Item #15

Reports by Mr. Kenike dated Dec. 29, 1931 on
"The Combustion of H_2S to S by Means of a Claus Kiln"

and by Dr. Hanisch, dated January 11, 1933 on
"Experiments Carried Out with the Aim to Recover Elementary Sulphur from Gases with a Low Content of Hydrogen Sulfide"

The Combustion of H_2S to S by Means of a Claus Kiln

The low reaction temperatures of 450°C. which have been observed when H_2S is burned with a deficiency of air to elementary sulphur and water vapor using a bauxite catalyst and a Claus kiln, are very surprising. The theoretical combustion temperature should be as high as 1800°C. The low actual temperature can be explained only by heat losses due to radiation.

A rough calculation was performed in order to determine whether the actual temperatures can be explained by the above mentioned heat losses due to radiation. The calculation confirms the presumption and shows that the theoretical calculated radiation losses are in compliance with the known heat losses in practice.

It can therefore be expected that if such a design of a kiln is employed which removes the heat of reaction more efficiently by a properly designed cooling system, the size of the kiln will become smaller or the output of a given kiln can be substantially increased. The fact is, however, that the catalyst allows the application of a higher output.

Method of Calculation

According to Dr. Legeber-Bremmitz a Claus kiln for a daily a production of 3 tons of elementary sulphur requires a volume of 30 cu. m. (compare sketch 1)

3 tons of elementary sulphur correspond with.

$$1000 \times \frac{3 \times 24.4}{32} = 2{,}300 \text{ cu. m. } H_2S$$

1 cu. m. H_2S + $\frac{1}{2}$ cu. m. O_2 = 1 cu. m. H_2O + 1.31 kg. sulphur + 2200 k. cal. Heat of reaction per hour = $\frac{2{,}300 \times 2{,}200}{24}$ = 210,000 kg. cal./hr

Since the process is carried out at a temperature of 450°C. it is to be assumed that the gases in the catalyst bed have a temperature of 450°C. too.

Heat content of the flue gases at 450°C:
1 cu. m. H_2S + 2.5 cu. m. air = 3 cu. m. of flue gases with 33% H_2O.

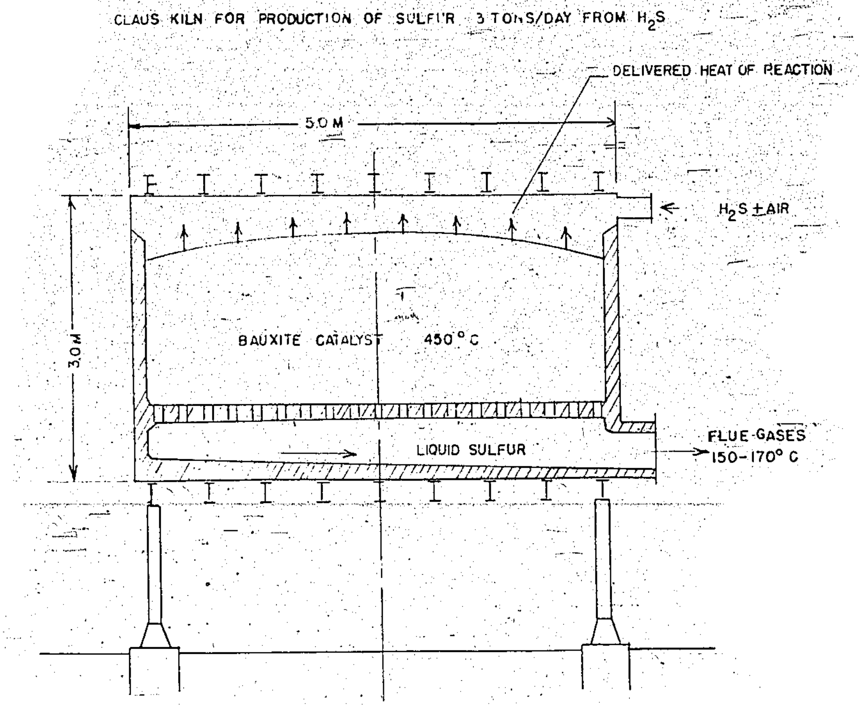
Heat content of the flue gases:
$\frac{2300 \times 450 \times 3.0 \times 0.34}{24}$ = 45,000 kg. cal./hr.

Heat of fusion of the sulphur and sensible heat in the sulphur present = 11,000 kg. cal./hr.

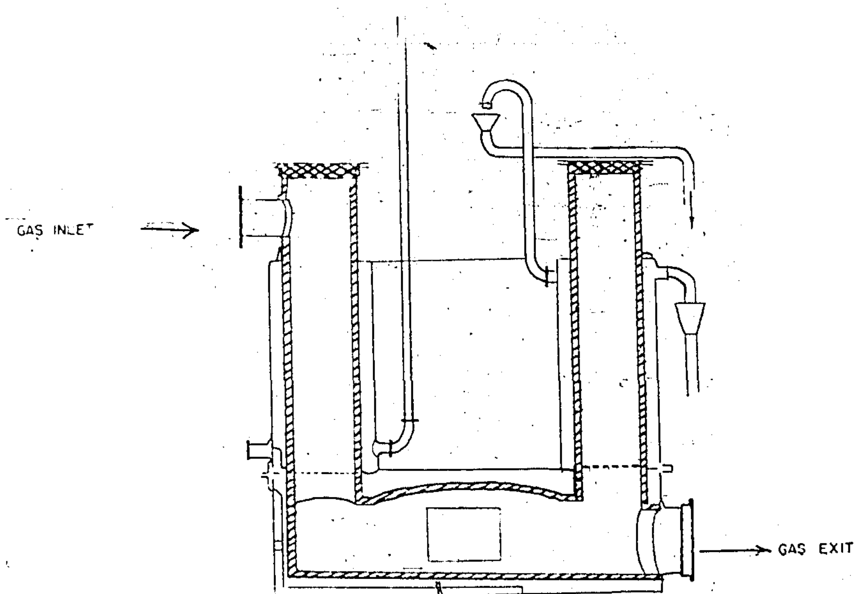
Heat of reaction which must be carried away by radiation
210,000-11,000-45,000 = 154,000 kg.cal./hr.

Surface of the brick-lined oven-mantle above the grate = 25m^2

Heat losses due to radiation approx. 25 x 1000 = 25,000 kg. cal./hr.



SKETCH I



SKETCH NO. 2

WATER COOLED CLAUS KILN

Heat losses of the unlined cupola:
154,000-25,000 = 129,000 kg. cal./hr.

Surface area of the unlined ceilings and of the unlined mantle is approx. 27 m^2. The surface area is enlarged by the girders, which support the brickwork. This enlargement is supposed to be approx. 30%, resulting in an actual area of 35 m^2 which is responsible for the heat losses due to radiation.
Heat losses per M^2 surface area:

$$\frac{129,000}{35} = 3,700 \text{ kg. cal./m}^2\text{/hr.}$$

The heat units are transferred from the surface area of the catalyst to the cover of the kiln. With a catalyst temperature of 450°C. the temperature of the mantle should be approxl 350°C. if the total amount of heat is transferred to the surrounding air. Assume a temperature of the air of 15°C. the coefficient of the heat transmission from the walls to the air must be a = 10; this is an absolutely normal value.

The flue gases leave the zone of reaction at a temperature of 450°C. and the kiln at 150°C. The surface area underneath the grate is approx. 36 m^2. By being cooled from 450°C. to 150°C. the flue gases deliver 31,000 kg. cal./hr. The heat loses per m^2 surface area are 860 kg. cal/m^2/hr. in that part of the reactor. The value is quite normal. The calculation shows that the performance of the claus-process depends on a large surface area of the kiln.

It can therefore be expected that, should the catalyst allow a higher velocity of the reaction, with a more efficient cooling of the catalyst bed the kiln could be of considerable smaller design or the output of a given size of the kiln could be inceeased. The cooling can be performed either by a water or a steam jacket or tube-kilns can be employed. Provision, however, must be made so that the temperature of the cooled walls is higher than the dew point of the gases (approx. 70°C.) in order to prevent corrosion by sulfurous acid. If iron is employed corrosion can be expected by sulfur vapors even if the temperatures are higher than those of the dew point of the gases. Aluminum is resistant against the influence of sulphur vapors or of condensed SO_2.

The attached sketch #2 shows the design of a Claus kiln which is equipped with a water cooled system.

Experiments Carried Out with the Aim to Recover Elementary Sulfur from Gases with a Low Content of Hydrogen Sulfide

The utilization of the waste gases, which are recovered by the desulphurization of the waste water of the Winkler-producers is carried out in such a manner, that it is added to the power gas in order to use its calorific value. Since the desulphurization experiments have shown that the H_2S-content of the waste gases can be considerably high under certain conditions--12-18% H_2S besides 4-10% H_2-- it seems to be possible to recover elementary sulfur by a partial combustion of the gases. (Compare experiments for the recovery of the sulfide-sulfur from the waste water of the Winkler producers). The experiments were carried out in a quartz tube of 20 mm diameter which was filled with granulated Bauxite as used in the factory for the production of catalytic hydrogen. In the beginning the volume of the catalyst was 200 ccm but a volume of 400 ccm. was applied for experiment #4 and the following. The tube was fixed in a vertical electrically heated furnace.

The gas mixture is prepared in a gasholder which has a capacity of 1 m^3 and the inside of which is coated with Sedraping. CO_2 and H_2 is furnished by high pressure cylinders, whereas the H_2S is prepared in a Kipp-apparatus. Since the sealing water continually extracts H_2S and CO_2 from the gas mixture, the H_2S and H_2-content of the gas to be converted was supposed to be equal to the experimentally determined content before the admixture of the air. The deposited elementary sulphur was recovered by a Woulf-bottle heated by a glycerine bath, later on the bottle was replaced by a beaker. A high percentage of the sulfur however was deposited as fine flocks at such places where as a result of more efficient cooling of the gases, the reaction water has been condensed. Due to such losses the compilation of a sulfur balance was not possible.

As soon as it was experienced that no considerable reaction took place between H_2S and CO_2 in the cold part of the condensing apparatus, gas samples were directly drawn from the sulfur recovering container. Tests 13 and 14 were performed in order to find whether a dry electrostatic precipitation of the sulfur particles carried by the gas is possible. For that purpose an electrostatic filter which had a diameter of 70 mm and was enveloped by an electric heating coil was arranged behind the sulfur recovering container and operated with 30,000 volts at a gas temperature of approx. 140°C. Neither a considerable sulfur precipitation nor a reaction between H_2S and CO_2 could be observed. The recovered sulfur was of a dark color caused by carried-over catalyst particles shortly after a fresh catalyst was applied, but showed a light yellow color after a short period of time. Its purity was not determined. At the end of an experiment, the catalyst was found to be coated with a black coal-like substance, but carbon could not be found by analysis.

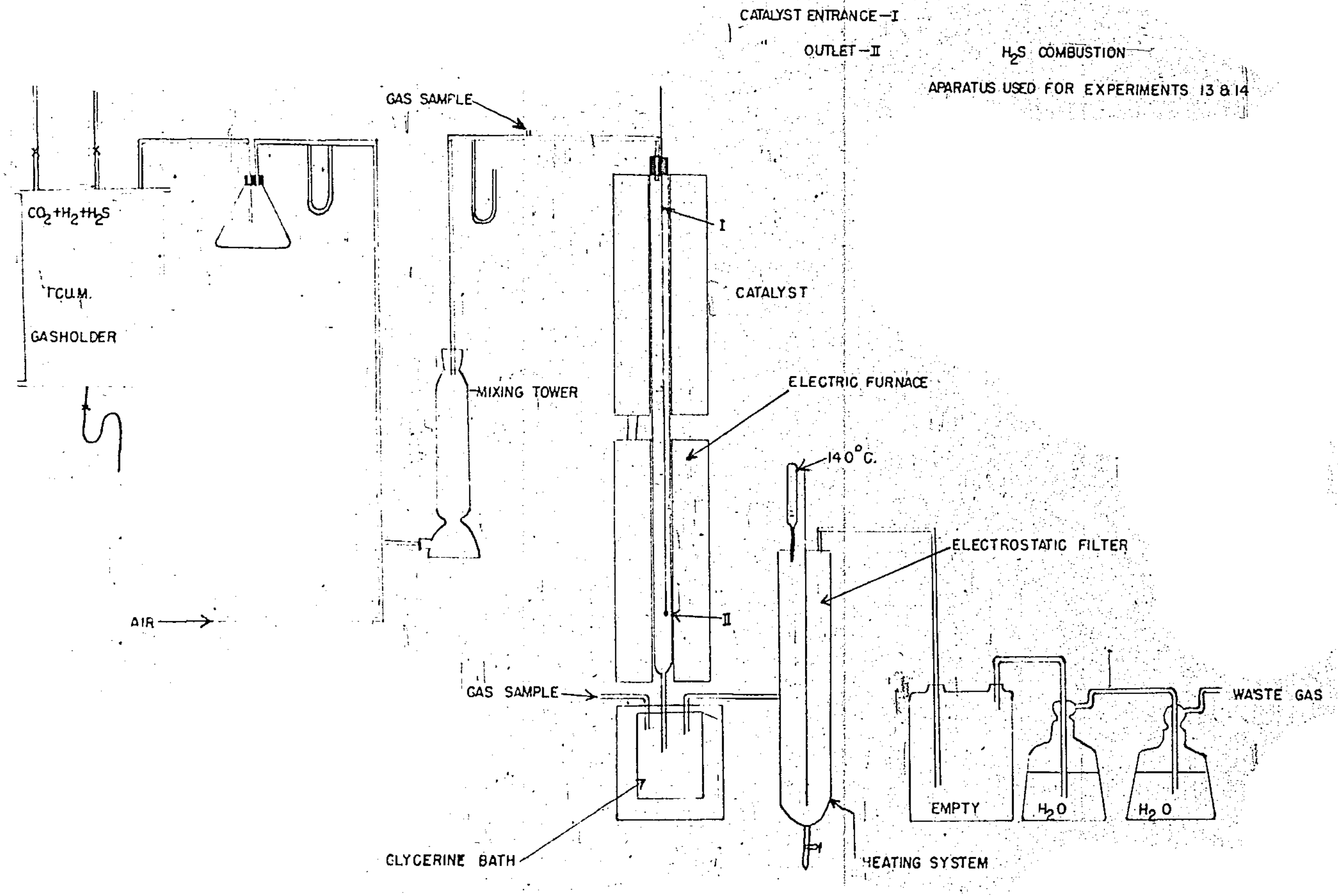
Tables 1 and 2 contain the results of the experiments. The numbers of the experiments represent the experiments of 1 day whereas the letters indicate the alterations which in most cases comprised 1-2 hours. Beginning with experiment 13 no hydrogen was added, the hydrogen (2-3%) which was present in the gas was formed during the preparation of the H_2S in the Kipp-apparatus.

The result of the experiments is as follows:

1. It is possible to recover elementary sulfur from gases which contain 10-15% H_2S besides more or less H_2 by a partial combustion with air and the application of a catalyst.

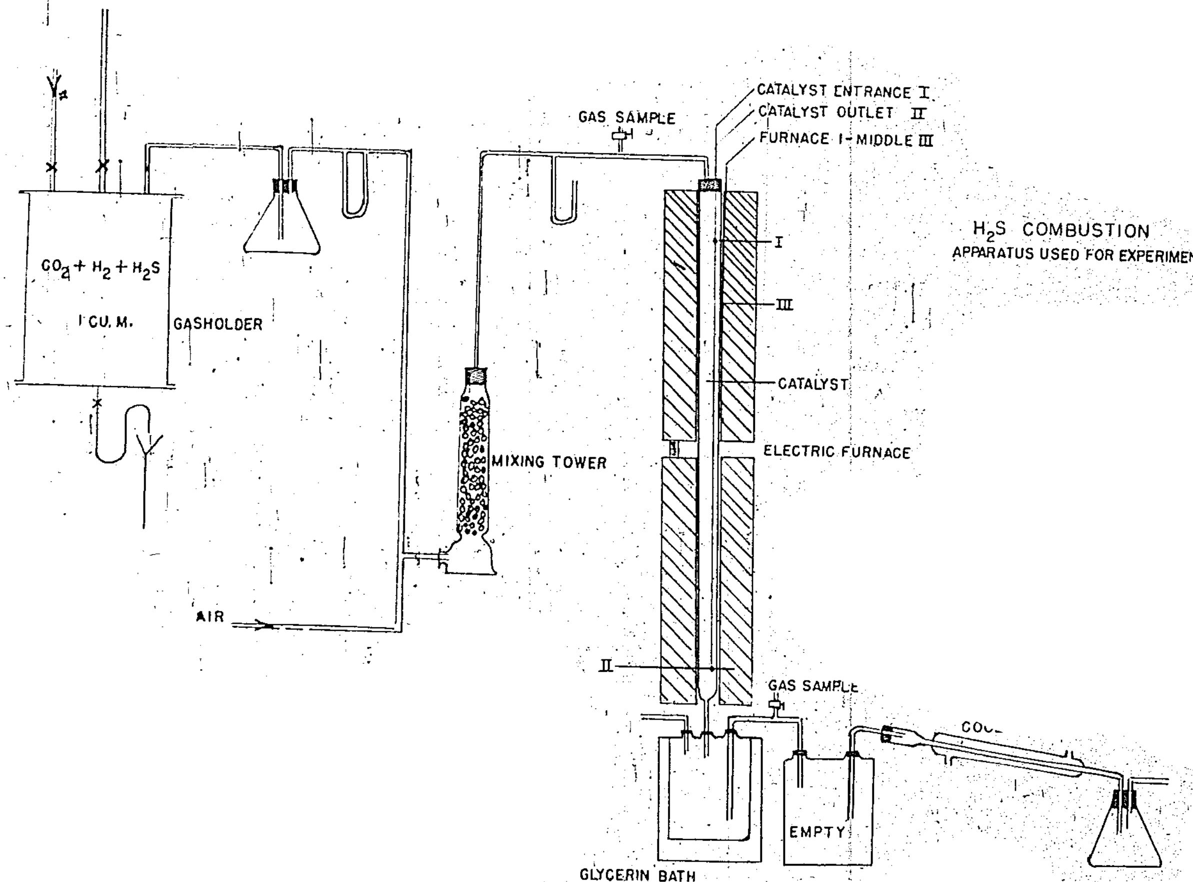
2. The lower the temperature of reaction the better the reaction and the precipitation of the sulfur. Reaction times below 3 sec. are possible. The temperature of reaction could be influenced by a more or less compensation of the heat losses by heating the quartz tube.

3. The efficiency of the process was as high as 98-99% calculated on the introduced sulfur, whereby not more than 2 g. S(H_2S + SO_2) remained in the waste gas.



H_2S COMBUSTION
APPARATUS USED FOR EXPERIMENTS 13 & 14

740



H_2S COMBUSTION
APPARATUS USED FOR EXPERIMENTS

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Table I and II

Experiment No.	Temperature Oven Before °C	After °C	Middle °C	Rates Gas l/hr.	Air l/hr.	Time of React. sec.	Crude gas H_2S %	H_2 %	Waste gas H_2S %	SO_2 %
1	460	410	455	68	26	1.5	8.0	?	0000	
2	500	400	485	31	13	3.2	12.2	11.6	13.3	5.[illegible]
3	410	310	395	31	13	3.2	10.9	17.3	45.0	4.[illegible]
4	435	345	405	31	13	5.8	14.4	16.6	56.0	6.[illegible]
5a	455	335	400	68	26	2.7	6.3	18.0	19.7	7.[illegible]
5b	440	320	400	68	26	2.7	13.9	18.4	66.0	13.[illegible]
5c	465	285	400	68	29.5	2.9	13.9	18.4	38.0	36.5
6	395	395	365	52	20	3.5	18.0	19.2	185	36.2
7	400	235	365	52	20	3.5	10.3	12.8	104	9.7
8a	430	320	400	52	23	3.4	14.5	11.4	85.5	14.6
8b	430	310	400	52	26	3.2			73.0	12.0
8c	435	310	400	52	30	3.1			40.0	10.0
8d	440	305	405	52	35	2.9			23.0	2.0
8e	440	305	405	52	40	2.8			15.0	3.0
9a	435	305	405	52	223	3.4			105	0.0
9b	445	305	405	52	30	3.1			72.0	4.0
9c	450	290	405	52	35	2.9	11.0	13.4	31.0	0.0
9d	460	280	405	52	40	2.8			12.5	0.0
9e	470	280	405	52	45	2.6			7.0	0.0
10a	420	285	365	52	45	2.6			3.5	40.[illegible]
10b	430	235	355	52	40	3.0	11.6	11.8	5.5	19.[illegible]
11	400	240	320	52	40	3.2	14.7	9.0	10.8	16.[illegible]
12a	380	255	310	52	40	3.2			5.9	28.[illegible]
12b	400	225	310	52	36	3.3	13.4	7.2	8.5	7.[illegible]
12c	375	185	300	31	31	4.8	13.0	9.6	6.6	29.[illegible]
13a	405	395	440	32	33	3.0		-	21.5	30.0
13b	425	395	450	32	38	2.8		-	18.6	38.2
13d	405	395	460	32	16	4.1	20.8	-	3.2	62.0
13d	365	395	455	32	12	4.5		-	10.6	10.3
14a	325	375	410	32	12	4.8	15.0	-	22.6	7.1
14b	335	350	400	32	14	4.6	13.2	-	9.5	12.7
15a	245	335	355	32	14.5	4.9	13.0	-	3.0	36.5
15b	300	345	365	32	10.0	5.3	13.0	-	2.8	10.1
15c	300	340	365	32	9.0	5.4	12.4	-	10.5	5.[illegible]
15d	300	340	365	32	10.0	5.3	12.4	-	12.5	4.5
16a	270	285	315	32	10.0	5.7		-	20.7	4.6
16b	265	275	310	32	12.5	5.4	11.5	-	15.2	4.[illegible]
16c	265	270	310	32	13.5	5.3		-	6.2	4.[illegible]
17a	235	265	270	32	13.5	5.6	15.4	-	6.3	2.[illegible]
17b	225	210	-	32	16.0	6.2	15.6	-	4.1	4.6
17c	230	180	230	32	14.5	6.1	15.6	-	1.2	7.5
17d	235	185	235	32	13.5	6.2	15.6	-	1.5	2.5
17e	230	185	230	32	14.5	6.1	13.3	-	9.0	6.0
17f	195	145	200	32	16.0	6.2	13.3	-	1.8	0.7
18a	150	155	200	45	22.0	4.4		-	1.6	4.2
18b	165	140	205	45	20.0	4.5	14.0	-	0.7	1.1
18c	175	145	235	60	26.0	3.2		3.6	1.1	4.5
18d	170	155	255	60	26.0	2.8	12.4	-	1.6	0.2