

REMOVAL OF HYDROGEN SULPHIDE FROM COKE OVEN GAS

BY THE STRETFORD PROCESS

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The removal of hydrogen sulphide from coke oven and other manufactured gases has been practised in many ways over the years. When these gases were first used for lighting and other purposes it was found that the sulphur dioxide and trioxide formed on combustion of the hydrogen sulphide contained in them were air pollutants that attacked paint, vegetation, rubber and synthetic fibers and caused discomfort to humans. Laws limiting the allowable concentration of hydrogen sulphide in manufactured gas were passed in England in 1860. These laws have been tightened as the years have gone on until now the hydrogen sulphide specification calls for a maximum of 0.5 grains per 100 cubic feet. With the advent of the use of natural gas most manufactured gas plants were shut down and coke oven gas produced in steel mill facilities was used without the hydrogen sulphide being removed in operations unaffected by the sulphur dioxide in the products of combustion. However, with coal now increasing in sulphur content and air pollution restrictions becoming more stringent, the steel industry is again considering ways of reducing the hydrogen sulphide content of the gas.

All coking coals contain sulphur compounds but the percentage of sulphur may vary from 0.3% to 3.0% or more. The amount and distribution of the sulphur compounds formed on carbonization will depend upon a number of factors including: (1) types and amount of sulphur compounds in the coal, (2) characteristics of the ash content of the coal and (3) conditions during carbonization including moisture content of the coal, temperature and time of contact between the gases and the hot coke. However, on an average 25 - 30% of the sulphur in the coal forms hydrogen sulphide in the gas and the amount present expressed in grains per 100 cubic feet is usually about 365 times the percentage of the sulphur in the coal. Hence, with a coal mix containing 0.8% sulphur the anticipated hydrogen sulphide content would be 296 grains per 100 cubic feet or 0.5% by volume.

Hydrogen Sulphide Removal Processes

The removal of hydrogen sulphide from coke oven gases has been practised with or without the recovery of the sulphur in a number of ways, but on this continent primarily by the iron oxide, Seaboard and Thylox processes.

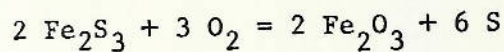
Iron Oxide Process In the iron oxide process the gas is passed through chambers or "boxes" in which there are one, two or three layers of wood shavings impregnated with hydrated iron oxide. A number of the boxes are employed in a unit and are valved so that the gas can pass through them in different sequences depending upon the sulphur

removing capability of each individual box. For example, No. 1 box would become fouled and have to be taken out of service. The gas would then go through 2 - 3 - 4 until the purifying material in No. 1 box was replaced and then the sequence would be 2 - 3 - 4 - 1.

The removal of the hydrogen sulphide is accomplished thus:



When the material is fouled to the extent that it is no longer effective it is removed and oxidized in the air:



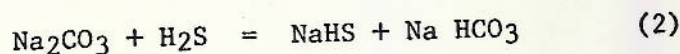
After a few revivifications the free sulphur in the material builds up to a level that makes it no longer practical to reuse it. Some revivification in place is accomplished by introducing enough air in the incoming gas to give a 0.5% concentration of oxygen in the outgoing gas.

While the process does give good hydrogen sulphide removal it has the following disadvantages:

1. No sulphur is recovered,
2. Changing the boxes is a time consuming, expensive job,
3. Spent oxide is difficult to dispose of, and
4. The area required for the boxes themselves and for storage of new and revivified material is considerable.

This process was used at Dofasco for a number of years when the hydrogen sulphide loading of the gas to the oxide boxes was about 75 grains because most of the hydrogen sulphide was being removed at a once-through final cooler not preceded by ammonia removal equipment. When it became necessary to remove the ammonia to reduce water pollution we knew that, with a hydrogen sulphide loading of 275 grains, we could no longer utilize the oxide boxes because of space limitations, but must go to another method.

Seaboard Process One process that was considered was the Seaboard process which utilizes soda ash as an absorbent and air as the desorbent. In this process gas enters a packed tower counter-currently to a stream of 3 - 3.5% sodium carbonate and the following reactions take place:



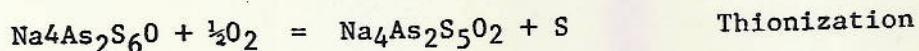
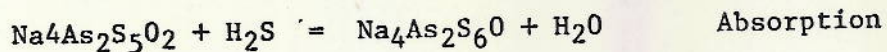
When the solution is blown with air in the bottom half of the same tower the second reaction is reversed and the H_2S liberated.

An efficiency of 80 - 85% can be obtained with one tower and 99% with two towers in series. However, the process has disadvantages that preclude its use under today's air and water pollution control requirements:

1. The hydrogen sulphide removed from the gas is blown into the air.
2. The hydrogen cyanide present in the gas is converted to sodium thiocyanate and some hydrogen sulphide is converted to sodium thiosulphate. The build up of these salts in the circulating liquor requires the dumping of the solution on a regular basis.

Thylox Process We also considered the Thylox process which has had wide use on this continent and in Europe. It is another liquid system in which hydrogen sulphide is removed from the gas and elemental sulphur is recovered. The gas is scrubbed with a weak solution of sodium thioarsenate at a pH of 7.5 - 8.0 in an absorber tower and the foul

solution blown with air in a Thionizing tower. There are several chemical reactions, but the principal ones are thought to be:



The sulphur froth produced flows to a sludge tank and then to a filter and autoclave. An efficiency of about 98% is obtained.

We rejected this process because:

1. High capital cost.
2. High cost of reagents.
3. Necessity of discarding solution due to formation of sodium thiocyanate and sodium thiosulphate.
4. Arsenate solutions are toxic and not particularly stable.

Stretford Process Because of the deficiencies of these and other liquid purification processes we looked further and finally chose the Stretford process which had been developed in the Stretford Laboratory by the North West Gas Board and the Clayton Analine Co. of England and sold in Canada by the Gas Machinery Co. It promised to remove the hydrogen sulphide at a high efficiency rate using water soluble, stable, non-toxic chemicals.

The gas flow through the Coal Chemicals plant is shown in Sketch No. 1. After indirect primary coolers, exhausers and detarrers the gas enters the hydrogen cyanide tower in which the hydrogen cyanide content of the gas is reduced by about 85 - 90%. The gas then passes through ammonia removal saturators, direct primary coolers and benzol washers before entering the two hydrogen sulphide towers in parallel. In these towers the hydrogen sulphide content of the gas is reduced from 275 grains per 100 cubic feet to less than one grain. The purified gas then goes to the boosters for pressurization of 10 p.s.i. and distribution throughout the steel mill. The plant is designed for a through-put of 28,000,000 cubic feet of gas per day. In a construction program now under way, which will increase the through-put to 42,000,000 cubic feet per day, additional hydrogen cyanide removal and Stretford process equipment is being installed as well as a final gas washer, which will be between the hydrogen sulphide towers and the boosters and will remove any chemical carry-over from the towers.

The flow diagram for the Stretford Plant is shown in Sketch No. 2. The two hydrogen sulphide towers (A) are 12'-0" diameter x 97'-0" high fabricated of mild steel. The bottom 24 feet of each tower is a delay tank from which the circulating liquor overflows to an oxidizing tank. Between the delay section and the packed section of the tower is a space of 4'. The inlet gas enters at this level. The packed section of the tower consists of four tiers of wooden grids each 11'-7" deep. A 2'-9" space is provided between tiers to assist in better distribution of the down-flowing liquor. This liquor is introduced at the top through eight low pressure spray nozzles extending below the gas outlet connection. The nozzles are designed to give an even distribution of the liquor over the top tier of grids without causing a spray that would aggravate the carry-over situation. The sprays are fed from a manifold on top of the tower accessible from a platform. A mist eliminator is located in front of the gas discharge nozzle. Each tower is designed to accommodate a gas flow of 600,000 cubic feet per hour.

The Stretford liquor is pumped from the pumping tank (B) to the top of the tower by centrifugal pumps (C) which have a capacity of 90,000 I.G.P.H. against a head of 100 feet. Two pumps are normally used - one for each tower - and the third one is maintained as a spare. The piping arrangement will permit the spare pump to be operated in place of either of the other two regular pumps.

The liquor leaving the towers passes through solution heaters (D) into oxidizers (E) - one for each tower. In the heaters which are equipped with stainless steel steam

coils, the temperature is brought to the desired level of 70 - 90°F. The oxidizers are 20'0" dia. x 24'0" high, fabricated of mild steel and internally coated on the bottom and sides with an epoxy resin. The liquor entering the tank is distributed over the bottom below the air diffusers and flows from the tank at a height to maintain a liquor depth of 20'-0". The sulphur froth released from the liquor by the air from the diffusers overflows an adjustable wier into the sludge tank (F).

On top of each oxidizer tank is an air manifold to which are connected 24 diffusers. The diffusers are mild steel inverted cylinders open at the bottom and with a stainless steel perforated top. The pipes connecting the diffusers to the manifold are jacketed at the top ten feet to prevent corrosion. Half inch diameter rods extend through these pipes to the floor of the tank to keep the diffusers in position and to allow for the removal and replacement of them when the tank is in operation.

The air manifold is fed with air by two positive displacement type blowers (G) each capable of compressing 60,000 c.f.h. They are driven by 100 H.P. motors. A third blower is connected to the blower discharge manifold as a spare.

The desulphurized solution from the oxidizers flows into a 18'-0" diameter x 24'-0" high pumping tank (B) fabricated of mild steel. To the conical bottom of this tank is connected the pipe leading to the inlet manifold of the Stretford solution pumps at the hydrogen sulphide towers. Connections are also provided to receive liquor from the slurry tank and the vacuum filters.

The sulphur froth, which contains about 5 - 10% sulphur, flows from the two oxidizers through stainless steel chutes into a 16'-0" diameter x 24'-0" high mild steel slurry tank (F). The slurry is pumped from the bottom of this tank to the vacuum filters by two 2,000 I.G.P.H. Moyno pumps.

The two vacuum filters (H) are C.E.E. rotary type with string discharge. Each has a filtering surface of 150 square feet and is capable of filtering the daily production of sulphur in about 8 hours. An inlet trough agitator is provided to keep the slurry in suspension and the drum drive is adjustable over a considerable range of speeds so that the proper cake depth can be maintained. Water sprays are used to wash the solution out of the cake in the filtering cycle. The filtrate and wash water flows back to the pumping tank and the filter cake falls into one of the two autoclaves through a tilting chute.

In the thermally insulated stainless steel autoclaves (I) the filter cake is brought up to a temperature of 130°C by internal and external steam coils containing steam at 50 p.s.i. desuperheated to 140°C. At this temperature the sulphur is melted and collects in the bottom of the autoclave. The liquid sulphur is discharged into an underground concrete sulphur holding tank (J) through steam jacketed valves and discharge pipe and the water is discharged into the sewer.

The sulphur is maintained in the liquid state in the holding tank by means of steam coils and pumped into sulphur tank trucks for shipment.

Hydrogen Cyanide Removal

The hydrogen cyanide removal step is not an integral part of the Stretford process but is a necessary adjunct if the gas to be processed contains hydrogen cyanide as all coke oven gas does. The reason for this will be explained later in the paper.

The removal is accomplished in a mild steel tower 14'-0" diameter x 55'-0" high. The bottom 10 feet of the tower serves as a reservoir for the scrubbing liquor. The reservoir has an inverted conical bottom with a bottom outlet connection for liquor flow to the circulating pumps and a valved drain connection. Just above the normal liquor level is a 36" gas inlet connection. A similar gas outlet connection equipped with a mist eliminator is provided at the top of the tower.

The tower contains two tiers of wooden slat packing each 12 feet deep.

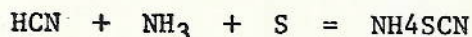
The scrubbing liquor is pumped by one of two 60,000 I.G.P.H. centrifugal pumps driven by 40 H.P. motors. The liquor enters the tower below the gas outlet connection through six low pressure spray nozzles which are designed, as the ones in the hydrogen sulphide towers, to give even distribution with a minimum of spray.

The circulating liquor is a suspension of water and filter cake from the discharge of the rotary filters which has been collected in an autoclave and pumped to the hydrogen cyanide tower by a Moyno reagent pump. The suspension is pumped into the tower, flows down through the packing and collects in the conical bottom. The entering gas which contains hydrogen cyanide, ammonia and hydrogen sulphide passes through the descending liquor and ammonium thiocyanate is formed. Actually the chemical reaction is in two steps with the sulphur reacting with the ammonia in the presence of hydrogen sulphide to form ammonium polysulphide which reacts with the hydrogen cyanide to form the ammonium thiocyanate. About every four hours a portion of the circulating liquor is discarded and more sulphur and water is added to maintain the proper volume of liquor.

The ammonium thiocyanate concentration of the discarded liquor is 10 - 20%. Originally it was intended that this liquor would be disposed of by spraying it on the incandescent coke in the near-by quencher station. Facilities were provided to pump the liquor to a holding tank and then automatically add it to the coke before the water quenching started. With 150 ovens pushed per day and the volume of liquor to be disposed of amounting to about 4,000 gallons per day the volume added per quench was not to be large and the delay in starting the quench was to be kept to a minimum. However, the plan had to be abandoned because the steam coming from the coke on the wharf had a very disagreeable odor and the condensate falling to the ground from the steam coming from the quencher station was highly corrosive.

Other means are currently being considered for the disposal of this effluent because the water pollution authorities will not tolerate the continual disposal of an effluent of this composition into the sewer system. The methods being considered include: (1) separation of the contained chemical compounds and (2) thermal destruction in an incinerator with cooling of the evolved products of combustion and collection of the solids in bag filters. Any of these processes promises to be expensive to build and operate and to offer little in the way of monetary return.

The hydrogen cyanide removal process is also expensive because of the chemicals necessary to remove the gas. From the formula:



it can be seen that every 27 pounds of hydrogen cyanide removed required 32 pounds of sulphur and 17 pounds of ammonia. In addition to this not all of the sulphur reacts with the hydrogen cyanide and is carried out in suspension in the discarded effluent. The operation considerably reduces the sulphur available to sell as a credit for the operation of the Stretford Plant.

Stretford Process Chemistry

The Stretford solution circulated over the hydrogen sulphide towers is made up of a number of chemicals:

1. Anthraquinone-disulphonic acid 2:7 (A.D.A.) - A dye industry byproduct manufactured in England. The 2:7 isomer is used rather than the 2:6 because of its greater solubility and reactivity with hydrogen sulphide and vanadium. A concentration of M/120 is used.
2. Sodium ammonium vanadate - In preparation of the solution the ammonia is evolved and sodium meta vanadate, NaVO_3 , is in solution. A concentration of M/60 is used.

3. Sodium citrate - Used to prevent formation of a complex vanadium-oxygen-sulphur compound precipitate that removes vanadium from solution. A concentration of M/60 is used.
4. Bellosol (Kalex OH) - A sequestering agent used to form a complex with any iron present and prevent it from combining with the citrate. A concentration of 2,700 ppm is used.
5. Caustic soda - Reacts with the carbon dioxide in the gas to form sodium carbonate. The total alkalinity is maintained at 30 g/l as carbonate.

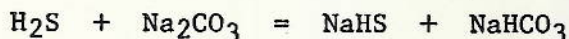
The solution is prepared in batches in a reagent tank and thoroughly oxidized in an oxidizing tank before being used.

The overall reaction of the Stretford process is the atmospheric oxidation of hydrogen sulphide to sulphur:

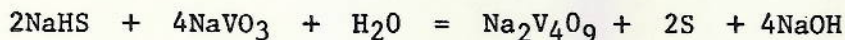


However, this reaction may be considered as taking place in several steps:

1. Reaction of the hydrogen sulphide with the alkali:



2. In the reaction tank of the hydrogen sulphide tower the hydrogen sulphide reacts with the vanadium:

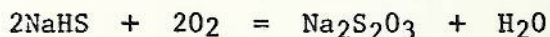


3. Also in the reaction tank the reduced vanadium is reoxidized by the ADA:



4. In the oxidizer the reduced ADA is reoxidized and the precipitated sulphur is driven to the top of the solution and leaves as a froth.

It would appear that if sufficient air is added and the alkalinity is maintained at the proper level that the solution could be effective indefinitely. However, that is not the case because of the formation of dissolved solids that finally build up to such a level that they interfere with the reactions. These solids are primarily sodium thiocyanate and sodium thiosulphate. Any hydrogen cyanide left in the gas after the hydrogen cyanide tower is absorbed in the alkaline Stretford solution and reacts with the sulphur present to form sodium thiocyanate, and any NaHS not reacting with the vanadate in the reaction tank is carried to the oxidizer and reacts with the oxygen there:



There are two choices - either to dump a portion of the solution daily when the concentration of the dissolved solids reach about 25% or to continue to use the solution until the concentration reaches about 40% and then change the entire solution. We have used the latter method despite the obvious disadvantage of having a period of time while the solution in one tower and one oxidizer is changed that the concentration of hydrogen sulphide in the exit gas will be considerably higher than desired.

The disposal of this discarded effluent is a problem in the same manner as it is in the disposal of the hydrogen cyanide tower effluent. The volume is considerably less - 150,000 gallons every 6-9 months instead of 4,000 gallons/day - but the concentration of the undesirable material is higher. In the past we have disposed of the effluent in the same way that it is disposed of in all other Stretford plants we know of - by putting it in the sewer, but that method of disposal is no longer acceptable. As soon as techniques and equipment are ready it will be disposed of by incineration or further chemical treatment.

Cost of Operation

An estimate of the direct cost of operating the plant is as follows:

Chemicals	\$0.007	per 1000 cu. ft. gas treated
Power	.003	
Steam and other utilities	.0005	
Manpower		
Operations	.003	
Chemical laboratory	.0008	
Supervision	.001	
Maintenance	<u>.002</u>	
	\$0.0173	

To this cost must be added the capital cost of the plant, and cost of spare and replacement parts, major maintenance items and disposal of the effluents, and from it can be subtracted the value of the sulphur produced. Because of a number of factors no attempt is made in this paper to present an estimate of the actual total cost per 1,000 cubic feet of gas treated.

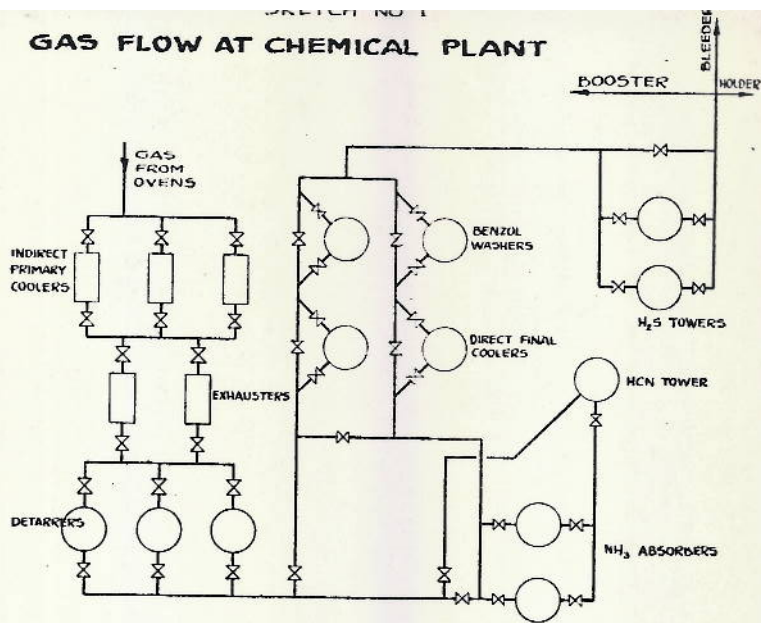
Conclusions

The costs indicated above are unquestionably high but so are other air and water pollution costs today. We have no operating costs of other liquid purification system such as the Thlox process that would be acceptable to air management authorities so we can not give comparative economic evaluation of the Stretford Process. However, it does do a good job in removing hydrogen sulphide from the gas and it does have a relatively low capital cost. It may find application at other plants such as ours where a low hydrogen sulphide concentration in coke oven gas is a necessity.

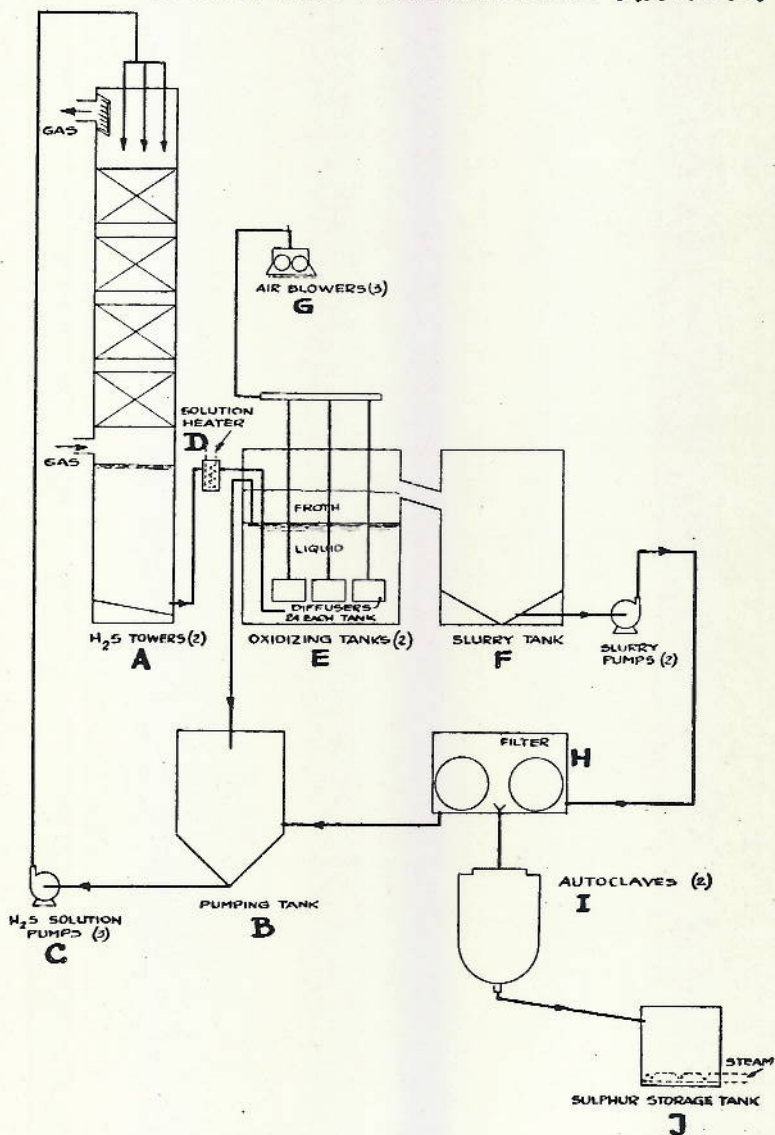
References

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2. Peter Ellwood "Meta Vanadates Scrub Manufactured Gas" Chemical Engineering, July 20, 1964, pp 128-130
3. Nicklin, T. and Brunner, E - "Hydrogen Sulphide Removal by the Stretford Liquid Purification Process" Paper presented at the 98th Annual General Meeting of the Institution of Gas Engineers, May 1961

GAS FLOW AT CHEMICAL PLANT



SKETCH NO 2
STRETFORD PROCESS FLOW DIAGRAM



DISCUSSION

D. E. BLACK

SUPERINTENDENT

DONNER-HANNA COKE CORPORATION

I would like to congratulate Mr. Ludberg on his informative review of Hydrogen Sulfide Removal by the Stretford Process.

Donner-Hanna has used a hot-actification process installation for over fourteen years for removal of sulfur from the gas stream. This installation consistently gives sulfur removal efficiencies of 90% or better. Its maintenance is minimal and operation relatively trouble-free in that it requires only minor attention and relatively few operational adjustments once it is "on the line" and a proper range of flows and temperatures is established.

The unit uses steam jets to establish its vacuum, and these are less troublesome than the average vacuum pump even though they require condenser capacity. Heat for the unit is recovered from the steam jets and from flushing liquor passed through heat exchangers before it is returned to the ovens.

This unit has handled up to 30 million cubic feet of gas per day and is currently handling 22 to 26 million cubic feet per day. Sodium carbonate addition for this unit averages about 200 pounds per day.

Solution disposal problems are minimal. Effective control of oven charging and maintenance of gas suction piping keeps oxygen to a low level in the gas stream and therefore the formation of sodium thiocyanate and thiosulfates in the carbonate solution is low.

There is an interesting study of the so-called "Ping-Pong Effect" in this review. Ammonia removal for water pollution control necessitated additional sulfur removal capacity. The sulfur removal by the Stretford Process required a cyanide scrubber. The cyanide scrubber and the Stretford Process both present solution disposal problems. This is something most of us have run into at one time or another -- the trading of one problem for another, "Ping-Pong Effect".

Each of these problems has a monetary value attached to it, and the challenge is for us as operators and engineers to solve these problems in a self-sustaining or profitmaking way. In the future, in an increasing number of cases, this will not be possible.

has answered many of our questions in pointing out its strengths and shortcomings from his operating experience. It demonstrates a one-step technique for sulfur removal from the gas stream into a saleable product. I am sure this process will receive close investigation by many of you.