14.08 moles x 64 lb./mole, or 901
pounds per batch. After sulfur dioxide addition is complete (as indicated
by the scale on which the cylinder is mounted), 93% sulfuric acid is added.
The required quantity is 14.08 moles x 98 lb./mole x 0.93 x 1 gal./15.28
pounds, or 84 gallons. At the conclusion of the reaction, the tank

contents will consist of about 1,350 pounds of precipitated sulfur, and an innocuous solution sodium sulfate. The sodium sulfate will be decanted off to the contaminated pond. The sulfur will be washed to remove sodium sulfate, then returned to the unloading hopper for melting.

Unloading Belt Conveyor

The unloading belt conveyor will be designed to handle 300 TPH of wet prilled sulfur; however, the average actual unloading rate will be about 75 LTPH.

The belt width of the proposed conveyor will be 30 inches and will travel on standard 35° troughing idlers as depicted in the attached cross-sectional drawing. The belt speed will be designed to operate at 350 feet per minute.

Other features of the belt conveyor include:

- A corrugated cover that will protect the belt contents from being blown off by high winds.
- A "hold-back" device that will prevent the inclined belt from running backwards and spilling sulfur in the event of a power failure.
- A zero speed switch which will be attached to the tail pulley of the belt conveyor. This device senses the speed of the belt and will sound an alarm if the belt slips or breaks.

Dust Collecting at Conveyor Discharge

The belt conveyor will discharge the wet prilled sulfur into a storage bin which will have an impingement-type wet scrubber attached to it. The wet scrubber will be arranged to force an induced draft (negative pressure) around the conveyor discharge opening. The scrubber will be sized to handle approximately 15,000 ACFM of ambient air. The scrubber will require about 10 GPM of water of which 9 GPM will be recirculated and 1 GPM will be bled off (blow down) to the SPCW contaminated water pond. It is proposed to construct the scrubber with type 316 stainless steel.

Screw Conveyor

It is proposed to use enclosed screw conveyors to transfer and feed the prilled sulfur to the melters. For design purposes, the screw conveyor for each melter will handle a maximum of 300 TPH but the normal rate will be about 75 LTPH. Prilled sulfur is wet and essentially dust-free, and therefore there is no threat of explosion. An extremely dusty environment of 35 ounces of dust per 1000 cubic feet is required for sulfur dust to be explosive. This situation will never happen with our material.

The screw conveyor will be about 25 feet long and 20 inches in diameter which will turn at a speed of about 100 RPM. See the attached design sketch and picture of a typical screw conveyor.
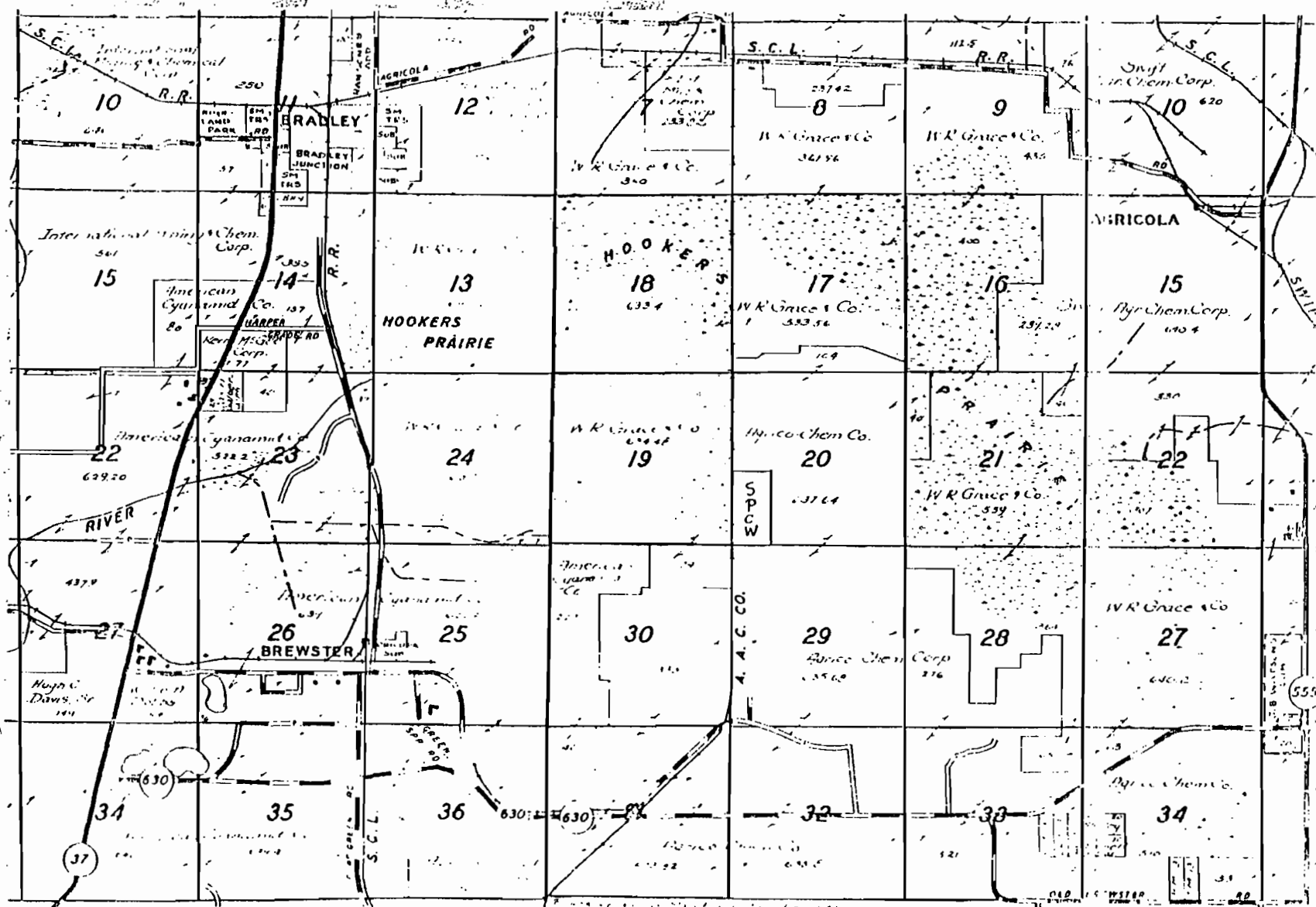
Product % Moisture	#/Ton Emission	2 Transfers W/O Control		2 Transfers - 90% Control		2 Transfers - 1-90% Control 1-50% Control	
		T.P.Y.	#/Hr.	T.P.Y.	#/Hr.	T.P.Y.	#/Hr.
0	0.40	268.8	67.2	26.88	6.72	80.64	20.16
1	0.12	80.64	20.1	8.06	2.01	24.19	6.05
2	0.038	25.54	6.4	2.56	0.64	7.66	1.91
3	0.01	6.72	1.7	0.68	0.17	2.02	0.50
4	0.005	3.36	0.8	0.34	0.08	1.01	0.25

Basis:

Ton = 2000#
Year = 8000 hours
Rate = 84 T/Hr.
#/Ton Emission Factor = Figure 6 of Dr. Dale Lundgren report dated 2/28/83

GULF DESIGN DIVISION

BADGER AMERICA, INC.

[A Raytheon Company]

TAMPA, FLORIDA

SPECIFICATION

FOR

FIELD PAINTING

AGRICO CHEMICAL CO.
PHOSPHORIC ACID EXPANSION
SOUTH PIERCE, FLORIDA

						CERTIFIED		
						ENG _____	DATE 1/3/80	
						_____	DATE 1-8-80	
II	JAN.9.80	CERTIFIED	GSD			CLIENT _____	DATE 1-9-80	
I	JAN.9.80	FOR CLIENT APPROVAL	GSD					
ISSUE	DATE	DESCRIPTION	CH'K'D	APP'D	SHEET 1 OF 17		SPE-8001-R-2	

GD-DE(H)-3-1 Rev. 1/76

SPECIFICATION FOR FIELD PAINTING

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8.0 SURFACE PREPARATION

9.0 APPLICATION OF PAINTS

10.0 STORAGE

11.0 RESOLUTION OF CONFLICTS

12.0 MISCELLANEOUS

13.0 LINE TABLE PAINT CODES

SELECTION TABLES

SPECIFICATION FOR FIELD PAINTING

1.0 DEFINITION OF TERMS

1.1 PAINTING shall include surface preparation, protection and clean-up as well as the application of primers, intermediate coats and top coats as prescribed in the specification.

1.2 SHOP: The term "Shop-Painting defines the miminum extent of the painting responsibility undertaken by the suppliers of major equipment, structural steel or piping (or any portion thereof), prior to the release of the equipment of materials to the contractor or owner.

1.3 CONTRACTOR shall mean Gulf Design Division acting for itself or on behalf of the OWNER.

1.4 OWNER shall mean the person or entity for whom the CONTRACTOR acts as AGENT or as an INDEPENDENT CONTRACTOR.

1.5 SUBCONTRACTOR shall mean the person, company or corporation supplying the necessary labor and/or materials for the performance of the work included under the SUBCONTRACT.

1.6 CONTRACTOR'S REPRESENTATIVE shall mean such person, for the time being or from time to time, duly appointed in writing by the CONTRACTOR to act as his representative.

2.0 SCOPE

2.1 This specification together with applicable drawings and requisitions, covers the basic general requirements for protective coatings of paint for equipment: piping, structural steel work and other associated items. The procedures and materials outlined in this specification are designed to assure thorough and complete painting of all areas specified in the invitation to Bid package.

2.2 The subcontractor shall provide all required material, labor, supervision, tools, equipment, scaffolding and/or other structures, miscellaneous consumable supplies, cartage, unloading, storage and such other services required to perform the work shown, described, indicated or implied within the paint requisition.

2.3 The subcontractor will obtain, at its own expense, all permits, licenses and inspections and shall comply with all laws, codes, ordinances, rules and regulations promulgated by authorities having jurisdiction which may bear on the work. This compliance will include Federal Public Law 91-596 more commonly known as the "Occupational Safety and Health Act of 1979".

3.0 GENERAL

The subcontractor shall be responsible for a thorough and complete fulfillment of all the requirements set forth herein:

3.1 All work shall be done in strict accordance with this specification, the design drawings, and the painting package, including manufacturer's printed instructions.

3.2 All work shall be done with proper equipment in good repair and by skilled workmen, according to recognized good painting practice. Excepting modifications made by this specification, all surfaces to be painted shall be prepared and painted in compliance with the Structural Steel Painting Council Specifications (Volume I: Chapter 16 and Volume II: Section 1,2,4, and 6). Copies of these may be obtained from: Steel Structural Painting Council, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213.

3.3 All painting shall be done in a careful workmanlike manner. The primer and paint shall be applied so as to prevent runs, drips, or sagging. The subcontractor shall correct all work found faulty under inspection.

3.4 Equipment shall be of the type approved by the Gulf Design representative. Unless a particular method is specified by the manufacturer of paints, the primer, intermediate and finish coats may be applied by brushing, spraying (conventional or airless) or roller coating. All air lines for spraying shall be equipped with proper moisture traps placed as far as practical from the compressor. All conventional spray pots shall be equipped with double air regulation.

3.5 The paint shall be prepared and applied in accordance with the requirements of the paint manufacturer. All ingredients in any container of paint shall be thoroughly mixed before use and shall be agitated as required during application to keep the paint in suspension. Zinc-rich paints shall be continuously agitated during application. Dry pigments and other additives which are separately packed shall be uniformly blended into paints. A skin which has formed on top of the paint shall be cut loose from the sides of the container and discarded before the mixing operation. If the skin is thick enough to noticeably affect the solids content, the paint shall not be used. All containers greater than 5 gallons shall be mechanically mixed. All mixing shall be done in accordance with SSPC Vol. 1 Chapter 4, "Practical Aspects, Use and Application of Paints" and/or with manufacturer's recommendations.

3.0 GENERAL (Continued)

3.6 Should inclement weather conditions occur or the ambient air conditions become of the kind detrimental to the cleanliness of the prepared surface and for the quality of the applied coating, all surface preparation operations and coating applications shall cease. When the conditions become proper, the surfaces shall be inspected and approved before coating application can be resumed. Areas damaged by such weather conditions must be repaired. Prime coats shall be applied the same day the surface is prepared. Each coat of paint shall be in proper state of cure and dryness before the application of the succeeding coat. Drying time shall be recommended by the manufacturer of paints.

See No
Sheet

3.7 Suitable enclosures to permit painting during inclement weather may be used if provisions are made to control atmospheric conditions artifically inside the enclosure, within limits suitable for painting throughout the painting operations.

3.8 The paint shall be applied at the manufacturer's recommended rates, but the minimum dry film thickness shall not be less than that specified in the Painting Selection Table. In the event the minimum dry film thickness has not been attained, the subcontractor shall apply an additional coat or coats until the minimum dry film thickness is attained. When steel is painted in hot weather, precautions shall be taken to assure that the specified dry film thickness of paint is obtained.

3.9 For most items (except concrete and wood) the surface preparation and priming shall be done by the "shop". In the event that any items does not have the required shop-primer, or equal, it will be the responsibility of the painting subcontractor to carry out the necessary surface preparation and application of primer, in addition to the final top-coating.

3.10 The subcontractor shall be responsible for protecting all buildings, structures and equipment from dropping of paint or other damage in his area of operation. He shall be responsible for damage done to automotive equipment, etc, as a result of painting.

3.C GENERAL (Continued)

   3.11 Painting shall not be performed on insulated pipe within three
        feet (3') of insulation operations, or on insulation whose
        covering and surface coat have not had time to set and dry.
        Painting shall not be performed on uninsulated pipe within
        one foot (1') of any type of connection until the connection
        has been made, except as directed by the Engineer.

   3.12 Locally mounted pressure gages, instrument relay boxes, etc.,
        having a factory baked enamel finish are to be protected
        prior to painting in the area, with clear plastic bags on
        instruments necessary to be read or by masking boxes and
        housings.

   3.13 Field Painting in the immediate vicinity of, or on, energized
        electrical and rotating equipment, and equipment and/or pipe
        in service shall not be performed without the approval of the
        Engineer.

   3.14 Field blast cleaning shall be avoided in process areas where
        existing machinery is present, that cannot be adequately
        covered. Agrico will determine when this condition exists.

   3.15 The Contractor's scaffolding shall be erected, maintained,
        and dismantled without damage to structures, machinery,
        equipment or pipe. Drop cloths shall be used where required
        to protect buildings and equipment.

   3.16 Contractor is responsible for the protection and eare of his
        equipment and materials, and any coating materials delivered
        to the job site.

   3.17 Rags and other waste material, soiled with paints, thinners and
        solvents shall be kept in tightly closed metal containers while
        on the job site and not in use.

4.0 COLOR SELECTION

     Finish colors shall be in accordance with the Paint Selection Table
     and shall be factory mixed (i.e., there shall be no job tinting by
     the Contractor).

5.0 INSPECTION OF SITE

     Bidders are instructed to inspect the facilities and subject items
     on the site. Ignorance of site conditions shall not be a cause of
     increase in contract price.

6.0 INSPECTION OF WORK

6.1 All work and material supplied under this specification shall be subject to inspection by Gulf Design or its representative. All parts of the work or material that are found unsuitable under this specification shall be corrected and/or replaced.

6.2 The film thickness of each coat shall be checked by each of the following methods:

6.2.1 During application, wet film thickness reading shall be taken with a wet film gauge.

6.2.2 When thoroughly cured, dry film thickness readings shall be made with a properly calibrated dry film thickness gauge. (Nordsen-Mikrotest gauge) When film thickness measurements are in conflict, the readings taken by the Gulf Design representative shall prevail.

6.2.3 Subcontractor shall provide, free of charge, to Gulf Design or its representative a dry film gauge for their use. Gauge may be used by subcontractor and returned each day to Gulf Design. Gulf Design will return gauge to subcontractor when job is completed.

6.3 Before application of the prime coat and each succeeding coat, all surfaces to be painted shall be subject to inspection and approval by Gulf Design representative. Any defects or deficiencies shall be corrected by the subcontractor before application of any subsequent coating.

7.0 SAFETY

7.1 Subcontractor is to follow all Agrico Safety and work rules.

7.2 All prudent precautions shall be taken to ensure the safety of personnel and property. The subcontractor shall insure that extreme caution is exercised when using oil or oil-based paints, cleaning fluid or cleaning compound, etc. in close proximity to oxygen piping, oxygen equipment, tanks, casings, etc. Heavy concentrations of volatile or toxic fumes must be avoided. In confined spaces, blowers or exhaust fans may be necessary. Where good practice dictates, masks, non-sparking tools and other such special equipment shall be used. The subcontractor shall consult Gulf Designs representative when any doubt exists regarding safety precautions for oxygen piping, equipment tanks, casings, etc.

7.0 <u>SAFETY</u> (continued)

7.3 The painting subcontractor shall remove all material and debris
    created by him and leave his work in a clean, finished condition
    which shall include cleaning of all drips and spills and the wa
    and polishing of all window glass stained during painting.

7.4 Before submitting his proposal, the subcontractor shall consult
    Gulf Design's representative to determine what limitations will
    enforced, in regard to the number of painters and other employe
    permitted to work at one time on various portions of the work.
    These limitations will be strictly enforced in order to safegua
    the operations of the plant.

7.5 After completion of all painting, the Contractor shall remove
    from job site all painting equipment, surplus materials, and
    debris resulting from this work.

8.0 <u>SURFACE PREPARATION</u>

8.1 All surfaces shall be sandblasted as specified. All jagged edge
    scale, slag, and flux shall be removed and all seams and unprime
    and abraded areas shall be treated in accordance with the degree
    preparation specified. All surfaces to be painted shall be clea
    prepared in accordance with the Steel Structures Painting Counc
    specifications.

8.2 Shop painted equipment and areas which require touch-up after
    erection, such as welds, burnbacks, and mechanically damaged
    areas, shall be cleaned by thorough power tool or hand wire
    brushing as specified in SSPC-SP-2 or 3-63.

8.3 Any carbon steel surface not primed shall be reblasted if any
    rust develops before painting, regardless of time after
    sandblasting.

8.4 The sandblasted surface shall be rendered dust free prior to app
    the primer.

8.5 Concrete and masonry surfaces shall be brushed free of dust,
    dirt and other foreign matter and be completely dry prior to
    coating. Concrete surfaces having a glazed appearance, such
    as produced by steel troweling, shall be etched with a 10 percen
    solution of hydrochloric acid (or muriatic acid) followed by
    water rinsing. Allow a minimum of 3 days drying time for
    masonry surfaces. Moisture content should indicate less than
    8 percent on a Delmhorst moisture meter (or equal) before
    coating. Surfaces which have pits or voids shall be grouted
    with a suitable mortar. Porous concrete block shall be filled
    with block filler prior to coating.

8.6 Wood surfaces shall be brushed free of dust and dirt and rough spots shall be sanded smooth. The wood surface shall be thoroughly dry at the time of priming. Wood surfaces shall be painted only if specifically recommended in the applicable specification.

8.7 All blasted surfaces shall be primed within six (6) hours after blasting is performed. Blasted surfaces left unprimed overnight or on which rain falls, shall be reblasted before priming.

8.8 Samples of surface preparation and of painting systems used shall be furnished by the Contractor and Sub Contractor to be used as a standard throughout the job, unless waived by the Field Engineer.

8.9 Surface preparation shall be done by one of the following methods in accordance with the SSPC Specification.

SPECIFICATION	NOMENCLATURE	DESCRIPTION
SSPC-SP-1-63	Solvent Cleaning	Removal of oil, grease, dirt, soil, salts, and contaminants by cleaning with solvents, vapor, alkali, emulsion or steam.
SSPC-SP-2-63	Hand Tool Cleaning	Removal of loose rust, loose mill scale, and loose paint to degree specified, by hand chipping, scraping, sanding, and wire brushing.
SSPC-SP-3-63	Power Tool	Removal of loose rust, loose mill scale and loose paint to degree specified, by power tool chipping, descaling, sanding, wire brushing, and grinding.
SSPC-SP-5-63	White Metal Blast Cleaning	Removal of all visible rust, mill scale, paint and foreign matter, by blast cleaning by wheel or nozzle (dry or wet) using sand, grit or shot. (For very corrosive atmosphere where high cost of cleaning is warranted.)
SSPC-SP-6-63	Commercial Blast Cleaning	Blast cleaning until at least two-thirds of each element of surface area is free of all visible residues. (For rather severe conditions of exposure.)

8.0 SURFACE PREPARATION (Continued)

SPECIFICATION	NOMENCLATURE	DESCRIPTION
SSPC-SP-7-63	Brush-off Blast Cleaning	Blast cleaning of all except tightly adhering residues of mill scale, rust and coatings, exposing numerous evenly distributed flecks of underlying metal.
SSPC-SP-10-63T	Near White	Blast cleaning nearly to white metal cleanliness, until at least 95% of each element of surface area is free of all visible residues. (For high humidity, chemical atmosphere, marine or other corrosive environment.)

All surfaces to be blast cleaned shall be dry and free from all deposits of oil, grease, or other contaminents which blasting will not remove.

9.0 APPLICATION OF PAINT

9.1 Paint shall be applied only on thoroughly dry surfaces and during periods of favorable weather, unless otherwise allowed by the paint manufacturer. Painting shall not be permitted when the atmospheric temperature is below 50°F, or when freshly painted surfaces may be damaged by rain, fog, dust, or condensation, and/or when it can be anticipated that these conditions will prevail during the drying period.

9.2 Paint shall not be applied when steel surface temperatures are beyond the limits specified by the manufacturer for the specific coating material being used.

9.3 Shop fabricated and assembled equipment and structural steel will be primed and have the intermediate coat applied in the shop. All equipment will be "touched-up" in the field before applying the recommended top coat.

"Touch-up" systems shall be same as original specification. Strict adherence to manufacturer's complete touch-up recommendations shall be followed.

9.0 APPLICATION OF PAINT (Continued)

9.4 The subcontractor shall exercise particular care to keep clean and unpainted all valve stems, piston rods, motor shafts and other such mo parts, in order not to impair their free movement. Any paint deposited on these parts shall be carefully and completely removed.

Equipment, nameplates, pressure gauges, instrument glasses, machined surfaces, electrical indicating devices, etc. shall be protected as approved or directed by the Gulf Design representative, shall not be painted, and shall be cleaned so that they are clearly legible.

Aluminum jackets on piping and equipment shall be protected and kept free of paint.

Galvanized electrical conduits shall not be painted unless specified in the requisition.

Galvanized surfaces will not require painting except where the shop galvanized coating is damaged during shipment, field handling, or welding. In these cases the damaged areas shall be thoroughly cleaned per SSPC-SP-2-63 and painted with one coat (3.0 mils) of zinc rich paint such as:

Carboline	-	Carbo-Zinc 11
DuPont	-	347-931
Matcote	-	Rust-Ban 193
Glidden	-	Glid-Zinc 104
Mobil	-	Mobilzinc 7
Prufcoat	-	Zinc Prime 500

(or approved equal)

9.5 Compatability of Primers and Topcoats

The subcontractor will be responsible for paint compatability over primers and intermediate coats, whether these are shop or field applied. Unless otherwise noted, shop primers and intermediate coats will be one or a combination of the products listed in Painting Selection Table.

9.6 Paint shall be applied primarily by spray. Brush or roller may be used where necessary to protect surfaces of equipment that does not require painting.

9.6.1 Air, Airless or Hot Spray

(1) The equipment used shall be suitable for the intended purpose, shall be capable of properly atomizing the paint to be applied and shall be equipped with suitable pressure regulators and gages.

9.0 APPLICATION OF PAINT (Continued)

        (2) Special care shall be taken with thinners and paint temperatures, so that paint of the correct formula reaches the receiving surface.

        (3) Nozzles, tips, etc., shall be of sizes and designs as recommended by the manufacturer of the paint being sprayed.

9.6.2 By Brush and/or Rollers

        (1) Top quality, properly styled brushes and rollers shall be used.

        (2) The brushing or rolling shall be done so that a smooth coat as nearly uniform in thickness as possible is obtained. Brush or roller strokes shall be made to smooth the film without leaving deep or detrimental marks.

9.7 Contact surfaces for friction type connections, to be made with high-strength bolts, shall be left unprimed, except when inorganic zinc primer is specified.

10.0 STORAGE

Materials shall be delivered to the jobsite, in the original packages, with seals unbroken with with legible unmutilated labels attached. _Packages shall not be opened until they are inspected by the Gulf Design Representative and required for use. All painting materials shall be stored in a clean, dry, well ventilated place, protected from sparks, flame, direct rays of the sun or from excessive heat. Paint susceptible to damage from low temperatures shall be kept in a heated storage space when necessary. The subcontractor shall be solely responsible for the protection of the materials stored by himself at the job site. Empty coating cans shall be required to be neatly stacked in an area designated and removed from the job site on a schedule determined by Gulf Design. Gulf Design may request a notarized statement from Contractor detailing all materials used on project.

11.0 RESOLUTION OF CONFLICTS

11.1 It shall be the responsibility of the Subcontractor to arrange meeting prior to the start of painting, between the painting Contractor, the Paint Manufacturer, whose products are to be used, and Gulf Design. All aspects of surface preparation, application and coating systems as covered by this specification will be reviewed at this meeting.

11.0 RESOLUTION OF CONFLICTS (Continued)

11.2 Clarification shall be requested promptly, from Gulf Design when instructions are lacking, conflicts occur in the specification, or the procedure specified seems improper or inappropriate for any reason.

11.3 Copies of all manufacturer's instructions and recommendations shall be furnished to Badger.

11.4 It shall be the responsibility of the Coating Manufacturer to have their factory representative meet in person with the Contractor and Gulf Design a minimum of three times during the job as a consustant on surface preparation, mil thickness of coating and proper application of coating unless meeting is determined to be unnecessary by Badger.

12.0 MISCELLANEOUS

12.1 All paint thinners, catalyzing agents and coating materials shall be products of the same manufacturer.

12.2 All paint shall be furnished in original containers with legible identification.

12.3 No thinners, unless specified by the manufacturer, or other than the oil component of the paint, shll be added to improve spreading or spraying characteristics of the paint.

12.4 Paint to be applied must not exceed the manufacturer's specified shelf-life.

13.0 LINE TABLE PAINT CODES

13.1 General Notes

13.1.1   All shop painting is to be done per Shop Painting Specification.

13.1.2   All field painting is to be done per Field Painting Specificatic

13.2 Code I   Uninsulated Carbon Steel And Low Alloy Steel Piping

13.2.1   Shop fabricated piping and fittings shall be shop primed. Primer shall be touched-up, intermediate and finish coats shall be applied in field.

13.2.2   Field fabricated and random piping shall be primed and finish painted in the field.

13.3 <u>Code II   Insulated Carbon Steel And Low Alloy Steel Piping</u>

Only exposed uninsulated attachments, such as brackets and supports, shall be primed and finish painted as follows:

13.3.1   Exposed attachments of shop fabricated piping shall be shop primed, and shall be touched-up. Intermediate coats and finish coats to be applied in the field.

13.3.2   Exposed attachments of field fabricated and random piping shall be primed and finish painted in the field.

13.4 <u>Code III   Partially Insulated Carbon Steel And Low Alloy Steel Piping</u> <u>(Such As Personnel Protection)</u>

13.4.1   Shop fabricated piping and fittings:

13.4.1.1 Entire piece shall be shop primed.

13.4.1.2 Uninsulated portions only shall be touched-up and finish painted in the field.

13.4.2   Field fabricated and random piping:

13.4.2.1 Uninsulated portions only shall be primed and finish painted in the field.

13.5 <u>Code IV   Carbon Steel Flanges On Stainless Steel And High Alloy Piping</u> <u>(Uninsulated Lines, and Exposed Portions Of Insulated Lines)</u>

13.5.1   Flanges shall be shop primed.

13.5.2   Flanges shall be touched-up and finish painted in the field.

SHOP PAINTING SELECTION TABLE

PAINT SYSTEM NUMBER 1 - EPOXY

Coat	Mfgr's No.	Type	Dry Film Thickness	No. Coats	Surface Preparation	Color
A.. Rust Oleum Company						
Primer	9369	Red Oxide Epoxy	2 mils	1	SP-5-63	Red
Intermediate	9391	Epoxy	2-3 "	1		White
Finish	9371	Epoxy	2-3 "	1		Dunes T
			6 mils*			
B. Rowe Coatings						
Primer	7-W-20	Epoxy Primer	3 mils	1	SP-5-63	
Intermediate	50-G-30	Epoxy	2-1/2-3 mils	1		White
Finish	5-G-67	Epoxy	2-1/2-3 "	1		Agrico T
			8 mils*			
C. Prufcoat Coatings						
Primer	545 Primer.	Epoxy	3 mils	1	SP-5-63	Red
Intermediate	545 Top Coat	Epoxy	2-1/2-3 mils	1		White
Finish	545 Top Coat.	Epoxy	2-1/2-3 "	1		Tan
			8 mils*			
D.. Sherwin-Williams Company						
Primer	B50N2	Kem Kromik	2 mils	1	SP-5-63	Red
Intermediate	B28W1	Latex	2 "	1		White
Finish	B-70	Epoxy	3-4 mils	1		Agrico T
			7 mils*			
E. The Glidden Company						
Primer	5461	Epoxy Chromate	2 mils	1	SP-5-63	Red
Intermediate	5555	H.B. Inter Epoxy	4 "	1		Gray
Finish	5240	Epoxy	2 "	1		Tan
			8 mils*			

*Indicates minimum total dry thickness in mils.
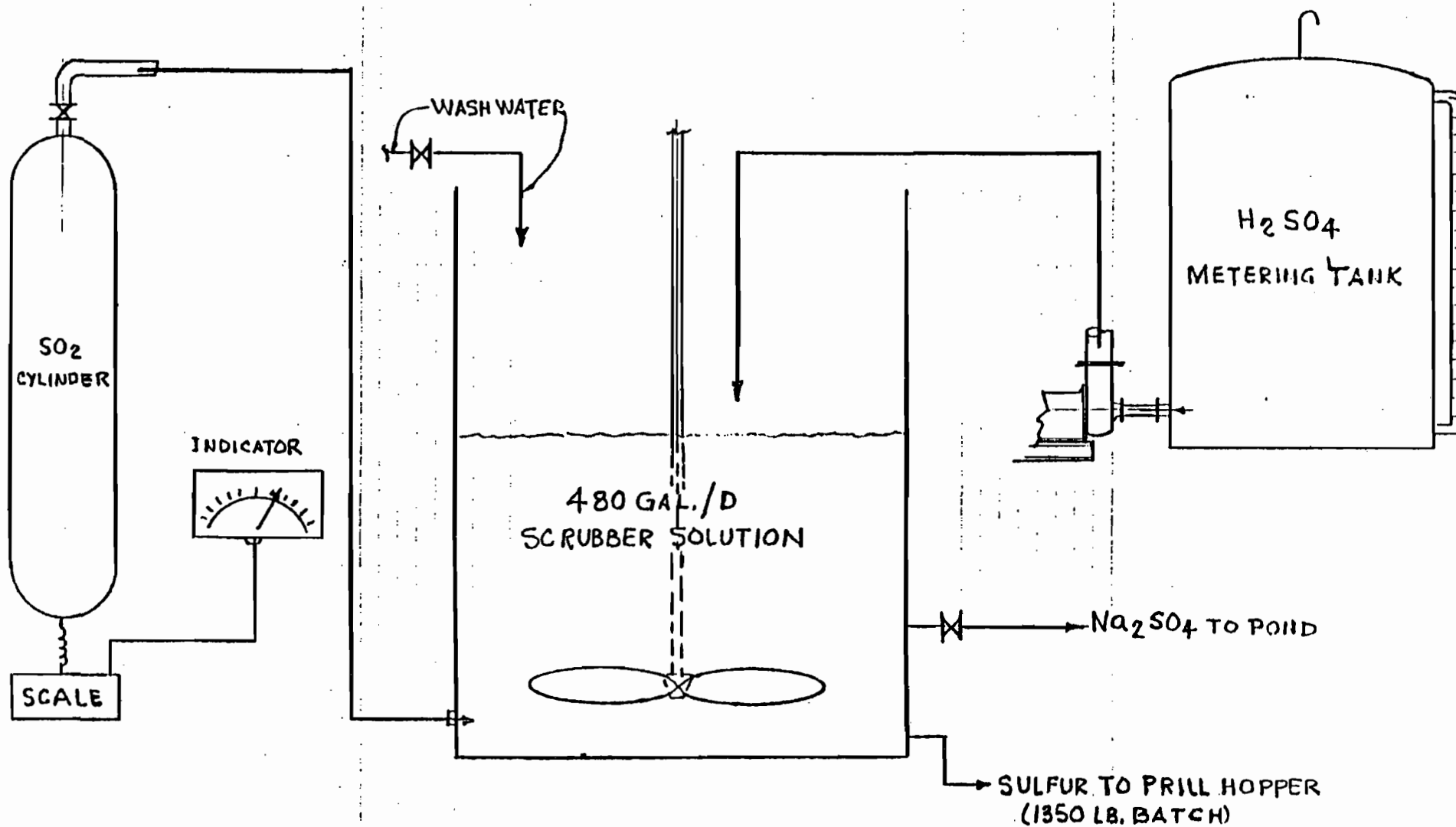No substitution of specified materials will be permitted.

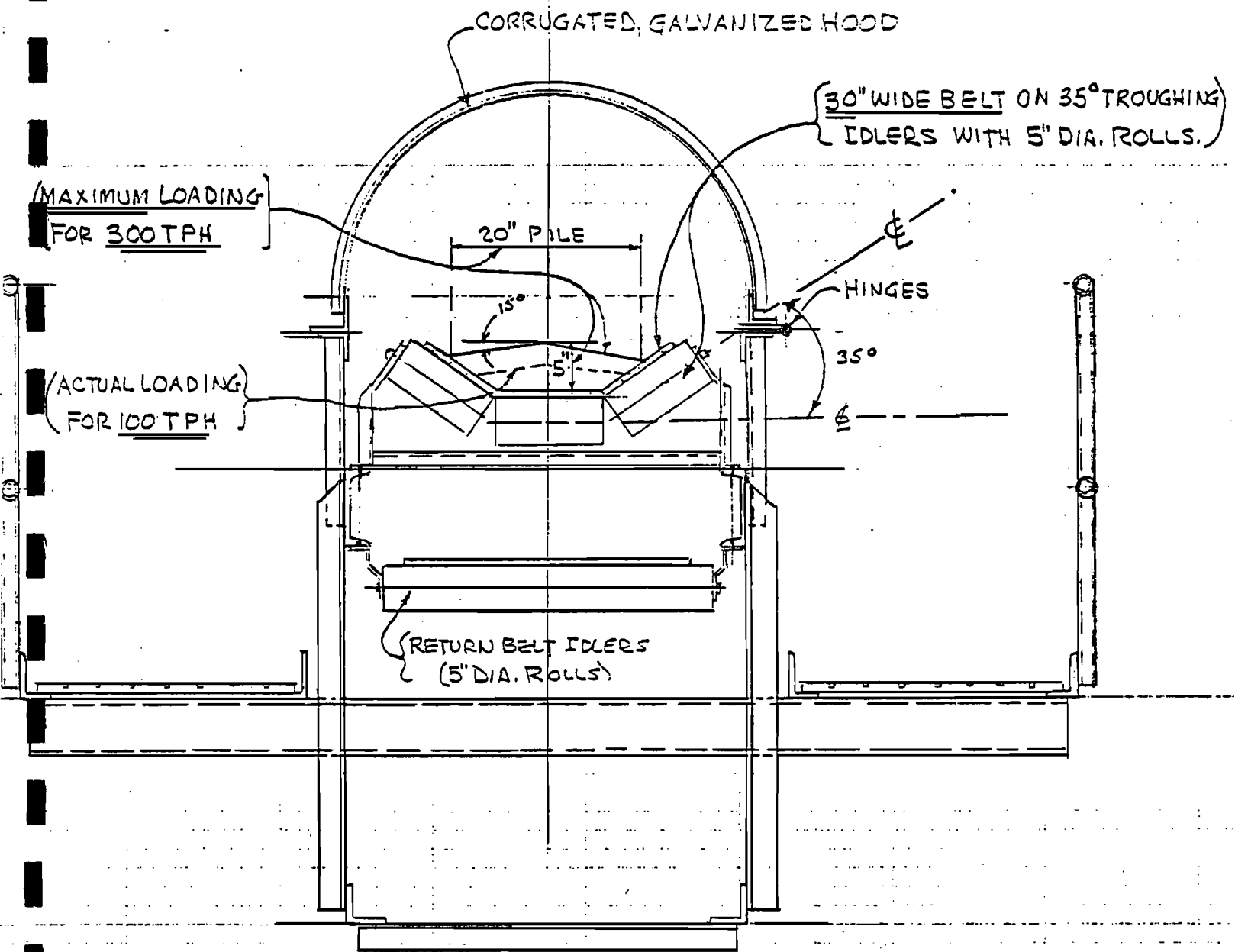## SHOP PAINTING SELECTION TABLE

PAINT SYSTEM NUMBER 2 - VINYL

Coat	Mfgr's No.	Type	Dry Film Thickness	No. Coats	Surface Preparation	Color
A. Rust Oleum Company						
Primer	9073	Zinc Chromate	2-3 mils	1	SP-5-63	Yellow
Intermediate	9079	Vinyl	3-4 "	1		Black
Finish	9071	Vinyl	3 "	1		Dunes Ta
			8 mils*			
B. Rowe Coatings						
Primer	7-Y-20	Vinyloid	2 mils	1	SP-5-63	
Intermediate	5-Y-30	Vinyl	2 "	1		White
Finish	5-Y-67	Vinyl	2 "			Agrico Tan
			6 mils*			
C. Prufcoat Coatings						
Primer	159-40	Vinyl weld	2 mils	1	SP-5-63	Red
Intermediate	'A' Series	Vinyl	2 "	1 /		552-xx-White
Finish	'A' Series	Vinyl	2 "	1		552-xx-Tan
			6 mils*			
D. Sherwin-Williams-Company						
Primer	B50N2	Kem Kromiks	2 mils	1	SP-5-63	Red
Finish	B69	Vinyl	3-1/2-4 mils	1		Agrico Ta
			5-1/2 mils*			
E. The Glidden Company						
Primer	5521	Vinyl cote primer	2 mils	1	SP-5-63	Red
Intermediate	5522	Vinyl	4 "	1		White
Finish	5523	Vinyl	2 "	1		Tan
			8 mils*			

*Indicates minimum total dry thickness in mils.
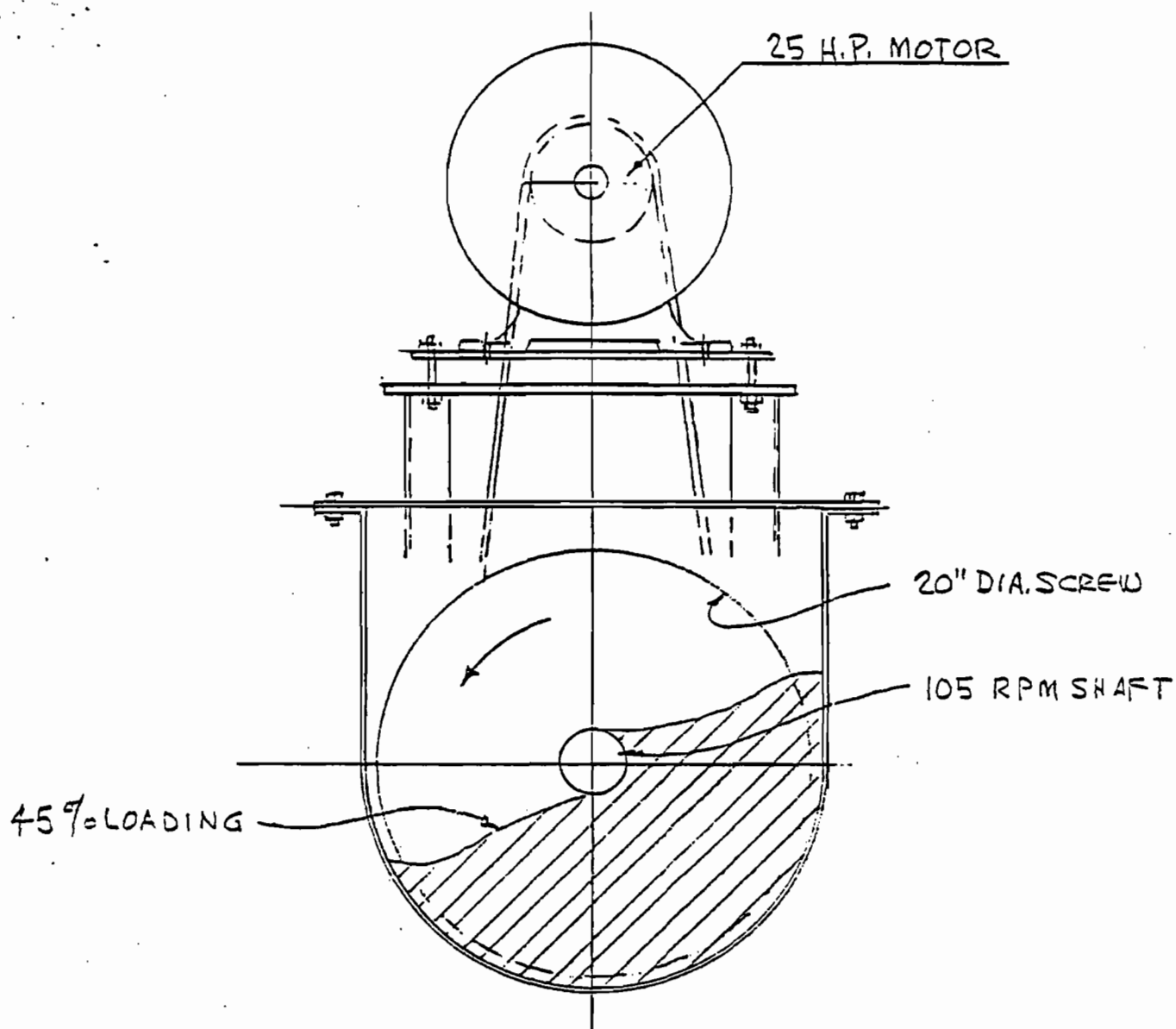
No substitution of specified materials will be permitted.

WASH WATER

SO₂
CYLINDER

INDICATOR

SCALE

H_2SO_4 METERING TANK

480 GAL./D
SCRUBBER SOLUTION

Na_2SO_4 TO POND

SULFUR TO PRILL HOPPER
(1350 LB. BATCH)

PRILLED SULFUR
H_2S SCRUBBER EFFLUENT TREATMENT

AT SOUTH PIERCE CHEMICAL WORKS

(8-22-83)

CORRUGATED, GALVANIZED HOOD

30" WIDE BELT ON 35° TROUGHING
IDLERS WITH 5" DIA. ROLLS.

MAXIMUM LOADING
FOR 300 TPH

20" PILE

15°

HINGES

35°

ACTUAL LOADING
FOR 100 TPH

5"

RETURN BELT IDLERS
(5" DIA. ROLLS)

TYPICAL CROSS SECTION FOR SULFUR UNLOADING BELT

(SCALE $\frac{3}{4}$"=1'-0)

(AT 300 TPH DESIGN RATE)

25 H.P. MOTOR

20" DIA. SCREW

105 RPM SHAFT

45% LOADING

SECTION THRU SULFUR HANDLING SCREW CONVEYOR

(300 TONS PER HOUR)

## Quik-Link conveyor screw with trough ends and hangers

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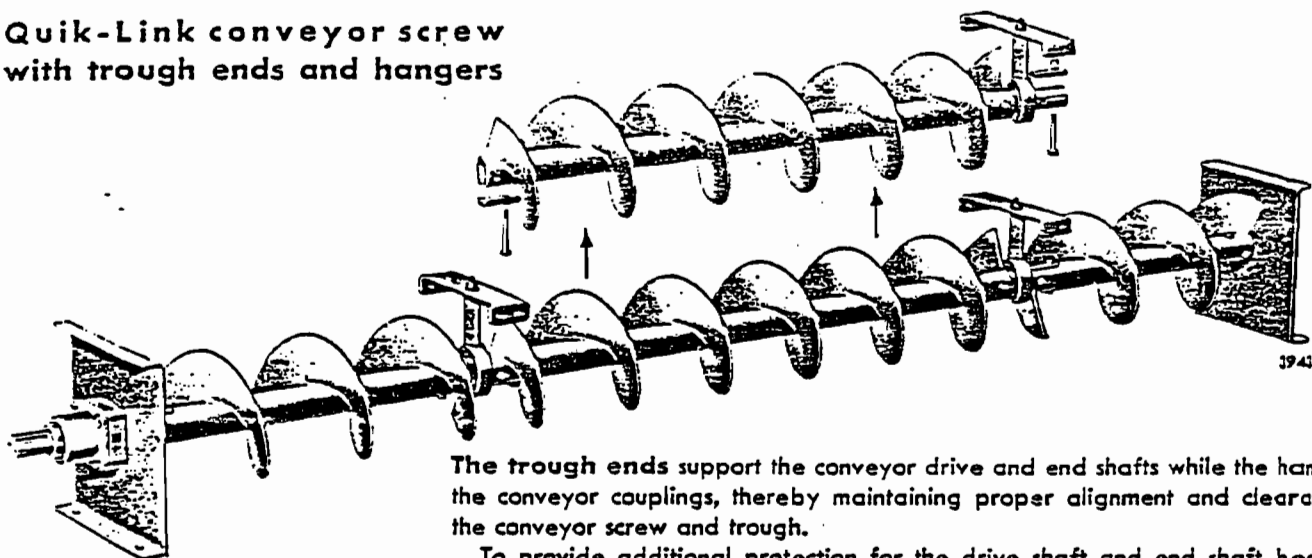
The trough ends support the conveyor drive and end shafts while the hangers support the conveyor couplings, thereby maintaining proper alignment and clearance between the conveyor screw and trough.

To provide additional protection for the drive shaft and end shaft bearings, for or against the material being handled, trough end seals are assembled between the flanged blocks and the trough end plates.

The overall operating efficiency of the conveyor is improved when the trough ends and hangers are fitted with ball bearings.

The Quik-Link conveyor screw can be readily lifted from the conveyor line, without disturbing other conveyor screw sections, after removing the Quik-Link key located at the end of the screw.

## Conveyor trough with inlet opening and discharge spout

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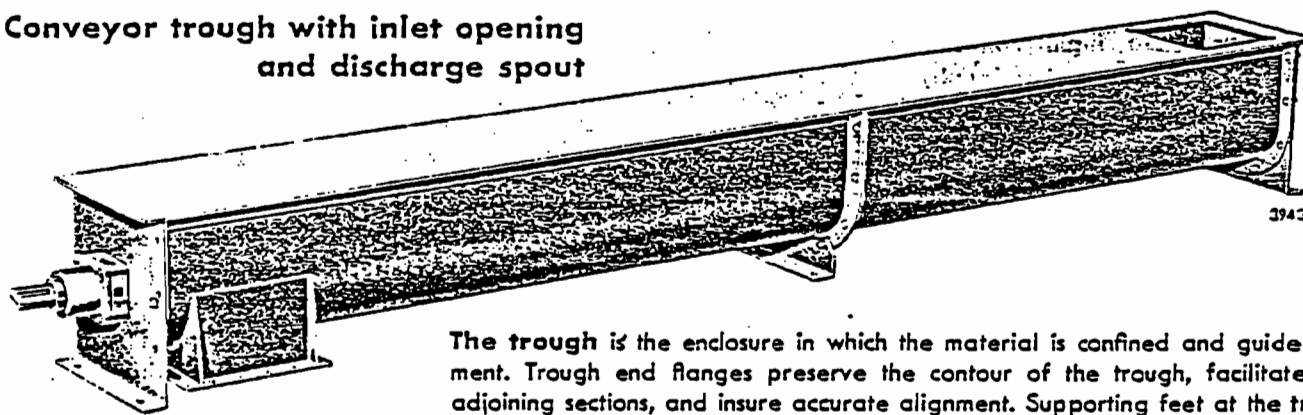
The trough is the enclosure in which the material is confined and guided in its movement. Trough end flanges preserve the contour of the trough, facilitate assembly of adjoining sections, and insure accurate alignment. Supporting feet at the trough joints or saddles located between the joints, support the intermediate trough sections.

Discharge spouts provide outlets for the material and direct its flow to bins or succeeding equipment. With more than one discharge point in a conveyor, selective control may be exercised by means of slide gates, made integral with the discharge spouts.

Trough covers with fasteners complete the conveyor enclosure. Material is fed into the conveyor through inlet openings in the cover.

Typical screw conveyor complete with drive

39440
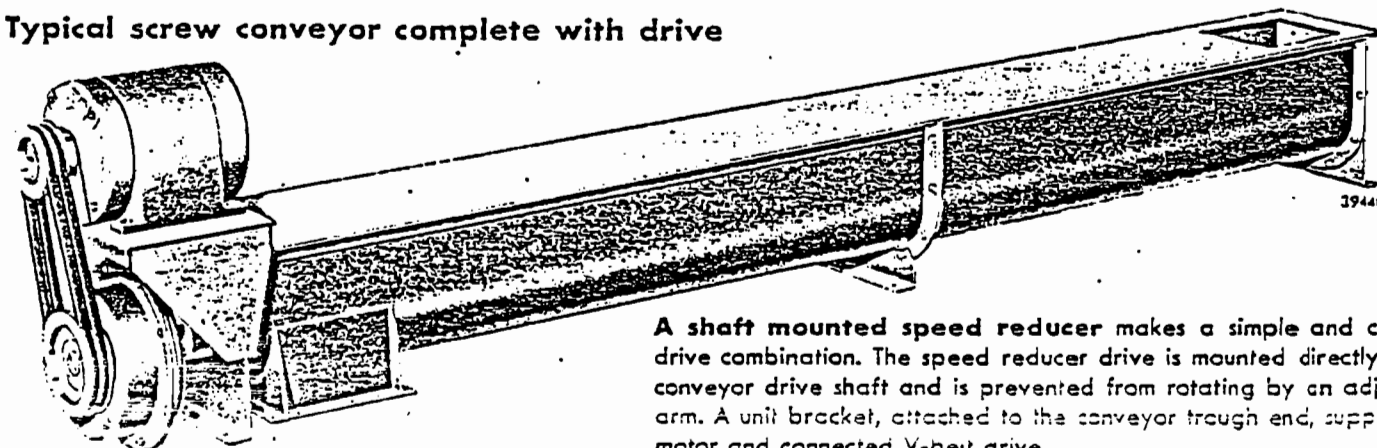
A shaft mounted speed reducer makes a simple and compact drive combination. The speed reducer drive is mounted directly on the conveyor drive shaft and is prevented from rotating by an adjustable arm. A unit bracket, attached to the conveyor trough end, supports the motor and connected V-belt drive.