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Hydrogen Sulfide Removal from Coke Oven Gas  
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HYDROGEN SULFIDE REMOVAL FROM  
COKE OVEN GAS

D7-018-013

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Corporate Research Department

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November, 1975

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## INTRODUCTION

This is the first progress report on hydrogen sulfide removal from coke oven gas. The purpose of this work is to solve our pollution problem in coke oven gas. The author has just finished the first stage of work -- laboratory phase. He is going to set up a pilot plant in order to learn more about practical use of this system in hydrogen sulfide removal. Emphasis was placed on the problem at Toledo because the problem there has been more serious than at Chicago.

There are some pre-restrictions before starting of this research project:

1. Six unused absorption towers are available in Toledo.  
We may use ~~it~~ <sup>them</sup> free.
2. Ammonia is one of the best H<sub>2</sub>S absorption media. We have to use it, since it is a by-product from our coke oven gas and available to us free.
3. We could not afford to buy the loyalty of existing patents. We have to try to develop our own.
4. The BOF dust and magnetite (from Wean System) are available for us free. It is our company's policy to let two evils cancel each other. We have to try them first.

This report contains the development of this research project, step by step, and possible recommendations. In order to save time for the reader, he does not have to read every page of this report. A reader only needs to read Introduction, Summary, Procedure, Conclusion, and Recommendation carefully. If he needs to know further information on certain areas, he can look for the specific sections in Result & Discussion, and Appendix.

### SUMMARY

The purpose of this project is to reduce the amount of  $H_2S$  in our coke oven gas in order to meet the newly EPA standard. To reduce the amount of  $H_2S$  has many many ways, and the earliest work could be traced back to 1850. The highlight of the whole story is that we found that the magnetite can be a catalyst to help air oxidize the  $H_2S$ . Hydrogen sulfide is absorbed by ammonia first, then oxidized by the help of magnetite and air. Ammonia can be either recycled or converted to fertilizer. Sulfur will be our by-product. The mechanism of overall reactions is very complicated, and we still could not find out the detail due to the limitation of the time and money.

## PROCEDURE

First of all, we should develop ways to determine the amount of  $H_2S$  in liquid phase and in the gas phase quantitatively. At first, sulfide electrode was assumed to be the best way to detect the amount of sulfide in the liquid phase; the gas chromatography was assumed to be the best way to detect the amount of  $H_2S$  in gas phase. Sulfide ion,  $S^{=}$ , reacts with many reagents in liquid state according to qualitative chemistry. However, in presence of  $CO$ ,  $CO_2$ ,  $SO_2$ , and unsaturated hydrocarbons, most of these reagents could not quantitatively determine the amount of  $H_2S$ . For example, iodine solution will react with unsaturated hydrocarbons. Later on EDTA Titration found to be more effective.

Both water and ammonia solution at different pH, temperatures, and concentrations, have tried in order to obtain a optimum conditions to absorb  $H_2S$  from coke oven gas.

Magnetite, BOF dust, and Pellet have been tried to destroy  $H_2S$  in ammonia solution, <sup>under</sup> ~~Under~~ various conditions; such as, different temperatures, different pH, and different media. The ways to regenerate ammonia and iron oxide also have been tried. Eventually, we hope this system can be a cyclic system to remove  $H_2S$  from coke oven gas continuously.

In addition, two simple ways to get rid of  $H_2S$  from coke oven gas has been proposed and tested. The purpose of spending extra time on those methods is, in case of invalidity of these BOF dust, magnetite, or pellet, we can have some ways to fulfill EPA's requirement at least.

## RESULT AND DISCUSSION

### Detection of H<sub>2</sub>S

The method, here, needs fast, reliable and relatively accurate method. Slow, delicated wet method is out of the question.

#### I. Sulfide Electrode

Sulfide electrode measures activity or concentration of sulfide in solution. Orion's sulfide electrode has been tried both by Mr. Frank Powers of Environment Department and Mr. Forrest Carmichael of our Department.

In order to re-test the sulfide electrode, some known concentration  $\text{Na}_2\text{S}$  solutions must be prepared. (Appendix 1). The concentration of  $\text{Na}_2\text{S}$  solution needs iodine solution to standardize. Again, iodine solution must be standardized by  $\text{As}_2\text{O}_3$  solution. (Appendix 1).

Beckman Company is famous for its pH meter and its electrodes.

~~two~~ <sup>Two</sup> methods have been tried:

#### A. Absolute Potential (S.C.E.)

The results from pH meter are as follows,

$$0.1 \text{ M } \text{Na}_2\text{S} = 847.5 \text{ mV}$$

$$0.01 \text{ M } \text{Na}_2\text{S} = 817.0 \text{ mV}$$

$$0.001\text{M } \text{Na}_2\text{S} = 785.0 \text{ mV}$$

According to electrochemistry,

$$E = E_b - 2.3 \frac{RT}{nF} \log A_S =,$$

where  $2.3 \frac{RT}{nF}$  is almost 29.6 mV here. Electronically, it

is pretty closed, since  $847.5 - 785.0 = 62.5$ , which matches



pretty well with 59.2 (2 x 29.6). However, in terms of absolute value, it is not accurate enough.

3 mV error means

$$3 = 29.6 \log \frac{A_{S=}}{A'_{S=}}$$

$$\log \frac{A_{S=}}{A'_{S=}} = 0.101 \quad \text{or} \quad \frac{A_{S=}}{A'_{S=}} = 1.263$$

That is a 26 percent error.

B. Substraction Method:

Add known concentration solution to an unknown solution and check the difference between potential.

Example: Add 1 ml 0.1 M Na<sub>2</sub>S solution each time to 0.01 M Na<sub>2</sub>S solution. 100 ml  
^

The

the results are as follows:

Original Value:	819 mV
After 1 ml (0.1 M):	821 mV
Add another 1 ml:	821.8 mV
Add another 1 ml:	823.0 mV
Add another 1 ml:	823.5 mV
Add another 1 ml:	824.6 mV

$$E_1 = E_b - 29.6 \log (\text{concentration}_1)$$

$$E_2 = E_b - 29.6 \log (\text{concentration}_2)$$

$$-\Delta E = E_1 - E_2 = -29.6 \log \frac{(\text{conc.}_1)}{(\text{conc.}_2)} \quad (\text{conc.}_1 / \text{conc.}_2)$$

After adding 5 ml (0.1 M),

Volume = 105 ml

Total amount of Na<sub>2</sub>S

= 0.01 Mole/liter ← x 0.1 liter

+ 0.1 Mole/liter ← x 0.005 liter

= 0.0015 mole

concentration<sub>1</sub> = 0.01 mole/liter

concentration<sub>2</sub> =  $\frac{.0015 \text{ mole}}{.105 \text{ liter}} = 0.01428 \text{ mole/liter}$

$$= -29.6 \log \left( \frac{0.01}{0.01428} \right) \quad (0.01/0.01428)$$
$$= -4.58 \text{ mV}$$

Actually, the change of potential from the pH meter is -5.6 mV. Again, it is not bad electronically. However, it is bad enough practically, since

$$29.6 \log \left( \frac{\text{conc.}_2}{\text{conc.}'_2} \right) = 1.02, \text{ or } \log \left( \frac{\text{conc.}_2}{\text{conc.}'_2} \right) = 0.0344$$

$$\text{conc.}'_2 = 1.08 \text{ } \times \text{ conc.}_2$$

Error is more than 8 percent.

Miss a paragraph (see back of this page)

1. If there is no interference (the presence of CO, CO<sub>2</sub>, ... or HCN), iodine titration is the best. Simple and accurate!
2. If there are some interferences, the activity of S<sup>=</sup> will change, and the accuracy would be even worse, no doubt. EDTA titration can alleviate this problem, and will be mentioned in the next section.

## II. EDTA Titration

EDTA titration can determine quantitatively the amount of S<sup>=</sup> in liquid phase or the amount of H<sub>2</sub>S in gas phase, even if there exists interferences.<sup>1</sup> The method to obtain PbS precipitation is as follows,

1. Dissolve Pb(AC)<sub>2</sub> in de-ionized water, and add acetic acid to make pH ~ 5.

2. Pass 12 ml at S.T.P. Mix 5 ml the unknown solution with that Pb(AC)<sub>2</sub> solution.

3. Collect the PbS precipitation and be ready for EDTA titration.

The method of EDTA titration is as follows,<sup>2</sup>

1. Add aqua-regia to dissolve the PbS precipitation.
2. Neutralize with 50 percent KOH solution to a pH of 7<sup>+</sup>.
3. Add pH=10 buffer solution to make pH=10.
4. Titrate with .917 N EDTA using Eriochrome Black T as indicator.

Titrate to a blue end point.

5. ML. EDTA  $\times 1.9$  = grams/liter of Pb<sup>++</sup>

6. From grams/liter of Pb<sup>++</sup>, calculate the amount of H<sub>2</sub>S or S<sup>=</sup>.

7. Similar method can be proposed to determine the amount of H<sub>2</sub>S in gas phase.

### III. Gas Chromatography

Gas chromatography owes its popularity to several of its inherent advantages to the analyst:<sup>3</sup>

1. The separation of mixtures contains many components, including homolog and isomers, is possible.
2. Results are obtained rapidly.
3. Only small amount of sample is required.
4. Method is reliable and relatively high quantitative and qualitative precision is obtainable.
5. It is easy to interpret the results.
6. The equipment required has relatively low initial cost, is inexpensive to operate and has a long, useful life.

We let the suppliers suggest which kind of column <sup>has</sup> to use, since the most difficult job in <sup>gas chromatography</sup> Gas Chromatography is how to choose the right column and the right condition. The data collection is usually just a routine work. Standard <sup>curves</sup> Curves were plotted, and the linearity at peak height was checked. Other variables, such as size of needles, <sup>ways</sup> of injections, flow speed and dosage were checked at the same time.

After talking to different salesmen and reading different catalogs, bulletins, three kinds of G.C. machines were tried. Reasons are as follows,

- (1) Fisher's: Cheap, lightweight.
- (2) Reaco's: Portable, with built-in gas bottles, able to adapt flame ionization detector.
- (3) Tracor's: Good reputation, especially for its sulfur detector.

The major difficulties in  $H_2S$  determination are:

1.  $H_2S$  can react with rubber bag.
2.  $H_2S$  can react with oxygen slowly.
3.  $H_2S$  can leak out of rubber bag.

From above, gas chromatograph machines prefer to be portable so that we can do the measurement on the spot. If a container is needed, Teflon bag will be the best.

4. There are some old literature mentioning that quantitative work in  $H_2S$  measurement could not be done, especially in the range of 0 - 2 percent. However, quantitative work in gas chromatography is mainly dependent upon which kind of column is used and what kind of condition is chosen. That's the reason why we shift the responsibility of choosing column and condition to the supplier. Results are as follows,

1. Tracor's

Tracor suggested "Dilute Coke oven gas twice with syringes. Use the flame ionization detector to do quantitative measurement." Two concentrations were run (1:2 ratio), and the peak heights were almost 1:2 proportion. However, there are additional problems,

- (1) Dilute twice may introduce unnecessary error.
- (2) The air in coke oven plant may include some  $H_2S$ . Unless, diluted by inert gas, interferences may introduce.
- (3) Open fire is danger at coke oven plant. We should try to avoid it.

2. Fisher's.

Fisher suggested "Use thermal conductivity detector with both molecular sieve column and porous polymer bead to do the quantitative measurement on  $H_2S$ ." The results were not too promising:

- (1) Standard deviation is high.
- (2) Head pressure is 131 psig. Usually, two hands are needed to inject the sample into septum. Therefore, the shape of the peak is unpredictable; double peak does occur sometimes. More expensive recorder have to be used in order to integrate the peak.

3. Reaco's

Thermal conductivity detector with a kind of molecular sieve column (Chromosorb 102) was suggested. The results are good:

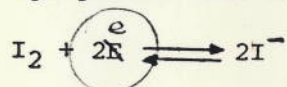
- (1) Has more uniform peak shape and better signal to noise ratio.
- (2) A flame ionization detector can add later on if needed.
- (3) Standard curve was almost a linear line.
- (4) It is portable.

However, the opening hole for syringe to the septum is too small.

Maybe this is the only thing inconvenient.

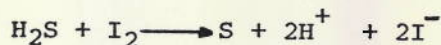
#### IV. Iodine Titration<sup>4</sup>

Iodine titration is the easiest and fastest method to determine H<sub>2</sub>S quantitatively, provided there is no interference or interferences are negligible. The reaction



is reversible. Substances with an oxidation potential much lower than that of iodine-iodide system are oxidized by iodine and can be titrated with a standard iodine solution (iodimetry).

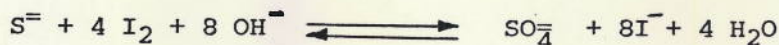
Hydrogen sulfide in acid medium is oxidized to sulfur by iodine:



A pronounced color change at the end point is obtained if starch is used as an indicator.

However, this method should be used very carefully.

- (1) The titration must not be in a alkaline medium, for part of the sulfide is then oxidized to sulfate



- (2) There are two important sources of error in iodine titration; air oxidation and the loss of iodine by volatilization. That is the reason the iodine solution should be always kept in a tight brown bottle. 0.1 M iodine solution after keeping in a tight brown bottle was found to be fairly stable for a reasonable length of time, say, 1 percent per month.

The major interferences include SO<sub>2</sub>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, S<sub>x</sub><sup>2-</sup>, H<sub>2</sub>O<sub>2</sub>, Fe<sup>++</sup>, and unsaturated hydrocarbon.

## Absorption Medium

As long as ammonia solution is the only  $H_2S$  absorption medium we have to use, an optimum condition and its properties have to be tested.

### I. $H_2S$ Solubility vs. Ammonia Concentration and Temperature.

← (Purged with (Pure  $H_2S$ ))

The apparatus is shown as Figure 1. The pure  $H_2S$  purged through the porous portion and formed small bubbles. If other than room temperature is needed, it is adjustable by the water bath (Figure 2).  $9^\circ C$ ,  $19^\circ C$ ,  $29^\circ C$ , and  $39^\circ C$  are the four temperatures we are interested; while 28 percent, 14 percent, 7 percent, 3.5 percent, 1 percent, 0.5 percent, 0.25 percent and 0.1 percent are the eight different ammonia concentrations we tested.

After bubbling with pure  $H_2S$ , a waiting period of 10 minutes was required before testing. The entire experimental data are too bulky to be included here. However, the conclusion are brief.

1. The solubility of  $H_2S$  in ammonia solution is almost the same if the concentration of ammonia is more than 1 percent. The solubility of  $H_2S$  in ammonia solution drops dramatically if the concentration of ammonia is less than 1 percent (see Figure 3). This information coincides with other research's result<sup>5</sup> very well. They recommended that the concentration of ammonia should be between 1 percent to 50 percent.

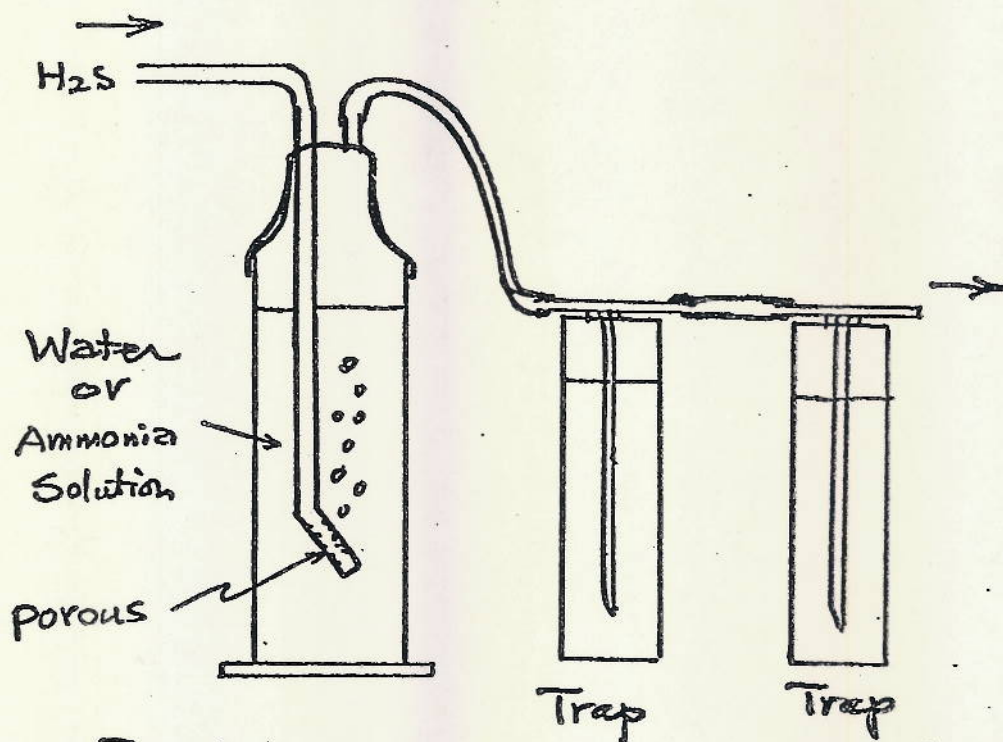


Fig. 1 Apparatus for  $H_2S$  Solubility Test in Ammonia Solution, or Water.

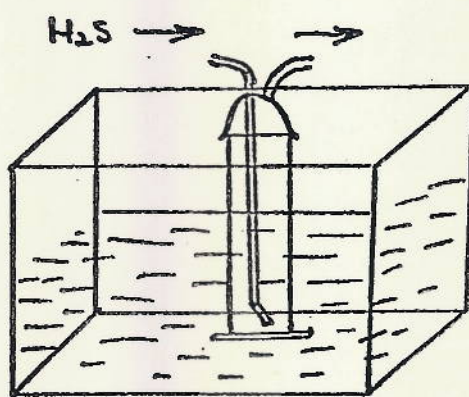
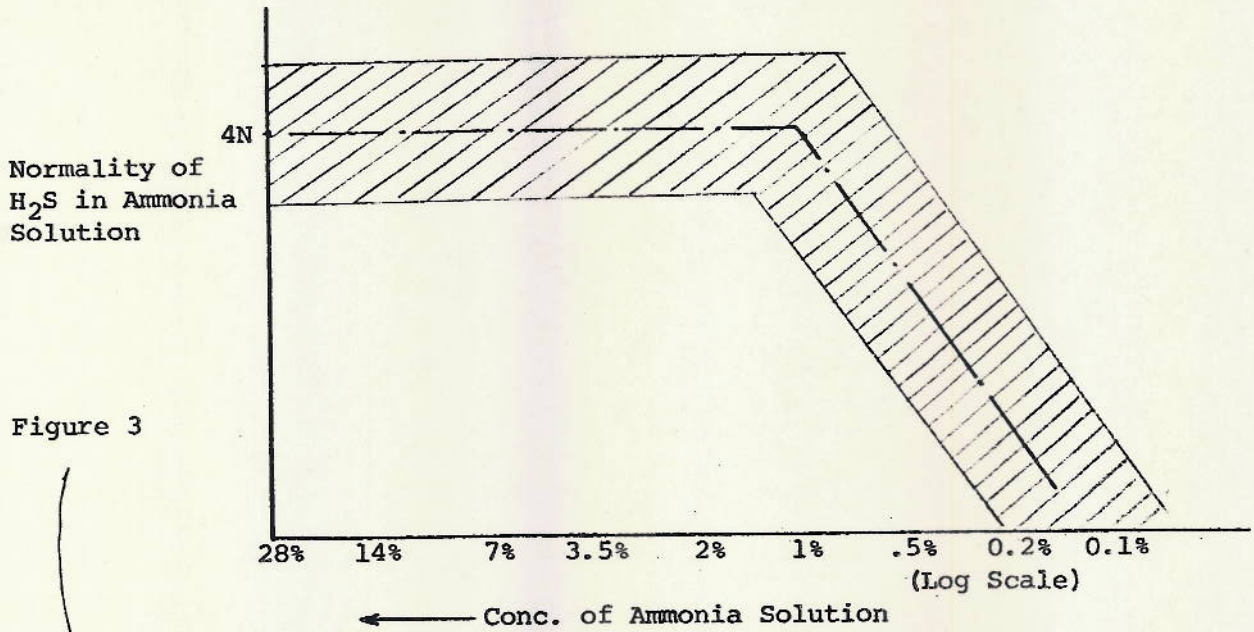


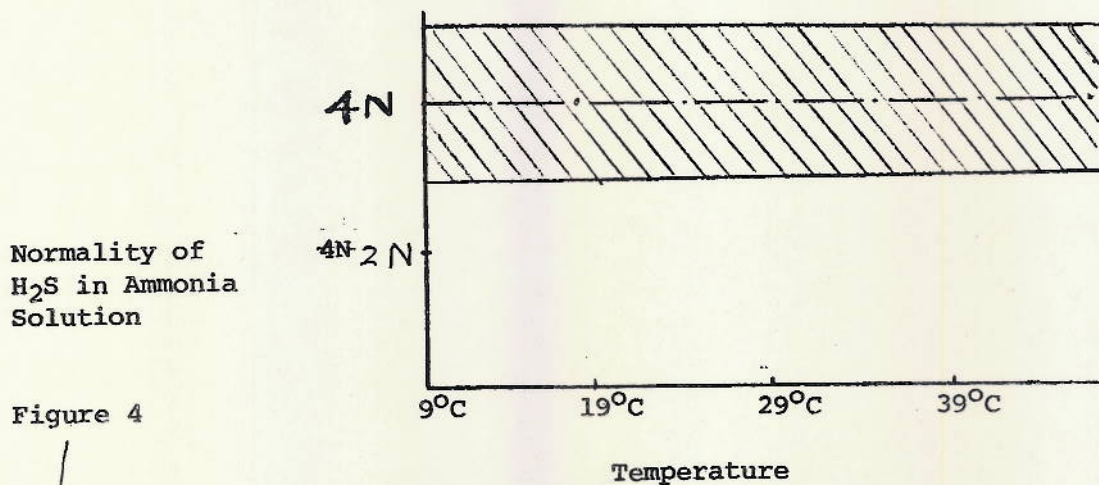
Fig. 2  $H_2S$  Solubility Test. Temperature can be adjusted by Water Bath.





Solubility of  $H_2S$  vs. Concentration of Ammonia

2. The temperature of ammonia solution will not affect the  $H_2S$  absorption too much (within our normal range). (Figure 4).



Solubility of  $H_2S$  vs. Temperature

3. Absorption reaction is fast.

In small scale, 5 minute bubbling with pure  $H_2S$  would get the same  $H_2S$  concentration as the 2 hour bubbling.

4. The lower the pH is, the lower is the solubility in ammonia solution.

The changing of pH is by adding of 1  $\text{NH}_2\text{SO}_4$  to the solution.

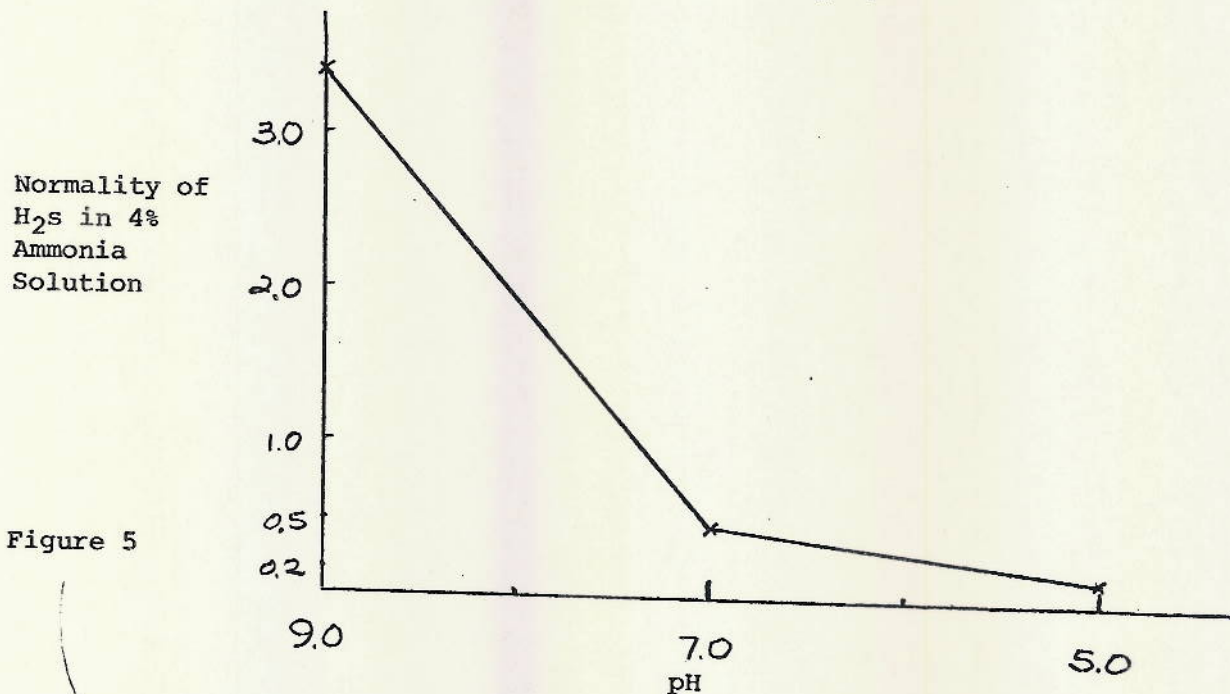


Figure 5

$\text{H}_2\text{S}$  Solubility in 4% Ammonia Solution vs. pH.

Moreover, the retaining ability of  $\text{H}_2\text{S}$  in 1 percent ammonia solution or over is so good. Usually, they can retain more than 70 percent  $\text{H}_2\text{S}$  overnight by leaving it exposed to air.

II.  $\text{H}_2\text{S}$  Solubility of Chicago Tap Water at Different Temperatures (Purge with pure  $\text{H}_2\text{S}$ ).

1. The lower the temperature is, the higher is the solubility.

(Figure 6)

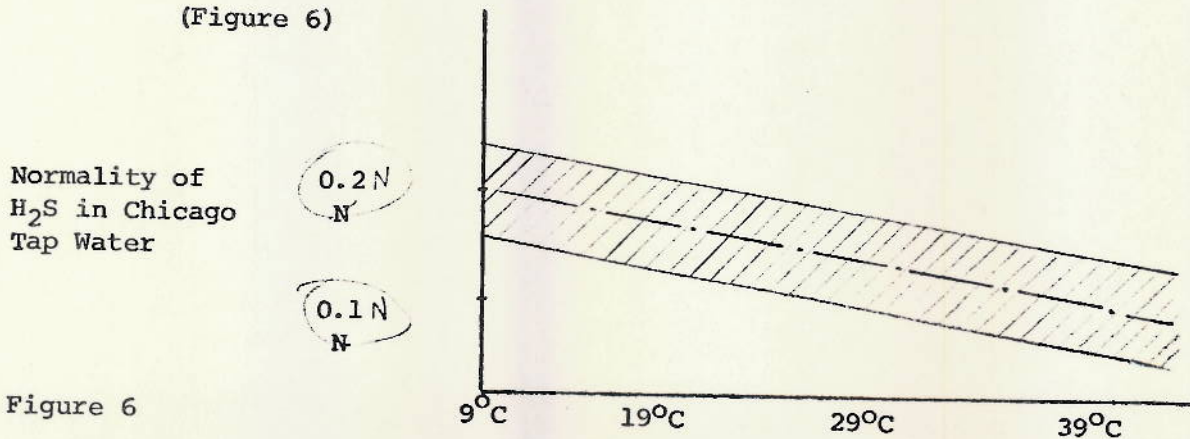


Figure 6

$\text{H}_2\text{S}$  Solubility in Chicago Tap Water vs. Temperature.

2. The higher is the temperature, the faster is the absorption.

However, the retaining ability of  $H_2S$  to tap water is so poor.

Usually, less than 5 percent  $H_2S$  is left after overnight exposure to the air.

III. The  $H_2S$  Absorption Ability of Ammonia Solution.  
(Purged with Air containing 1 percent  $H_2S$ )

Only room temperature data were collected. Three different concentrations, 1 percent, 4 percent and 8 percent ammonia solutions were being tested. The whole system is as shown in Figure 7. The absorption column is approximately 1 inch in diameter and 14 inches in length. The rate of ammonia solution flow speed <sup>was</sup> is about 560 ml/min. The rate of gas flow was about 400 c.c./min. by setting the gas flow meter from Air Product as follows,

{ E 29-D-65 mm at 5 ( $H_2S$ )  
E 29-D-150 mm at 1 (Air)

Under the above setting, the  $H_2S$  content <sup>was</sup> is about 600 grains/100 cu. ft., or about 1 percent. The content of  $H_2S$  in the ammonia solution <sup>is was</sup> is measured by iodine titration.<sup>4</sup> The  $H_2S$  content in the gas mix <sup>is was</sup> is measured by Tutwiler method (see Appendix II). Tutwiler method is not too accurate. However, it can give us a qualitative answer. The result is in Table I, II, and III.

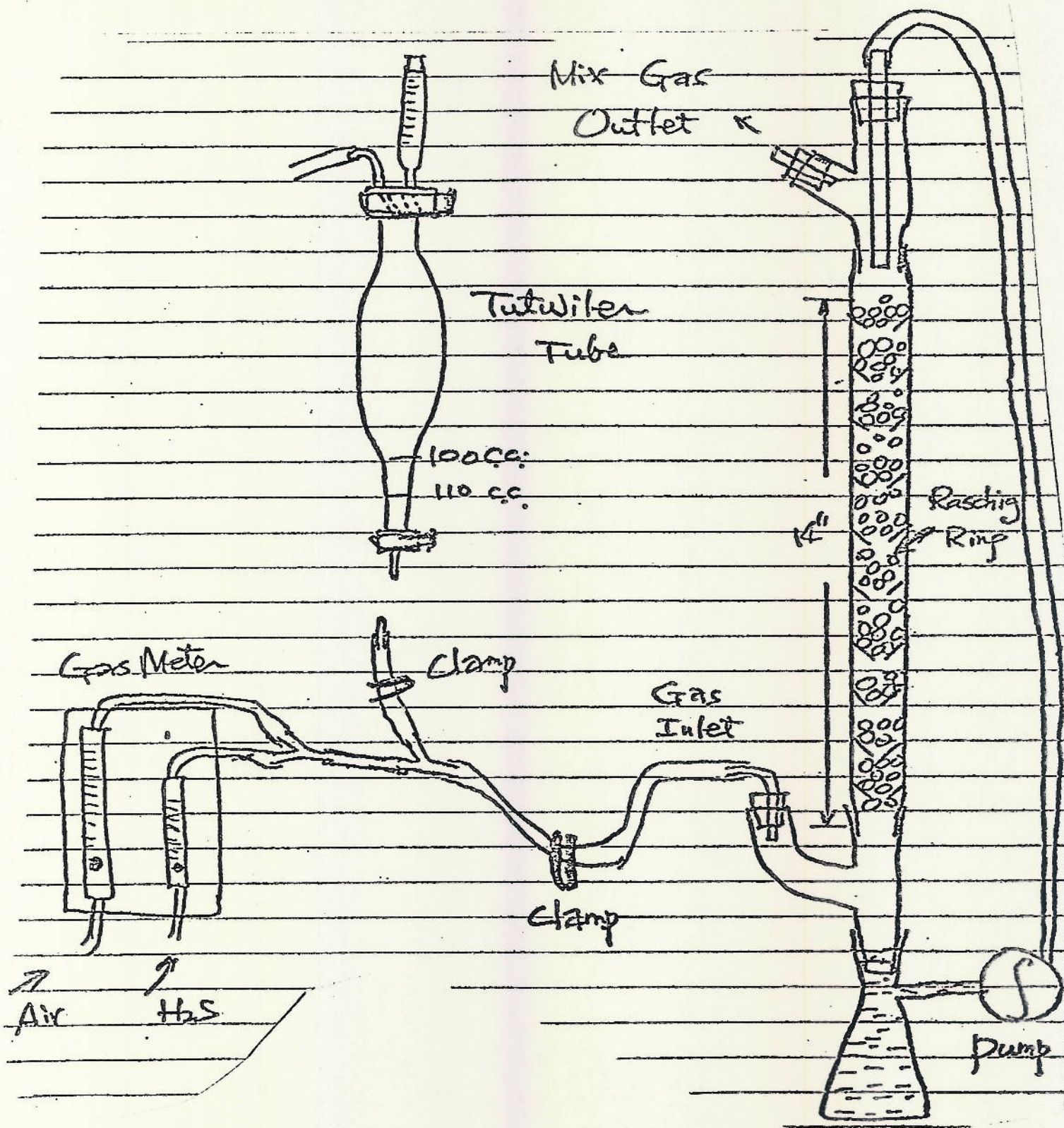


Fig. 7 Apparatus for  $H_2S$  Absorption Ability Test.

Table I H<sub>2</sub>S Absorption Ability of 1 percent Ammonia Solution.\*

Concentration of H <sub>2</sub> S in Ammonia Solution	Tutwiler Method	Lead Acetate Test Paper
Fresh Solution	< 20 grain/100 cu. ft.	
	< 20 grain/100 cu. ft.	No
	< 20 grain/100 cu. ft.	
With 0.118N H <sub>2</sub> S	< 20 grain/100 cu. ft.	
	< 20 grain/100 cu. ft.	No
	< 20 grain/100 cu. ft.	
With 0.25N H <sub>2</sub> S	< 30 grain/100 cu. ft.	
	< 40 grain/100 cu. ft.	Yes
	< 50 grain/100 cu. ft., > 20 grain/100 cu. ft.	
With 0.378N H <sub>2</sub> S	< 210 grain/100 cu. ft.	
	< 230 grain/100 cu. ft.	Yes
	< 200 grain/100 cu. ft. > 180 grain/100 cu. ft.	
* Blank	< 20 grains / 100 cu. ft.	

More than 200 grains/100 cu. ft. in the coke oven gas is not allowed by EPA, so the experiments stopped there.

Table II. H<sub>2</sub>S Absorption Ability of 4 Percent Ammonia Solution \*

Concentration of H <sub>2</sub> S in Ammonia Solution	Tutwiler Method	Lead Acetate Test Paper
Fresh Solution	< 20 grains/cu. ft.	
	< 20 grains/cu. ft.	No
	< 20 grains/cu. ft.	
With 0.244N H <sub>2</sub> S	< 20 grains/cu. ft.	
	< 30 grains/cu. ft.	No
	< 30 grains/cu. ft.	
With 0.465N H <sub>2</sub> S	< 20 grains/cu. ft.	
	< 30 grains/cu. ft.	No
	< 40 grains/cu. ft.	
With 0.588N H <sub>2</sub> S	< 20 grains/cu. ft.	
	< 30 grains/cu. ft.	No
	< 30 grains/cu. ft.	
With 0.741N H <sub>2</sub> S	< 60 grains/cu. ft.	
	< 70 grains/cu. ft.	Yes
	< 80 grains/cu. ft., > 50 grain/100 cu. ft.	
With 0.87N H <sub>2</sub> S	190 grains/cu. ft.	
	220 grains/cu. ft. > 180	Yes
	190 grains/cu. ft.	grain/100 cu. ft.
*Blank:	20 grains/100 cu. ft.	

From Table II, the upper limit of H<sub>2</sub>S content in 4 percent ammonia solution is higher than that of 1 percent ammonia solution.

Table III H<sub>2</sub>S absorption Ability of  
8% Ammonia Solution\*

Concentration of H <sub>2</sub> S in Ammonia Solution	Tutwiler Method	Lead Acetate Test Paper
Fresh Solution	< 20 grains/100 cu. ft.	No
With .286N H <sub>2</sub> S	< 20 grains/100 cu. ft.	No
With .571N H <sub>2</sub> S	< 20 grains/100 cu. ft.	No
With 1.177N H <sub>2</sub> S	< 20 grains/100 cu. ft.	No
With 1.33N H <sub>2</sub> S	< 60 grains/100 cu. ft., > 20	Yes
With 1.666N H <sub>2</sub> S	< 100 grains/100 cu. ft., > 50	Yes
With 1.905N H <sub>2</sub> S	< 90 grains/100 cu. ft., > 70	Yes
With 2.105N H <sub>2</sub> S	< 160 grains/100 cu. ft., > 120	Yes
	< 200 grains/100 cu. ft., > 170	Yes

Now, we know that the higher is the concentration of ammonia solution, the higher is the upper limit of H<sub>2</sub>S content in ammonia solution which is still usable as an absorption medium. In the next chapter, we will find out that higher content in ammonia solution would end up better efficiency for magnetite to oxidize H<sub>2</sub>S.

IV. The H<sub>2</sub>S Absorption Ability of Chicago Tap Water

(Purge with Air Containing 1 percent H<sub>2</sub>S)

The blank and Inlet Gas mix measurements are the same as previous sections. After pumping for 20 minutes in order to get equilibrium in the system, we measured both the H<sub>2</sub>S content in the outlet gas and in the Chicago Tap Water. The result in Table IV is not promising.

Table IV. H<sub>2</sub>S Absorption Ability  
of Chicago Tap Water

Concentration of H <sub>2</sub> S in Water	Tutwiler Method		Lead Acetate Test Paper
With 0.049N H <sub>2</sub> S	380	340	Yes
	400	350	

Now, we know that water is a very poor H<sub>2</sub>S absorption medium.

There is no reason trying to use water anymore.

## Ways to Destroy H<sub>2</sub>S

We know the every chemical reaction is reversible reaction. Ways of destroying H<sub>2</sub>S in order to remove H<sub>2</sub>S permanently is necessary. Ammonia solution should be either recovered or converted to something useful, such as fertilizer. For years, human being know that H<sub>2</sub>S can be removed by reactive with iron oxide, and the iron oxide, here, is usually Fe<sub>2</sub>O<sub>3</sub>. Our iron oxides to be tested mainly would be BOF dust and magnetite from Riverdale's Wean System. Both BOF dust and magnetite are the junk in our Company. It is our Company's policy hoping to cancel two evils at the same time. In the project proposal, H<sub>2</sub>S was planning to be absorbed by ammonia first, and then reacted with iron oxide to form iron sulfide. The iron sulfide either discarded without offending EPA requirement (if possible) or through aeration to regenerate iron oxide and released free sulfur. Of course, lots of technical difficulties will be involved. Those problems are parts of the job we need to solve in our project.

In order to detect the reaction, two methods were proposed.

### 1. Direct method:

Let iron oxide react with H<sub>2</sub>S (in ammonia solution). Use iodine titration to measure the amount of H<sub>2</sub>S from time to time and compare with a blank run.



2. Indirect Method:

Try to detect the presence of  $\text{Fe}_2\text{S}_3$ .  $\text{Fe}^{+3}$  is a group III cation. If there is the reaction,  $\text{Fe}_2\text{S}_3$  should be able to dissolve in acid media pH  $\sim 5$  to form  $\text{H}_2\text{S}$  which can be detected by iodine titration. Indirect method was tried first, since it is easy to perform.

I. BOF Dust (Indirect Method)

A. Preparation of BOF Solution

Weigh approximately 120 gr. BOF dust and make up to 500 ml. volume by dilution with  $\text{H}_2\text{O}$ .

B. Reaction

Adjust the pH of BOF dust solution to 5 and 10. Add ammonia solution which is saturated with  $\text{H}_2\text{S}$  slowly, and adjust the pH.

After finishing mixing, start time counting. Re-adjust pH to 5 if necessary. Use iodine titration to determine the amount of  $\text{H}_2\text{S}$ .

C. Result

Table V. Reaction between BOF Dust and H<sub>2</sub>S.

<u>pH</u>	<u>Time</u>	<u>Presence of Fe<sub>2</sub>S<sub>3</sub></u>
5	20 Mins.	None
	2 Hours	None
	24 Hours	None
<hr/>		
10	20 Mins.	None
	2 Hrs.	None
	24 Hrs.	None

Without the presence of Fe<sub>2</sub>S<sub>3</sub> does not mean that there is no reaction between BOF dust and H<sub>2</sub>S. It only means that our proposed Fe<sub>2</sub>S<sub>3</sub>, end product, never shows up. Maybe other kind of end products would be produced. Since this method is a necessary condition, not a satisfactory condition, we changed to direct method later.

B. Magnetite (Indirect Method)

The magnetite is the end product from Wean System, and is so dirty and with fouling odor. See Appendix III for way of cleaning. The method used to test the reaction between magnetite and H<sub>2</sub>S is the same as previous BOF dust.

Table VI. Reaction between Magnetite and  $H_2S$ .

pH	Time Duration	Presence of $Fe_2S_3$
5	20 Mins.	None
	2 Hrs.	None
	24 Hrs.	None
10	20 Mins.	None
	2 Hrs.	None
	24 Hrs.	None

Again, there is no  $Fe_2S_3$  presence. We have to look for some other method to prove whether there is reaction or not.

### III. Pellet (Iron Ore)

We hope pellet can react with  $H_2S$  in ammonia solution. So that, we can have some way to remove  $H_2S$  and recycle ammonia solution in case of failure of other methods. Pellet requires to maintain its shape after prolong dipping in ammonia solution.

#### A. Experiment

70 gr. Pellet was put into a tight plastic bottle with 70 ml. ammonia solution (with  $2.7 NH_2S$ ) for four days. After 4 days, the ammonia solution was titrated against some 0.2N iodine solution. Results are in Table VII.

Table VII. Reaction between Pellet and H<sub>2</sub>S.

NH <sub>4</sub> OH Solution	pH	NH <sub>4</sub> OH Solution Consumed (ml)	Normality of H <sub>2</sub> S in Ammonia Solution
Original	8.8	3.5	2.87 N
After 4 Days	9.0	3.7	2.70 N

$$(2.87 - 2.70) \text{ N} \times 70 \text{ ml.} = 11.9 \text{ meq}$$

$$\frac{1}{70 \text{ gr.}} \times \frac{11.9}{1000} \times 34 \times \frac{1}{2} = 2.89 \text{ mg H}_2\text{S}/1 \text{ gr. Pellet}$$

In other words, each gr pellet can remove at the most 2.89 mg H<sub>2</sub>S. This is far from enough, although the pellet is strong enough to maintain its strength after dipping in ammonia solution. In this respect, we have to look for different method or different material.

#### IV. Magnetite (Direct Method)

This method is the most successful method so far in our laboratory, and, of course, the most important method. In this section, we only mention how we found magnetite can be a H<sub>2</sub>S scavenger. We will discuss the detail, characteristics and its mechanisms, in next chapter.

This time we use direct method because we would like to know whether there is really existing any reaction or not. The Apparatus is shown in Figure 8. We let 200 gr Magnetite react with 200 ml. Ammonia solution.

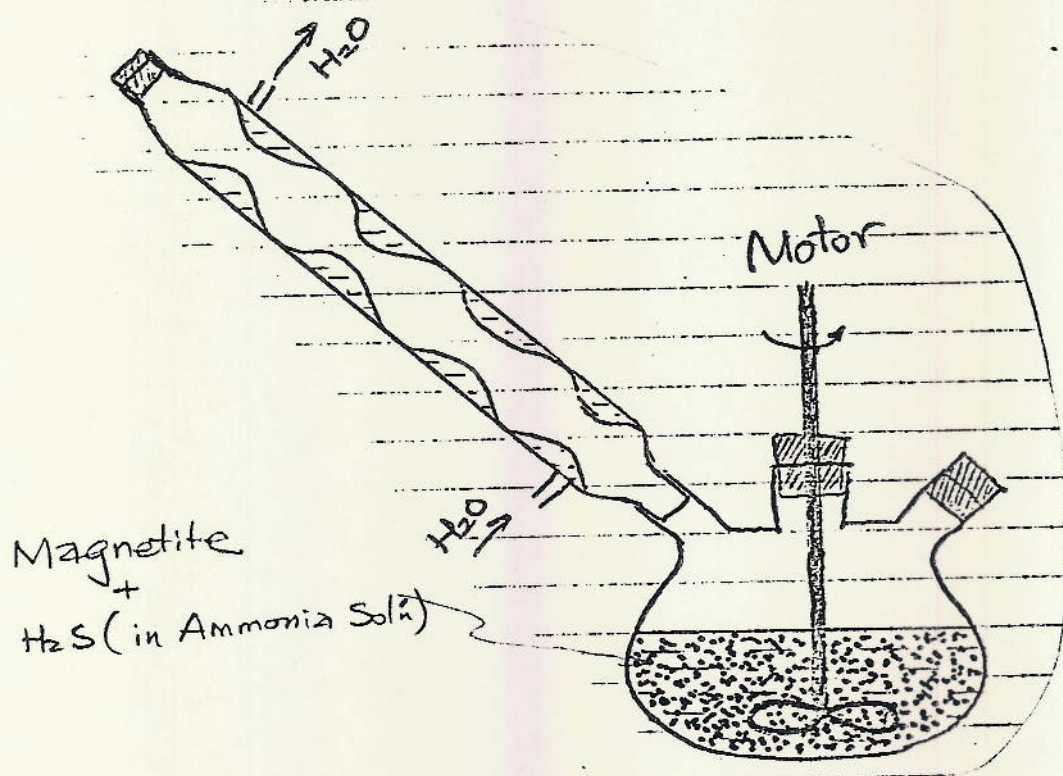


Fig. 8 Reaction Flask for Magnetite and H<sub>2</sub>S (in Ammonia Solution)

Since NH<sub>4</sub>OH solution (Sat. with H<sub>2</sub>S) keeps losing H<sub>2</sub>S or NH<sub>3</sub> into the air during stirring, we have to run "control". "Control" operated the same way except there was no magnetite in the solution.

After 20 minues, 1 hour, 2 hours, 20 hours and 24 hours, measure the content of H<sub>2</sub>S by iodine titration. Results are in Table VIII and Figure 9.

Table VIII. Reaction between Magnetite and H<sub>2</sub>S (Direct Method).\*

	Time Duration	pH	Amount of NH <sub>4</sub> OH Solution	Conc. of H <sub>2</sub> S in Ammonia Solution
Control	0 Minutes	8.8	3.5 ml.	2.86 N
	20 Minutes	8.8	3.6 ml.	2.78 N
	1 Hour	8.9	3.7 ml.	2.70 N
	2 Hours	8.9	3.8 ml.	2.64 N
	20 Hours	9.0	4.4 ml.	2.28 N
	24 Hours	9.0	4.5 ml.	2.22 N
Magnetite + NH <sub>4</sub> OH (Sat. with H <sub>2</sub> S)	0 Minutes	8.8	3.5 ml.	2.86 N
	20 Minutes	9.1	6.3 ml.	1.59 N
	1 Hour	9.2	7.3 ml.	1.37 N
	2 Hours	9.3	8.5 ml.	1.18 N
	21 Hours	9.4	17.1 ml.	0.58 N
	24 Hours	9.7	21.1 ml. +	0.47 N

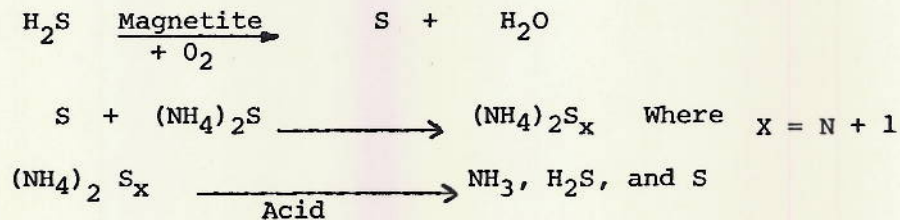
Apparently, there is reaction between magnetite and H<sub>2</sub>S. Magnetite can be a H<sub>2</sub>S scavenger.

\*Titrate against 50 ml 0.2 N Iodine Solution.

+Not too accurate. Use "drop method" due to insufficient solution. That is "drops of NH<sub>4</sub>OH solution vs. drops of iodine solution".

## Characteristics of Magnetic Reaction and its Mechanism

As long as magnetite can be H<sub>2</sub>S scavenger, we should find out its optimum reaction conditions and its major mechanism, since they are useful information during setting up the pilot plant. Magnetite is the end product of Wean System, which changes the pickling solution into harmless magnetite for Riverdale plant, and has a very complicated chemical composition. (Appendix IV). From last section and more detail study, it is found that magnetite can serve as a catalyst which can oxidize H<sub>2</sub>S through the help of oxygen in the air. As we know, H<sub>2</sub>S is not easy to be oxidized by air directly. Blow air into H<sub>2</sub>S solution (dissolved in water, or ammonia solution) can only drive out the H<sub>2</sub>S. The catalytical reaction of magnetite, more or less, coincides with what other researcher found <sup>5</sup>. Some other research chemist found that a mixture of iron sulfide, nickel sulfide, lead sulfide can be the catalyst to oxidize the H<sub>2</sub>S by the help of air.<sup>5</sup> The intermediate product, sulfur, dissolves into ammonia solution to form polysulfide.



We will discuss the characteristics of magnetite reaction, its major mechanism, and how to extract sulfur from our scrubber, ammonia solution, step by step.

I. Characteristic of Reaction:

A. Reaction Rate Vs. Temperature

Just like other chemical reactions, the higher is the temperature, the faster is the reaction. Figure 10 shows a typical reaction between magnetite and  $H_2S$  in different temperatures. Although amounts of sulfide after 24 hours are not the same. It is because of the escaping speed of  $H_2S$  into the air is different due to the temperature difference.

B. Reaction Rate Vs. pH

It is found that the lower the pH, the faster is the reaction. However, the solubility of  $H_2S$  in ammonia solution drops dramatically, and it becomes not practical to let them react at low pH.

C. Amount of  $H_2S$  Removed Vs. Quantity  
of Magnetite

It is found that the amount of  $H_2S$  removed is proportional to the amount of magnetite use, provided the Conc. of  $H_2S$  in ammonia solution and the surface condition of the magnetite are the same. Figure 11, 12 and 13 are three examples at different temperatures.



D. Reaction Vs. Surface Condition of Magnetite

Same as other solid catalysts, the cleaner is the magnetite surface the faster is the reaction and the more is the amount of hydrogen sulfide removed. Figure 14, 15 and 16 are the typical examples.

E. Efficiency of Magnetite Vs. Concentration of H<sub>2</sub>S in Ammonia Solution

We found that the higher is the concentration of H<sub>2</sub>S in ammonia solution, the higher is the efficiency of magnetite. In other words, the more is the amount of H<sub>2</sub>S can be oxidized per unit weight of magnetite per pass. No reason is given here. The readers are going to learn more in the next section. Figures 17, 18, 19 and 20 composed typical examples.

II. Mechanism of Reactions

Although many famous chemical processes nobody knows why and are still in use, we hope we can understand some basic principles in order to help us to establish our pilot plant. The detail of mechanism may be too hard to study due to the limitation of time and money. In case of this process becomes very useful to human beings and adopted by major steel industry, there will be somebody else to try to find out the detail of reactions. The famous

Kreb's Cycle\*, which won Nobel prize, can be a good example. Although Kreb's Cycle has been modified many many times and become more and more sophisticated, the credit still goes to Mr. Kreb. First, we may propose the overall mechanism of reactions judged by our chemical sense and our experience in this project. Then we may design some experiments to test the overall mechanism. The proposed one can be wrong, and never be a perfect one; however it still can give us some useful information to establish the pilot plant.

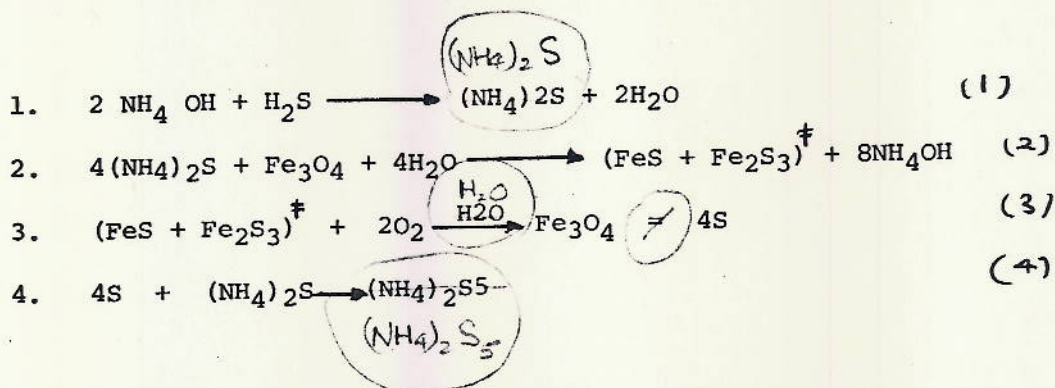
The first thing tried to find out is what is the intermediate compound. We know that there must be an intermediate compound due to the reaction between  $H_2S$  and magnetite. What is it? Then the intermediate compound oxidize to release sulfur and recover the magnetite. That's why we need to soxlet the magnetite in order to recover the magnetite after each reaction, and the amount of magnetite never changes. The second thing tried to find out is what is the rate of overall reaction and, what is the order of each separate reaction? After we know this information, we can predict the reaction rate under different conditions.

The third thing needs to know is where is the chemical equilibrium and what is the equilibrium constant. If we do know this information we can use the magnetite more effectively. We can discuss step by step from each stape work we have done, and deduct the result.

---

\*Metabolism Cycle. See any biochemistry textbook.

Mr. Victor Beaucaire proposed a brief overall mechanism as follows,



The reason why we can propose this way is that magnetite got to participate this entire reaction, since there is at least 10% metal oxide <sup>reacting</sup> should react with H<sub>2</sub>S during nitrogen run which will be mentioned later.

#### A. X-Ray Diffraction

X-Ray Diffraction is the best tool to identify new compounds in solid state. Our way to identify or find out the intermediate compound was to let the H<sub>2</sub>S (in ammonia solution) react with magnetite under inert gas, say N<sub>2</sub>. Then, used the X-ray diffractometer to get the diffraction pattern and wished to have a miracle. Of course, the sample should be under inert atmosphere protection during taking the X-ray diffraction pattern. With such unstable complex, we <sup>do</sup> will not expect to identify it. However, we expected to get some odd peaks if possible. The amount of intermediate compound supposed to be enough to be detected by X-ray diffraction. Usually, X-ray diffraction can detect an impurity which is more than 3% in its medium under normal conditions.

Unfortunately, we tried and could not get any sign of presence of intermediate complex compound. Though we are positively sure there is such intermediate complex compound from various sources. We have to give up this wish. An evidence that such kind of intermediate compound does exist is that a filter paper with such end product (between  $H_2S$  and magnetite running under  $N_2$ ) caught fire after being dried in the decicator and expressed to the air. Maybe, that intermediate compound has <sup>huge</sup> hope lattice constant. Maybe that intermediate compound has a distorted lattice constant. Maybe that intermediate compound can react with oxygen such vigorous that no more such intermediate ~~existive~~ <sup>existing</sup> during taking the diffraction pattern. We know that no system is perfect especially our temporary air protection system. Maybe the X-ray diffractor at IITRI is such lousy that no such signal can be picked up.

B. Reaction Under  $N_2$

Figure 21, Figure 22, Figure 23, and Figure 24, are the typical examples of magnetite reacting with  $H_2S$  (in ammonia solution) under nitrogen atmosphere. The concentration of  $H_2S$  in ammonia solution are different. However, per unit weight of magnetite, same amount of  $H_2S$  is consumed. This phenomenon is different from what we saw in Figure 17, Figure 18, Figure 19 and Figure 20, since the reaction stops at reaction (2).

In other words, only reaction (2) has been completed, and nothing else. That would explain why they consumed the same amount of H<sub>2</sub>S. (FeS + Fe<sub>2</sub>S<sub>3</sub>)<sup>‡</sup> is the so called intermediate compound. Naturally, maybe the intermediate can be in other form.

Moreover, the order of reaction and the reaction rate constant can be derived. Initial slopes can be obtained from charts independently.

$$- \frac{d(S^{\equiv})}{dt} = K \cdot (S^{\equiv}) \cdot X = K' \cdot (S^{\equiv})$$

where (S<sup>≡</sup>) indicates the concentration of (NH<sub>4</sub>)<sub>2</sub>S plus the concentration of free H<sub>2</sub>S. X indicates the available surface area of magnetite, and K' = K.X

1. Initial concentration of H<sub>2</sub>S = 1.31 N

$$- \frac{d(S^{\equiv})}{dt} = K' \cdot (0.65) = \frac{0.7}{14} = 0.05 \quad (5)$$

$$\text{If } n = 2 \quad K' = 0.14$$

$$\text{If } n = 3 \quad K' = 0.18$$

$$\text{If } n = 4 \quad K' = 0.25$$

2. Initial Concentration of H<sub>2</sub>S = 2.00 N

$$- \frac{d(S^{\equiv})}{dt} = K' (1) = \frac{1}{7} = 0.14 \quad (6)$$

$$K' = .14 \quad \text{If } n = 2, 3 \text{ and } 4$$

3. Initial Concentration of  $H_2S = 3.00 N$

$$-\frac{d(S^{\equiv})}{dt} = K' (1.5) = \frac{1}{4} = 0.25 \quad (7)$$

$$K' = 0.12 \quad \text{If } n = 2$$

$$K' = 0.07 \quad \text{If } n = 3$$

$$K' = 0.05 \quad \text{If } n = 4$$

From the above, it seems that reaction (2) is second order to the concentration of  $(S^{\equiv})$  and the reaction rate constant has to be 0.14.

4. Initial Concentration of  $H_2S = 1.73 N$

$$\text{slope (From Figure 24)} = \frac{1.73 - 0.76}{9} = \frac{.97}{9} = 0.108$$

$$-\frac{d(S^{\equiv})}{dt} = K' (0.865)^2 = 0.108$$

$$.748 K' = 0.104$$

$$K' = 0.138$$

Very very consistent.

5. Initial Concentration of  $H_2S = 1.73 N$

Only half amount of magnetite is used here.

(50 gr.)

$$\text{Slope (Figure 25)} = \frac{1.73 - 0.78}{20} = 0.0475$$

$$\frac{d(S^{\equiv})}{dt} = K (0.865)^2 \quad \left(\frac{1}{2} \times \right)$$

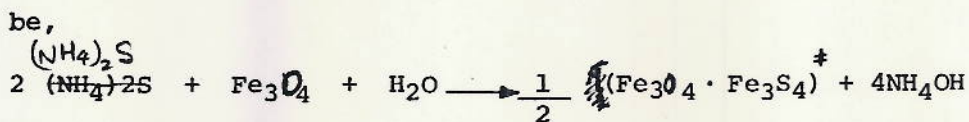
$$= \frac{1}{2} K' (0.748) = 0.0475$$

$$K' = 0.129$$

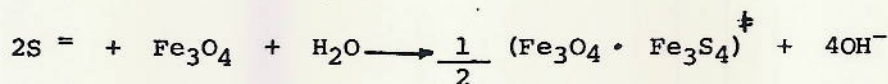
Still pretty consistent.

From here, we can establish that the reaction rate should also be proportional to the first order of the amount of magnetite.

At the first glimpse, it seems funny that how the reaction rate can be proportional to the second order of  $(S^-)$  concentration instead of fourth order. However, it is possible, since most of the chemical kinetic theory is still in its childhood period. And, there are lots of impurities in magnetite. How do we know the intermediate compound got to be  $(FeS + Fe_2S_3)^\ddagger$ ? Maybe it can be in some other form, especially the reaction happened on the surface of a particle. Maybe the reaction (2) should



or



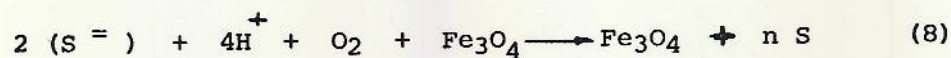
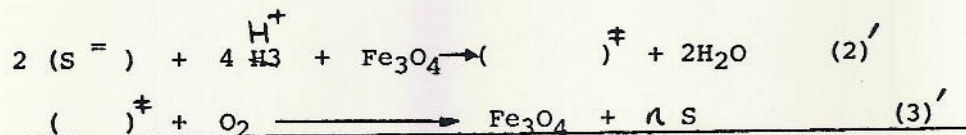
Nobody knows. Maybe there is another intermediate compound  $XO_2$ , where X is a metal, preceding Reaction (2) to cause second order reaction. The detail should leave to whoever interests in it.

### C. Reaction in Air

Reaction in the air, without inert gas protection, is the summation of reaction (2), reaction (3) and reaction (4). The reaction rate constant in (3) should be very, very fast and hard to estimate,

since the overall reaction is so fast and the overall reaction rate constant is the product of the reaction rate constant in (3) times the reaction rate constant in (4).

The combination of reaction (2) and (3) can be as follows,



X                      where  $n < 2$

$$K = \frac{S}{(S^=)^2 \cdot X}$$

The reasons are

1. We assume part of  $Fe_3O_4$  is not covered by sulfur and can be re-usable. The ratio between original available surface area to the re-usable surface area should have a certain value. Therefore, the usable  $Fe_3O_4$  surface area can be denoted by X.
2. The output sulfur, S, should have a quantity n and n is less than 2, since some of the sulfur become polysulfide. There is a chemical equilibrium between  $(S^=)$ , S and polysulfide.

From figure 17, Figure 18, Figure 19, Figure 20, and Equation (8),



$$K_1 = \frac{(0.15)}{(0.71)^2 \cdot X} \quad (9)$$

$$K_2 = \frac{(0.85)}{(1.5)^2 \cdot X} \quad (10)$$

$$K_3 = \frac{(0.35)}{(0.87)^2 \cdot X} \quad (11)$$

$$K_4 = \frac{(0.7)}{(1.17)^2 \cdot X} \quad (12)$$

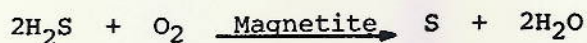
If we let  $N = 1$ ,  $K_1 \approx K_2 \approx K_3 \approx K_4$

that means the order of sulfur in the overall reaction should be 1.

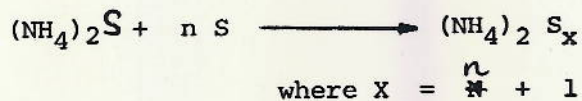
A very important information is here - the amount of sulfur released by the catalytical oxidation reaction is proportional to the second order of the initial concentration of  $H_2S$  in ammonia solution.

### III. How to Decompose Polysulfide

As mentioned before, after catalytical oxidation of  $H_2S$  by air and magnetite, sulfur is released.



The sulfur apparently re-dissolved into ammonia solution and formed polysulfide.



One of the characteristic attributes of carbon in organic chemistry is its ability to undergo unlimited covalent combination with itself. Sulfur, as well as some Group III and Group IV elements, has the same ability. Polysulfide, which is not well-known to most of the chemists, is one of those self-covalent combined sulfur compounds. The author, through some effort, eventually identified that the yellowish material in the ammonia solution happened to be polysulfide, which is coincided with some other researcher mentioned in other places <sup>5,6,7</sup> ~~5,6,7~~.

A. Identification of Polysulfide

Polysulfide which has the structure of  $R - S - (S)_n - S - R$ , where R can either hydrogen or alkyl group and n can be zero or other integers. Polysulfide has different chemical properties than sulfide. Polysulfide can be easily decomposed to yield sulfur by acid,  $S_n^{2+}$  ~~S<sub>n</sub><sup>2+</sup>~~ reaction, or by heat <sup>6,7</sup> ~~6,7~~, just like polythionic acid. And the -S-S- bond can be detected by NMR, UV and Raman Spectra. The wet chemistry of polysulfide is hard to be obtained. However, the author used his wet chemistry knowledge and made a list.

Table IX. Wet Chemistry for Polysulfide

<u>Reagents</u>	<u>Results if there is H<sub>2</sub>S only</u>	<u>Actual Result</u>
(1) Pb(AC) <sub>2</sub>	Black <del>pp<sub>te</sub></del> <sup>ppte</sup>	Brownish Red ppte
(2) FeSO <sub>4</sub>	Brownish Black <del>pp<sub>te</sub></del> <sup>ppte</sup>	Solution changes to light brown color
(3) CuSO <sub>4</sub>	Brown <del>pp<sub>te</sub></del> <sup>ppte</sup>	Solution changes to green color
(4) Zn(AC) <sub>2</sub>	White <del>pp<sub>te</sub></del> <sup>ppte</sup>	Solution changes to light brown color

Obviously, H<sub>2</sub>S in ammonia solution after reacting with enough magnetite formed a new compound which is entirely different from sulfide. In ordinary situation, polysulfide usually mixed up with sulfide, since not that much magnetite was used.

Polysulfide as mentioned before, structure -S-S- bonding, can be detected by NMR, UV, and Raman Spectra. Among them, Raman Spectrum, especially Raman spectrascopy with laser beam, would be the best instrument to identify it. However, it is hard to find an available Raman spectroscopy nearby Mid-east area. Figure 26, and Figure 27 are the UV spectra for

7,8  
polysulfide which are coincided with what the other author found ~~7,8~~.  
The peaks around 280 mu are the characteristic peak for -S-S-  
bonding. Different solvent can shift the peak somewhat, but not too  
much.

B. Decomposed by Acid

Polysulfide, just like polythionic acid, can be decomposed  
easily and yielded sulfur by adding acid. The reaction  
mechanism is too bulky to discuss here; however, it is a  
nucleophilic reaction,  $S_N^2$ . Adjust pH to 2.0 - 3.0 we can  
get all the sulfur precipitation. One of the disadvantages  
is that, the end product in our case got to be the  $(NH_4)_2SO_4$ ,  
and the ammonia can not be re-cycled without extra cost.

C. Decomposed by Heat

Just like polythionic acid, polysulfide is not a stable  
compound, and can be easily decomposed by heat ~~7,9~~<sup>7,9</sup>. Apparatus  
is shown in Figure 28.

An experiment was run. The original concentration of that  
solution is 0.71 N\*, and the original pH is 10.1. The  
polysulfide solution changed from yellow to dark brown after  
boiling for several minutes. Then, turned to green.

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\*Use iodine solution for titration, and consider all polysulfide as H<sub>2</sub>S.

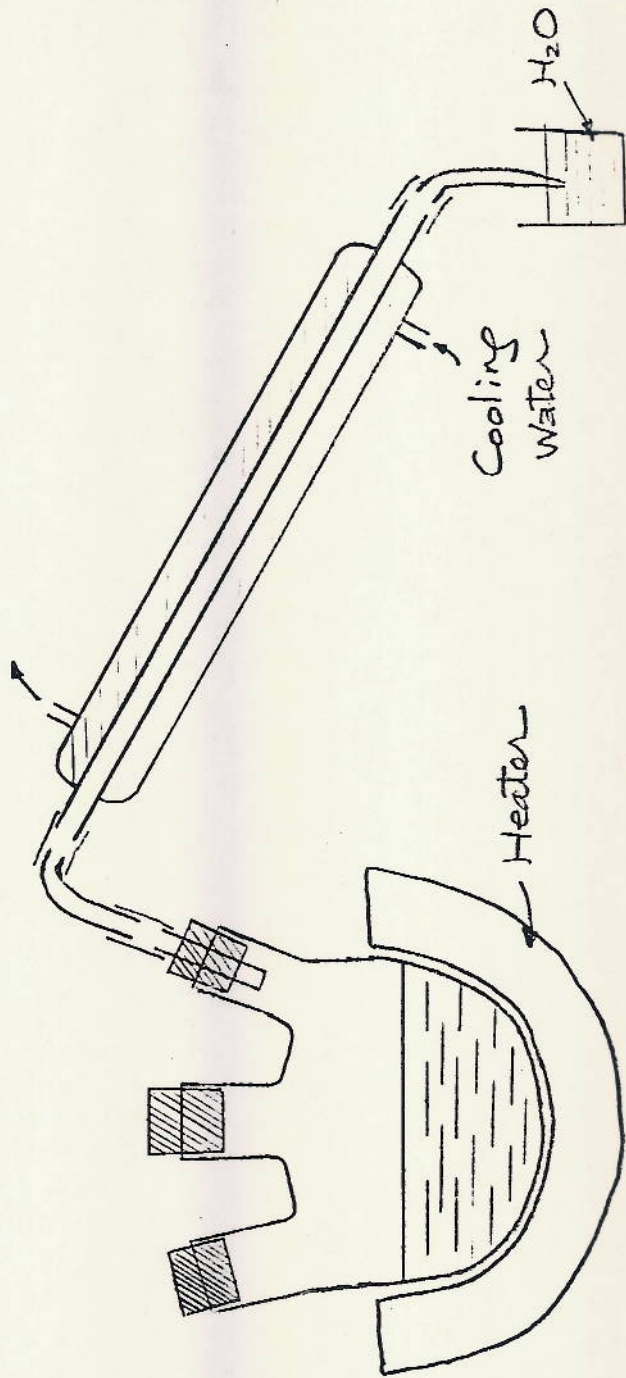


Fig. 28 Decomposition of Polysulfide by Heat.

Finally, it turned to yellowish turbulence solution. At this stage, there is almost no more  $H_2S$  and ammonia left in the solution. Sulfur can be filtered out by ordinary filter paper. Why change the color from yellow to dark brown and then to green before turning to yellowish turbulence? We don't know so far. Maybe there are lots of short-life-time intermediate compounds during the entirely reaction.

The author believes that the decomposition of polysulfide by heat can be accerlerated by catalyst or by using autoclave. More research work can be done in this area.

## Other Trials and Two Alternatives

### I. Other Trials:

The author based on some of his chemistry knowledge and the chemical sense to do some trial tests to see whether there are some other simple ways to destroy  $H_2S$  or not.

#### A. Oxidation by Air:

Blowing air into ammoniacal  $H_2S$  solution simply drives out the  $H_2S$ , even if in the presence of  $Al_2O_3$ .  $Al_2O_3$  is an organic <sup>and</sup> catalyst <sub>^</sub> is used very widely.

#### B. Oxidation by $SO_2$

In the laboratory,  $SO_2$  can be generated by adding concentrated  $H_2SO_4$  to  $Na_2SO_3$  crystals. (Figure 29)

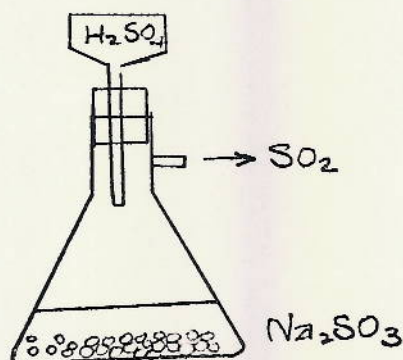


Figure 29 *Generation of  $SO_2$*

Bubbling  $SO_2$  through ammoniacal  $H_2S$  solution again, simply drives out the  $NH_3$ , and  $H_2S$ . There was no sulfur precipitation come out. The fundamental reason is that the  $SO_2$  gas is not easily dissolved into ammonia solution. Reaction rates between heterogeneous phases is usually low.

C. Chlorine Gas

Chlorine can be obtained by adding concentrated  $H_2SO_4$  to  $MnO_2$ . (Figure 30). The apparatus is similar to Figure 29. At first, we hope chlorine can replace sulfur and regenerate sulfur. However, bubbling chlorine gas through could only

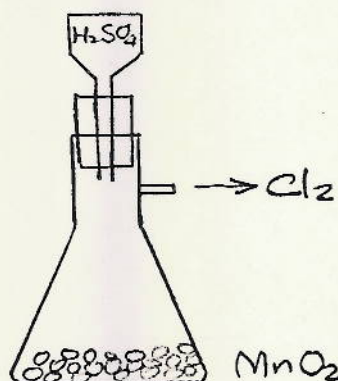


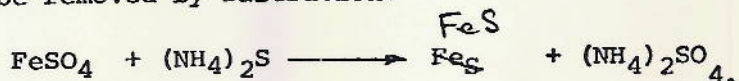
Figure 30 Generation of  $Cl_2$

drive out  $H_2S$  and  $NH_3$ , and no sulfur precipitation observed.

II. Two Alternatives

A.  $H_2S$  Removed by Pickling Solution.

This is <sup>the</sup> easiest method and only requires the lowest initiation capital spending. The only major facilities need to buy is a storage tank and a reaction tank. Iron sulfide precipitation can be removed by filtration.



or



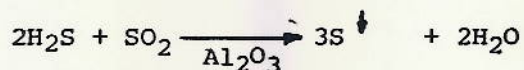
Pyrite,  $Fe_2(SO_4)_3$  or  $FeS$ , can be sold to Stauffer Chemical



Company, Westport, Connecticut. They can pay somewhere between \$2 to \$3 per ton. However, judging from our H<sub>2</sub>S amount and coke oven gas production, we can have 30 to 50 tons pyrite produced per day. The pickling solution from our Riverdale Plant and Gary Steel Plant will not be enough. We got to collect pickling solution from other sources. Moreover, the shipping of pickling solution depends upon trucks. The shipping of pyrite depends upon railroad. Unless we are going to build huge storage tanks and warehouses, we will have trouble during either a railroad strike or truck strike. Therefore, unless other methods failed to mature, we will not use this method.

B. Oxidation by Sulfite.

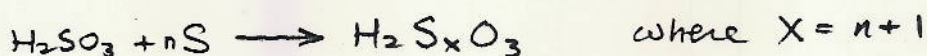
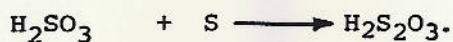
Recall the famous volcano reaction:



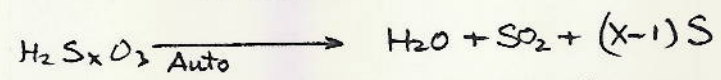
Although the yield is low, it is where the free sulfur came from. From kinetic point of view, the best way to let volcano reaction become fast and complete is let them react in the liquid phase. In other words, we should change the form of SO<sub>2</sub> to sulfite. SO<sub>2</sub> can dissolve very easily in cold water.



However, the sulfur will not precipitate out this way. This is a very bad disadvantage. It redissolved by sulfurous acid, and formed thiosulfate, or polythionic acid.



Thiosulfate is relatively stabler than polysulfide. We should use either acid or autoclave to break it down.



The sulfur, our by-product, can be burned to regenerate  $\text{SO}_2$ .

The flow sheet is in Figure 31.

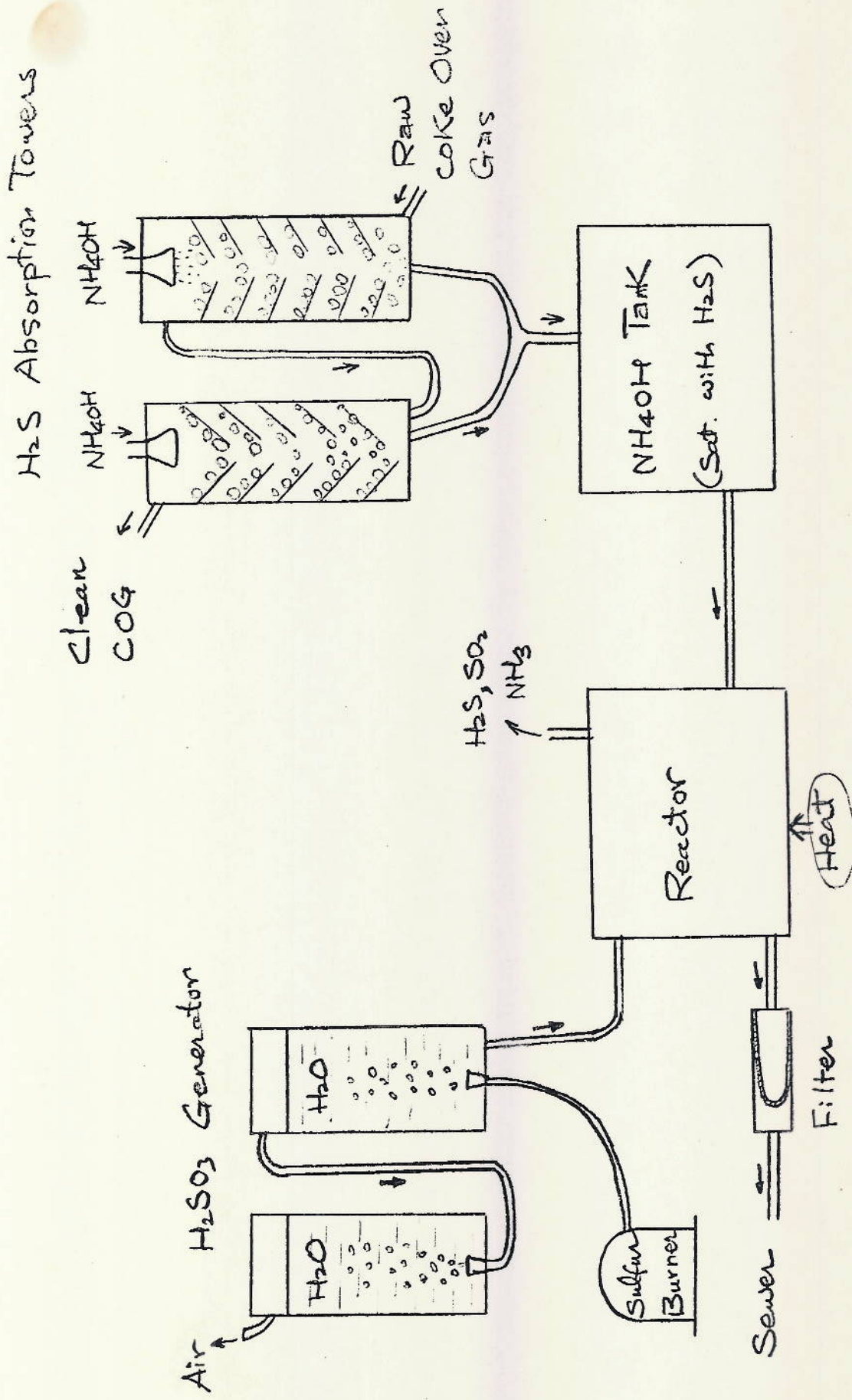


Fig. 31 Decomposition of ~~Raw coke Oven Gas~~ <sup>H<sub>2</sub>S</sup> by Sulfite.

## RECOMMENDATION

Based on the laboratory results so far, a pilot plant or a pre-pilot plant should be considered for further information on practical use of this method.

However, in dealing with <sup>(1)</sup> why magnetite can be a catalyst? <sup>(2)</sup> how long a time can magnetite be used over and over again without getting poisoned?<sup>3</sup>  
<sup>(3)</sup> How can we obtain a fast way to clean up magnetite? and <sup>(4)</sup> Whether we can make a better artificial catalyst by mixing optimum amount of different metal sulfides? Those are still good research topics laid before us.

Further work can be done and worth to be tried in the future if magnetite proves to be a good oxidation catalyst for  $H_2S$ .

APPENDIX I

A. Preparation of Solutions:

1. 25% SAOB (Sulfide Anti-Oxidant Buffer).

-- from Instruction Manual "Sulfide Ion Electrode", Orion Research.

40 gr. NaOH

160 gr. Sodium Salicylate

36 gr. Ascorbic Acid

Dissolved in approximately 500 ml. water and make up to 2-liter.

2. Iodine Solution (0.1 M or 0.2 N)

-- from Kolthoff's Textbook of Quantitative Inorganic Analysis.

Put 40 gr. KI in a weighing bottle and dissolve into 10 ml. H<sub>2</sub>O.

Add approximately 12,500 gr. re-sublimized iodine (need accurate reading). Transfer to a 500 ml flask and make up to the mark.

Store it in a brown bottle.

12.5730 gr. iodine was weighed.

$$\frac{12.5730}{126.91} = 0.09907 \text{ M (as I}_2\text{)}$$
$$= 0.198 \text{ N}$$

3. Arsenious Oxide Solution (0.1 M or 0.4 N)

-- from Kolthoff's Textbook of Quantitative Inorganic Analysis

Dissolve exactly 1.9782 gr. of pure AS<sub>2</sub>O<sub>3</sub> in a 20 ml 1 N NaOH.

Add 1 N H<sub>2</sub>SO<sub>4</sub> until neutral or slightly acid to litmus paper.

Transfer to a 100 ml volumetric flask and make up to the mark.

4. Na<sub>2</sub>S solution

--from Instruction Manual "Sulfide Ion Electrode" Orion Research.

(0.1 M) Weigh 24 gr. Na<sub>2</sub>S x 9 H<sub>2</sub>O. Dilute with 25 percent

SAoB solution to 1 liter (0.01 M). Take 100 ml 0.1 M Na<sub>2</sub>S

solution and dilute with 25 percent SAoB solution to 1 liter

(0.001 M). Take 100 ml 0.01 M Na<sub>2</sub>S solution, and dilute with

25 percent SAoB to 1 liter.

B. Standardization

39.8 ml iodine solution was required to neutralize 20 ml  $AS_2O_3$  solution.



$$40.01 = 39.8 \cdot x$$

$$x = \frac{40}{39.8} = 0.1005 \text{ M}$$

$$= 0.2010 \text{ N (Concentration of Iodine Solution)}$$

This reaction is a reversible reaction: arsenious oxide can only be titrated with iodine solution at pH value between 9 and 4. During titration, lots of acid releases out and needs to add NaOH from time to time.

30.9 (0.1 M)  $Na_2S$  solution needed in order to neutralize 30 ml iodine solution.

$$30.9 \times x = 30 \times 0.1005 \text{ M}$$

$$x = \frac{30.0}{30.9} \times 0.1005 = 0.09905 \text{ M}$$

$$= 0.198 \text{ N}$$

(Concentration of  $Na_2S$ )

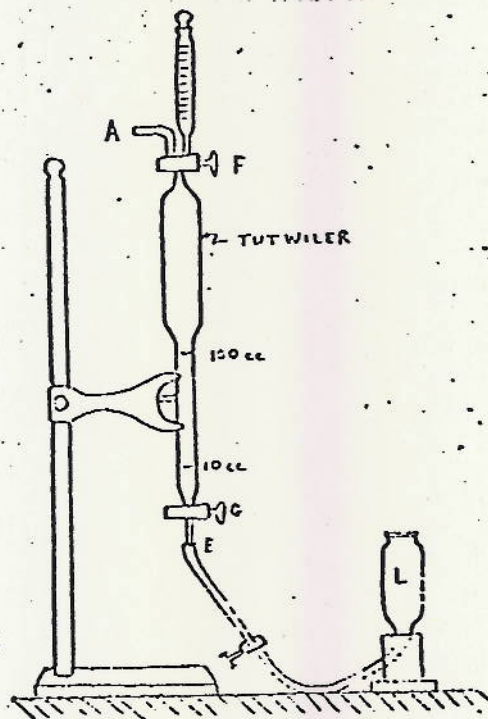
APPENDIX II



## H<sub>2</sub>S IN COKE OVEN GAS

Displace the air by drawing starch solution through the bottom of the Tutwiler. Take in 110 cc. of gas sample through the top of the Tutwiler subtracting 1/10 of the reading to correct to 100 cc. Titrate a small amount at a time with .01345 N Iodine solution to a blue end point.

Titration -  $(1/10 \text{ of the titration}) \times 100 = \text{Grains of H}_2\text{S per 100 cu. ft.}$



Rinse the graduated cylinder portion of the Tutwiler twice with .01345 N Iodine solution, fill the cylinder and record the reading. Put on the ground glass top. Fill the leveling bulb, L, with starch solution. Raise L, open cock G, open F to A, and close F when the starch starts to run out of gas inlet tube A. Close G. Purge the gas sampling line and connect it with A. (If the gas contains dust or tarry matter, it should be filtered through a tube of glass wool or cotton.) Lower L and open F (to A) and G. When the liquid level is past the 100 cc. mark, close G and F, and disconnect the sampling tube at A. Open G and bring the starch solution

to the 100 cc. mark by raising L; then close G. Quickly open and close F to bring the gas in the burette to atmospheric pressure. Open G, bring the liquid level down to 10 cc. mark by lowering L. Close G, clamp the rubber tubing near E and disconnect it from the Tutwiler.

Titrate slowly with the Iodine solution through F, shaking after each addition until a faint permanent blue end point is reached. Record the Iodine reading, subtract from the first reading, and call it D.

With every fresh starch solution run a blank. Fill the Tutwiler with starch up to 100 cc. mark. Close F and G. Lower L and open G. When the level reaches the 10 cc. mark close G. Titrate the same way as during a test to the same end point. Call the Iodine used C.

$$100 (D - C) = \text{Grains of H}_2\text{S per 100 cu. ft.}$$

#### SOLUTIONS USED

.01345 N Iodine - 1 ml = 100 grains of H<sub>2</sub>S per 100 cu. ft. -  
Weigh .8538 grams of Iodine as closely as possible. Dissolve 12.5 grams of Potassium Iodide (KI) in as little water as possible. Dissolve the Iodine in the KI. Dilute to 500 ml. Let stand overnight before titrating. Store in a brown bottle.

Starch indicator - (1) Dissolve 15 g. of soluble starch or 27 g. of any starch in 150 ml of water. Add 0.3 g. of phenylmercuric acetate. Add this slowly to 3 liters of boiling water. Cool. Decant the clear portion if soluble starch was not used. Add 50 g. of KI.

(2) Mix 1000 ml of saturated NaCl solution (filtered), 160 ml of glacial acetic acid, 40 ml of water and 6 g. of starch. Bring slowly to a boil and boil for two minutes.

(3) Add 1 g. of soluble starch to 100 ml. of water and heat to boiling. Add 1 g. of boric acid. Cool. Use about 3 ml for each titration. If regular starch is used boil 5 minutes and decant if necessary.

#### REACTIONS AND EXPLANATIONS

Iodine dissolves in KI giving a triiodide ion. The slightest excess of iodine reacts with starch to give a blue color. The blue colored substance, which loses its color when heated and regains it when cooled, is not a true chemical compound. The iodine is absorbed on the colloidal starch in the water. Iodine also reacts with water:  $I_2 + H_2O \rightarrow H^+ + I^- + HIO$ . Strong bases shift the reaction to the right and therefore must be avoided when titrating with iodine solutions. Since HIO decomposes in light giving off oxygen, iodine solutions must be kept in dark bottles.

There are many different starches and even more methods of making starch solutions. It is important to add a preservative if the starch is to be stored to prevent the formation of molds.

A small amount of alcohol can be used to get the iodine into solution quickly. To standardize an iodine solution the best standard available is pure arsenic oxide ( $As_2O_3$ ). Other standards are potassium permanganate, potassium dichromate and metallic copper. A standardized sodium thiosulfate solution is acceptable as a standard.

The first method for  $H_2S$  is only good because of its brevity. The second method is a bit more accurate and takes a little longer. The gas volume can be corrected to standard if ambient temperature and pressure are taken. An even longer and more accurate method is found in Methods... of U.S.S. using  $CdCl_2$  and a gas meter.

Running time: 7-8 minutes for Method 1.

Method source: "Gas Analysis and Testing of Gaseous Materials"  
1944, p. 339.

Last change: None

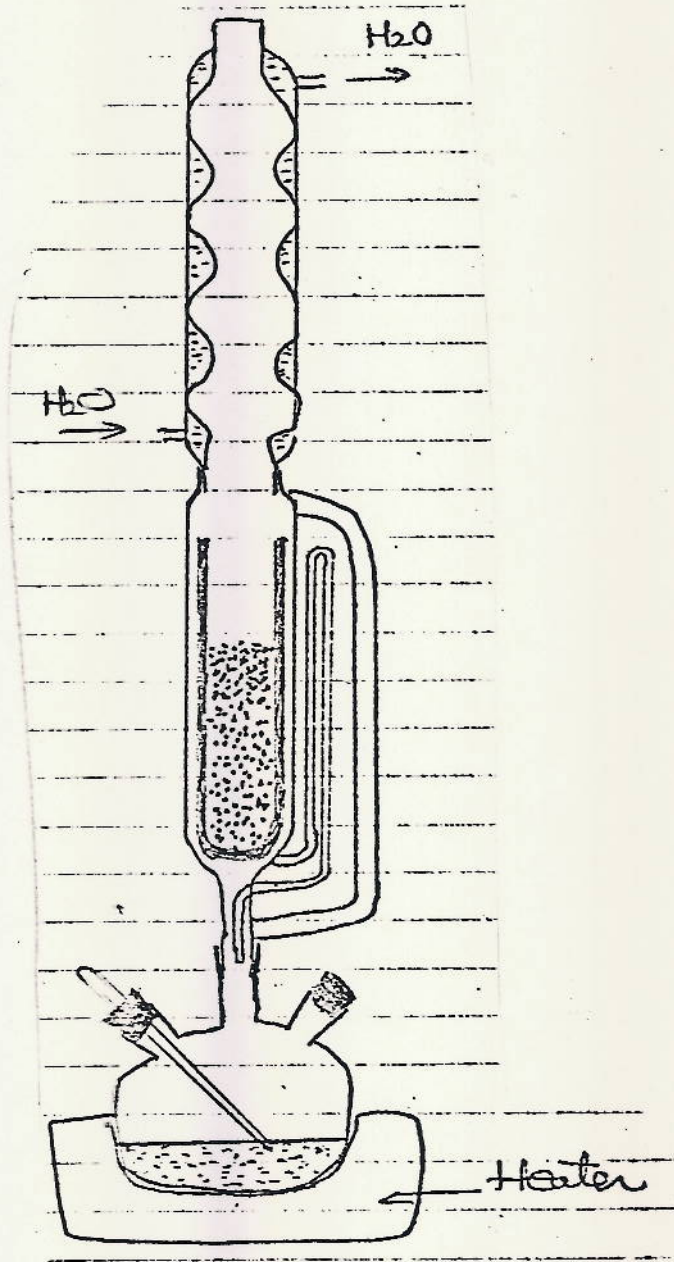
APPENDIX III

WAY OF CLEANING

1. Get 1 pound (approximately) magnetite and put it into a 1000 ml. beaker.
2. Add some acetone (approximately 500 ml) into the beaker. Stir.
3. Filter it.
4. Take out the magnetite, and add some more acetone. Re-stir.
5. Filter again.
6. . . . .

Repeat steps 4 and 5 until the acetone in the trap is colorless and clear.

7. Dry in the air, (flatten the magnetite on a sheet of paper and leave it exposed to air for 1 hour) until no acetone odor.
8. Use Soxlet (hexane as solvent) to do the final cleaning.  
Solet it overnight.



APPENDIX IV



CHEMICAL COMPOSITION OF MAGNETITE

The chemical composition of magnetite is so complicated. Detail study is almost impossible due to the limitation of time and money. However, the following information can give us a rough idea:

1. X-Ray Spectroscopy

The composition of elements is as follows:

Date 3/16/71

Wet Cake % H<sub>2</sub>O 65.2%

Dry Cake Analysis

Fe	38.1%
Zn	1.29
Cu	.032
Ni	.05
Cr	.02
Mn	.27
Al	.54
Ca	9.4
Mg	.58
Pb	.11
Si	1.38
Hexane Soluble	1.28
Smoke on ignition	None

2. X-Ray Diffraction (Powder Method)

Remarks

$\alpha$ - crist.

$\alpha$ - quartz

FeO

Fe<sub>3</sub>O<sub>4</sub>

VS

$\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

CaCO<sub>3</sub>

Tr.

ZnCO<sub>3</sub>

Fe<sub>4</sub>(Fe CN<sub>6</sub>)<sub>3</sub>

Zn(CN)<sub>2</sub>

---

S - Strong

M - Moderate

W - Weak

Tr. - Trace

+ - Present

3. X-Ray Diffraction (Diffractometer)

Mo-K<sub>α</sub> Radiation

2θ	height	Ni (holder) 4-850	Magnetite 11-614	Stishovite SiO <sub>2</sub> 15-26	Zinc sulfite hydrate 11-281	Wustite Iron-Oxide FeO 6-615	ZnFe <sub>2</sub> O <sub>4</sub> 1-1108	ZnFe <sub>2</sub> S 1-1108
13.7	1.5		2.966 (70)	2.96 (100)	2.99		2.97 (25)	
15.1	1.5				2.67			
16.15	13		2.53 (100)			2	2.53 (100)	2.54 (100)
16.4	12					2.49 (20)		
19.1	19				2.14	2.15 (100)		
19.9	9.5	2.03	2.09 (70)	1.98 (35)				
23.	5	1.76						
24.2	2		1.71					
25.4	4.5		1.61 (85)					1.62 (70)
27.1	15			1.53 (50)	1.51	1.52 (60)		
27.6	9		1.48 (85)				1.48 (30)	1.49 (30)
31.3	5					1.30 (25)		
33.3	3	1.25				1.24		
37.8	2		1.09 (60)					
38.8	3	1.06				1.08 (15)		
42.2	2.5					0.99 10		
43.4	5					0.96 15		
47.8	3	0.88						

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## CONCLUSIONS

The following conclusions resulted from the chemical study of H<sub>2</sub>S removal.

- Iodine titration is the easiest way to measure the amount of H<sub>2</sub>S both in gas phase or liquid phase, provided there is no interference. The major interferences are CO, CO<sub>2</sub>, SO<sub>2</sub>, unsaturated hydrocarbon, . . . . and HCN.
- EDTA Titration and Gas Chromatography proved to be effective devices to measure the amount of H<sub>2</sub>S in liquid phase and gas phase even if there are interferences existing.
- Ammonia solution is a very good H<sub>2</sub>S absorption medium and white water is not. The conc. of ammonia should be somewhere around 8 percent.
- Boiling perhaps is the best way to recycle ammonia and H<sub>2</sub>S and decompose the polysulfide and recover sulfur.
- Magnetite is a good catalyst to assist air to oxidize the H<sub>2</sub>S.