TECHNICAL SUPPORT DOCUMENT FOR THE RECOMMENDED LOWEST ACHIEVABLE EMISSION RATE FOR SO$_2$ EMISSIONS FROM COKE–OVEN GAS COMBUSTION

TECHNICAL SUPPORT DOCUMENT FOR THE RECOMMENDED

LOWEST ACHIEVABLE EMISSION RATE FOR SO_2 EMISSIONS

FROM COKE-OVEN GAS COMBUSTION

Prepared by the U.S. Environmental Protection Agency,
Division of Stationary Source Enforcement

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Section I. INTRODUCTION

This document presents a description of technology for the desulfurization of coke oven gas. It is intended to provide guidance to EPA technical staff and policy makers in the implementation of significant deterioration and new source review policies of EPA. The information is also intended to be useful in the development, revision, or the enforcement of existing State Implementation Plan (SIP) standards. This document has been prepared in conjunction with an Office of Enforcement memorandum, "Guidance for Establishing the Lowest Achievable Emission Rate for SO_2 from the Combustion of Coke-Oven Gas, January 5, 1977."

EPA has not yet developed a New Source Performance Standard (NSPS) for this source category.

Coke-oven gas (COG) is produced during the coking of metallurgical coal in by-product coke ovens. As a result of the coking process a fraction of the sulfur contained in this coal (25-30%) is transferred to COG in the form of hydrogen sulfide (H_2S), carbon disulfide (CS_2), and carbonyl sulfur (COS). Upon subsequent combustion these gases release SO_2 to the ambient air. It is the purpose of COG desulfurization systems to reduce the amount of SO_2 emitted to the ambient air by the removal of sulfur compounds from COG prior to combustion.

COG principally consist of hydrogen and light hydrocarbons, as illustrated in Table 1. Depending upon its exact composition, which in turn depends upon coal analysis and coke oven operation, COG has a heating value of 500-560 Btu/scf and an average molecular weight of about 10. Very importantly it typically has a sulfur content of 250-600 gr H_2S/100 dscf and 5-25 gr/dscf of total

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TABLE 1

COKE OVEN GAS ANALYSIS

Component	Range, %	Mean, %
Hydrogen	55.83-59.69	57.69
Methane	24.28-26.94	25.40
Nitrogen	4.52- 8.94	6.67
Carbon Monoxide	3.78- 5.24	4.25
Ethylene	2.01- 2.31	2.16
Carbon Dioxide	1.58- 2.02	1.72
Ethane	0.68- 0.82	0.76
Oxygen	0.38- 0.87	0.59
Hydrogen Sulfide	0.38- 0.59	0.43
Benzene	0.01- 0.19	0.11
Propylene	0.12- 0.17	0.14
Propane	0.06- 0.12	0.08
Acetylene	0.04- 0.10	0.08
Naphthalene	0.00- 0.02	0.01
Carbonyl Sulfide	0.006	0.006
Carbon Disulfide	0.0009	0.0009
Hydrogen Cyanide	0.008- 0.12	0.10
Argon	traces	traces

organic sulfur (the sum of RSH, COS, & CS_2). One useful rule of thumb is that the H_2S concentration in COG, expressed in gr/100 dscf, is approximately 365 x %S in coal[1]. The volume of COG produced in the coking process is in the range 10,000 - 13,000 scf per ton of coal charged[2], again ranging with initial coal volatility and coking practice. Therefore, a coke battery producing 500,000 tons of coke per year (e.g., a four meter tall, 77 oven battery) will produce about 8.6 billion scf of COG annually. SO_2 emissions are in direct proportion to COG consumption. When burned by itself, uncontrolled, coke-oven gas will produce 5.7 - 11.5 tons of SO_2 per 1000 tons of coke pushed at 250-500 gr H_2S/100 dscf, respectively. A 100 tpy SO_2 emission rate from COG combustion is equivalent to coking 8700 tons per year of coal producing COG of 500 gr H_2S 100 dscf or 87,000 tons per year at 50 gr H_2S/ 100 dscf. New coke production in excess of 100,000 tons/year will produce more than 100 tpy SO_2, even within the allowable level of all SIP's in the United States. Hence, even under the most stringent SIP, new coke battery construction is subject to New Source Review LAER criteria in SO_2 non-attainment area.

It should be understood that coke-oven gas is almost never consumed at one point in a coke plant. Where coke batteries are heated (underfired) with COG, typically, only 40-45% of total COG production is needed for this purpose. Distribution to in-plant boilers, steel heating furnaces, open hearth furnaces, COG flairs, and to out-of-plant consumers is the rule. One average distribution for a major steel producer is shown in Figure 2. Therefore, desulfurization is effected at the point of generation by removal of H_2S and organic sulfur. The existence of a distribution system for coke-oven gas poses a
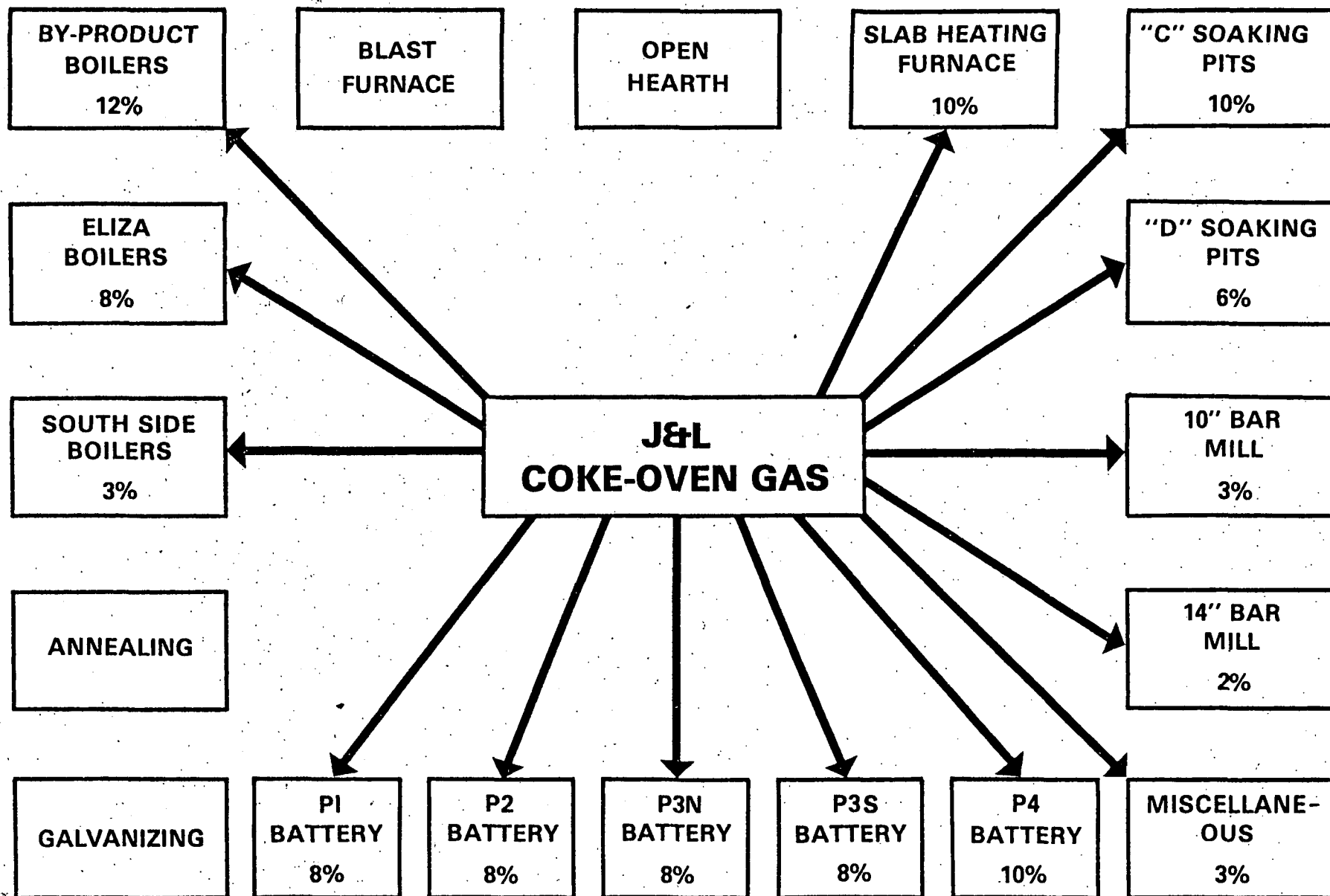
FIGURE 1. 1973-1974 COG DISTRIBUTION OF J&L PITTSBURGH WORKS

complex issue for the EPA regional engineer. At each use point, SIP emissions standards for SO_2 may exist. An industrial boiler may be limited to 1.2 lb $SO_2/10^6$ Btu; a soaking pit to 1000 ppm SO_2. On an average basis then, it is conceptually possible for SO_2 emissions from COG combustion within an integated steel mill to comply with an existing SIP despite the non-existence of a direct COG regulation. Dunlap & Massey[4] note that 500 gr H_2S/100 dscf is approximately equivalent to a 1.3% S coal. Upon combustion in a boiler this fuel will produce about 2 lb $SO_2/10^6$ Btu; when burned in a reheat furnace the waste gas stream will contain approximately 1000 ppm SO_2. However, since all new coke-oven gas will be consumed, the Offset Policy applicability determination shall be made for the total gas volume itself. Each end use stream, of which an integrated mill may have dozens, is not to be separately considered against the 100 tpy criterion.

STATE IMPLEMENTATION PLAN REQUIREMENTS FOR COKE-OVEN GAS DESULFURIZATION

The SIP's for California, Kentucky, Pennsylvania, Ohio, New York, and West Virginia require COG desulfurization. Coke plants are also located in states which do not have SIP's for coke-oven gas. These are Illinois, Indiana, Alabama, Tennessee, Minnesota, Wisconsin, Colorado, Michigan, and Utah. The most stringent SIP standards are shown below:

	COG	TAIL GAS	TOTAL
California	50 gr/100 scf [a]	500 ppm SO_2	∿51 [c]
Pennsylvania	——	——	50 gr/100 scf [b]
Kentucky	10 [a]	2000 ppm SO_2	∿20-35 gr/100 scf [c]
Lorain, Ohio	——	——	35 [b]

(a) H_2S

(b) Total Sulfur

(c) No regulation per se. This is the equivalent total.

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The Kentucky coke-oven gas SIP is apparantly the most stringent in the U.S. However, it applies only to "Priority I" areas, which are defined by the SIP as having (SO_2) ambient levels in excess of 0.04 ppm (annual) and 0.17 ppm (24-hr). The 2000 ppm process emission limit, when applied to acid or Claus plant tail gas implies a sulfur recovery efficiency of 95-98%, depending upon process details. The Kentucky SIP is equivalent to 20-35 gr H_2S/100 dscf of COG produced. To comply with the Kentucky SIP all of the liquid oxidation and absorption methods of Section II are available. High efficiency sulfur recovery is necessary to comply with this regulation if liquid absorption is chosen.

The Pennsylvania SIP regulates total sulfur, as H_2S. Hence, for an organic sulfide level of 15-20 gr/100 scf, this regulation is as stringent in overall allowable SO_2 as the Kentucky SIP. But, the Pennsylvania rule is more flexible in that only the total equivalent SO_2 emission rate is fixed. The rule applies Commonwealth-wide. The Ohio SIP for U.S. Steel, Lorain requires certain process streams to the less than 35 gr "H_2S"/100 dscf overall, including tail gas emissions. This regulation is about as stringent as the Kentucky SIP.

The California SIP is the most stringent with respect to tail gas emissions, requiring 99.5% sulfur yield. In fact, Kaiser Steel chose a liquid oxidation-no tail gas process in order to comply with this rule. The rule allows 50 gr/100 scf of H_2S in the COG and places no organic sulfide limit.

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Section II.   CONTROL TECHNOLOGY

Each of the technologies for coke-oven gas desulfurization involves two separate steps: (1) the removal or stripping of H_2S and related sulfur compounds from the coke-oven gas and (2) the recovery of the stripped compounds as elemental sulfur, sulfuric acid, or ammonium sulfate. Available systems fall into two broad categories: liquid absorption followed by Claus or acid plant sulfur recovery or liquid absorption plus liquid phase oxidation of reduced sulfur gases. Altogether, there are at least six basic technologies commercially available in the U.S. for removing reduced sulfur from coke-oven gas as shown in Table 2. In addition, there exist a number of technologies for recovering this sulfur. Improving the sulfur recovery from both Claus plant tail gas (via tail gas treatment) and sulfuric acid plants must be considered as part of these desulfurization technologies. These processes are shown in Table 3.

A.   LIQUID ABSORPTION TECHNOLOGIES

1.   Vacuum Carbonate Process

This process uses a solution of sodium carbonate to wash countercurrently an upward rising flow of COG in an absorption tower. The absorber removes H_2S, HCN, and CO_2 but not COS or CS_2, from the coke-oven gas. The rich solution is then steam stripped in a second tower, called the actifier, which releases the acid gases overhead and regenerates the lean absorbing solution. In the Vacuum Carbonate process the steam stripping is accomplished under partial vacuum in order to lessen the steam demand. The basic process flowsheet is shown in Figure 2.

Table 2.   COKE OVEN GAS DESULFURIZATION TECHNOLOGIES

STEP 1 - SULFUR REMOVAL	STEP 2 - SULFUR RECOVERY	PRINCIPAL U.S. VENDORS
Liquid Absorption		
Vacuum Carbonate	Claus Process	Koppers Co.
Sulfiban	Sulfur Recovery	Applied Tech. Corp. (BS&B)
	or	
Diamox	Sulfuric Acid Production	Mitsubishi Chemical Industries
Carl Still	Claus, Acid or Stretford	Dravo Corp.
Liquid Oxidation		
Stretford	Elemental Sulfur	Wilputte Corp.
Takahax A,B	Elemental Sulfur	Chemico and/or Nippon Steel
Takahax C,D	Ammonium Sulfate	

Table 3. CLAUS PLANT TAIL GAS TREATMENT TECHNOLOGIES

	SYSTEM CHEMISTRY	VENDOR
SCOT	S and SO_2 hydrogenation, amine absorption to concentrate H_2S, feed to Claus inlet	Shell
IFP - 1	Catalytic conversion of H_2S and SO_2 to elemental sulfur	Institute Francis Petrol
BEAVON	S, SO_2 hydrogenation and COS, CS_2 hydrolysis to H_2S, Stretford sulfur recovery	R. M. Parsons
WELLMAN-LORD	Sulfite/bisulfite absorption and concentration of SO_2	Davy Powergas

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STEAM JET EJECTORS

CLEAN COG
30 gr H_2S/100 SCF

NO. 1
150 psig stm
317,000 lb/DAY

NO. 2
150 psig stm
143,300 lb./DAY

ACID GAS TO
TREATMENT
55-70% H_2S
5-15% HCN
15-18% CO_2
5% H_2 ETC.

VAPOR CONDENSER

INTER CONDENSER

AFTER CONDENSER

(5.7 gal/ton CCAL)

(3.02 gal/ton COAL)

17,200 gal/DAY

H_2S ABSORBER   ACTIFIER

SOUR COG
500 gc H_2S/100 SCF
60 gr HCN/100 SCF

ABSORPTION SOLUTION
BLOWDOWN (QUANTITY
VARIABLE)

TOTAL VACUUM JET
CONDENSER BLOWDOWN
55,400 gal/DAY (CONTAINING
HCH, H_2S, CO_2)

38,200 gal/DAY

FIGURE 2. PROCESS FLOWSHEET: VACUUM CARBONATE PROCESS BASED ON 60 MILLION SCF/DAY COG AND 93 PERCENT SULFUR COLLECTION EFFICIENCY (REFERENCE 18)

GAS
ACID GASES
FOUL SOLUTION
ACTIFIED SOLUTION
CONDENSATES
FLUSHING LIQUOR

GAS OUTLET
MIST SUPPRESSOR
SECONDARY STAGE
PRIMARY STAGE
12
GAS INLET
MAKE UP
TO CRUDE LIQUOR STORAGE

FLUSHING LIQUOR
FLASH SOLUTION
SECONDARY STAGE | PRIMARY STAGE
STEAM
WATER
VENT
WATER
STEAM
NA_2CO_3
CONDENSATE
WATER

STEAM
EJECTOR
EJECTOR
STEAM
ACID GASES T HCN REMOVAL S

ABSORBER
SOLUTION CIRCULATING TANK
PUMPING TANK
FRESH SOLUTION MIXING TANK
SOLUTION COOLER
ACTIFIER
SOLUTION COOLER
FLASH SOL. HEATER
VAPOR CONDENSER
FLUSHING LIQUOR TO FLASH SOL. HEAT EXCHANGER
INTER CONDENSER
AFTER CONDENSER
CONDENSATE TANKS AND PUMPS
VAPOR KNOCK OUT DRUM

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KOPPERS COMPANY, INC
PITTSBURGH PA.
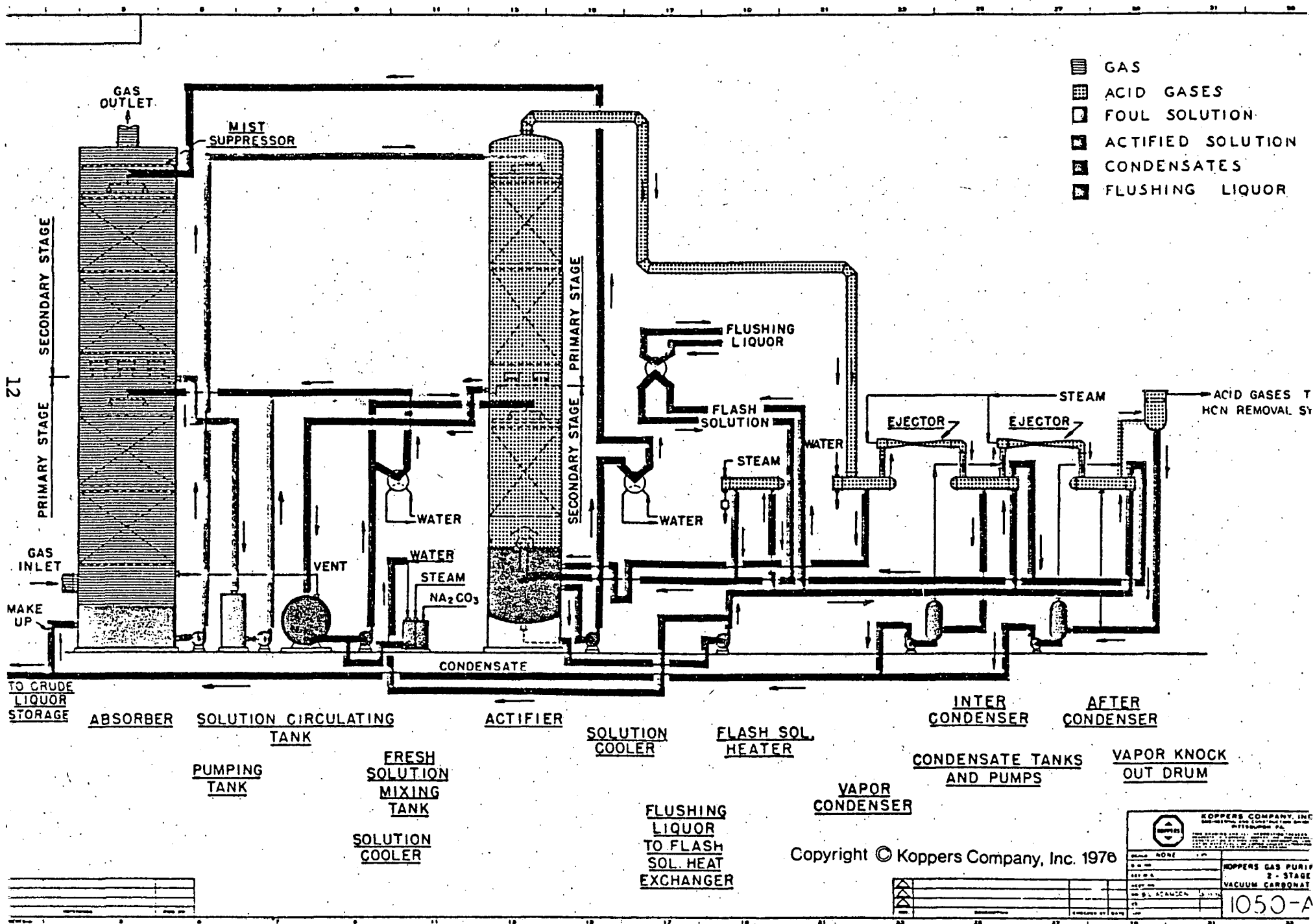KOPPERS GAS PURIF
2 - STAGE
VACUUM CARBONAT
1050-A

FIGURE 3.

Recently, the Koppers Co. has proposed a two stage vacuum carbonate process (Figure 3) which is intended to produce still lower sweet gas levels of H_2S. Koppers maintains that by a double stage H_2S absorber (see Process Appendix) bench scale levels of $\leq$ 10 gr H_2S/100 dscf have been achieved[5]. Koppers is offering this technology to stay competitive in the COG desulfurization field.

The single stage vacuum carbonate process is capable of reducing COG H_2S levels to 30-35 gr/100 dscf[5,6], independent of inlet concentration. Hence, foul gas concentrations of 500 gr/100 dscf will be desulfurized by 93%. However, COG with H_2S concentrations of 250 gr/100 dscf will be desulfurized only 86% to reach the 35 gr/100 scf level. On the other end of the efficiency spectrum, U.S. Steel's Clairton Works produces one H_2S stream containing 2000-4000 gr/100 scf and it is desulfurized $\sim$ 97% by a Vacuum Carbonate plant[7]. Due to these unusually high H_2S inlet levels, the driving force for H_2S absorption at this Clairton Works Vacuum Carbonate plant is correspondingly high.

A number of vacuum carbonate plants, summarized in Table 4, have been constructed over the years, and there is no doubt as to the H_2S removal efficiency or basic reliability of the technology. A major concern for the Vacuum Carbonate process has been HCN - caused corrosion in Claus sulfur recovery plants used in conjunction with the Vacuum Carbonate process[8]. Serious corrosion and catalyst fouling at Burns Harbor and Wierton[5] caused major downtimes at each facility. It is generally recognized now that HCN must be removed from the acid gas stream leaving the still prior to admittance to a Claus plant. In acid plants, however, conversion of H_2S to sulfuric acid may not require HCN

Table 4. VACUUM CARBONATE PLANTS

PLANT	COKE OVEN GAS CAPACITY (MMSCFD)	SULFUR RECOVERY
Bethlehem Steel		
• Burns Harbor	120	Claus Plant, HCN Destruct
• Lackawanna	50	Acid Plant
• Sparrows Point	60	Acid Plant (down now)*
• Bethlehem	X (down)	None for V.C. Plant*
• Johnstown	X (down)	None for V.C. Plant*
National Steel		
• Wierton	70	Claus Plant, HCN water wash
U.S. Steel-Clairton		
• Keystone V.C.	90	Two Claus Plants, HCN
• No. 1 V.C.	60	water washing
Inland Steel	50	Claus, water wash for HCN

*There are or will be Sulfiban-Claus technology at these plants.

removal because HCN combustion in acid plant converters is higher than in Claus sulfur recovery plants. (The first stage in the Claus plant intentionally only partially combusts incoming H_2S to SO_2 so that combustion is really occurring in an oxygen-lean environment. Consequently, HCN will not destruct in the Claus burner.) Section IIB discusses HCN removal techniques in more detail.

For the single stage Vacuum Carbonate process the best coke oven-gas desulfurization produces a clean gas of 30 gr H_2S per 100 dscf of COG produced. No organic sulfur is removed. See Section III for a discussion of organic sulfur in COG. Double absorption Vacuum Carbonate has been shown capable of achieving as low as 10 gr H_2S/100 dscf.

2. The Sulfiban Process

This is a technology developed by Black, Sivalls & Bryson, Inc. and Bethlehem Steel Corporation. Sulfiban is sold by Applied Technology Corporation (ATC), a subsidiary of B.S.& B.

As with Vacuum Carbonate, Sulfiban is a liquid absorption/steam stripping-solution regeneration process. It produces at the outlet of the still column an acid gas rich stream containing H_2S, reduced organic sulfur gases, CO_2, and HCN which must be treated in the same manner as the Vacuum Carbonate acid gas stream. Sulfiban employs an amine absorber solution ($\sim$ 15% monoethanol amine, "MEA") for sulfur removal. Its still column operates at atmospheric pressure.

Due to the formation of certain salts, Sulfiban employs a reclaimer for

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distillation of a side stream of the MEA which is returned to the absorber for salts recovery. As described by Williams and Homberg[9], the key variables in the achievement of sweet gas H_2S levels are still column and reboiler steam rates, absorber solution temperature, and the liquid circulation rate. Figure 4 taken from this reference illustrates the strong dependence on liquid circulation rate of outlet H_2S concentration. It is true of <u>all</u> the liquid absorption processes that the sweet gas H_2S level is a variable; high lean solution acid gas levels and low liquid circulation rates detract from the best achievable levels. The control of these variables allows an operator to lower operating costs. Therefore, continuous monitoring of sweet gas levels will be needed to insure continual emissions performance.

Sulfiban plants have been constructed at three locations in Pennsylvania (see Table 5 for details) with commitments at three other locations. Each of these facilities was brought on stream during 1975-1976, and then brought down because of mechanical start-up problems. These experiences are described in an attachment (see the Process Appendix from the vendor) and are summarized here[10].

<u>Shenango Inc. - Neville Island, Allegheny County</u>

> Purchase order in spring 1973 - Start-up in May 1975 with a spray tower absorber - Conversion to a packed tower absorber by December 1975 to decrease outlet from 30 gr/100 scf to <10 gr/100 scf - Plant taken down in winter 1975-6 for winterizing, installation of recycling cooling water system aimed at increasing still column efficiency (see letter), putting in epoxy lining in still (HCN corrosion protection), and correcting for improper still column tray construction - Scheduled to be on-stream in February 1977.
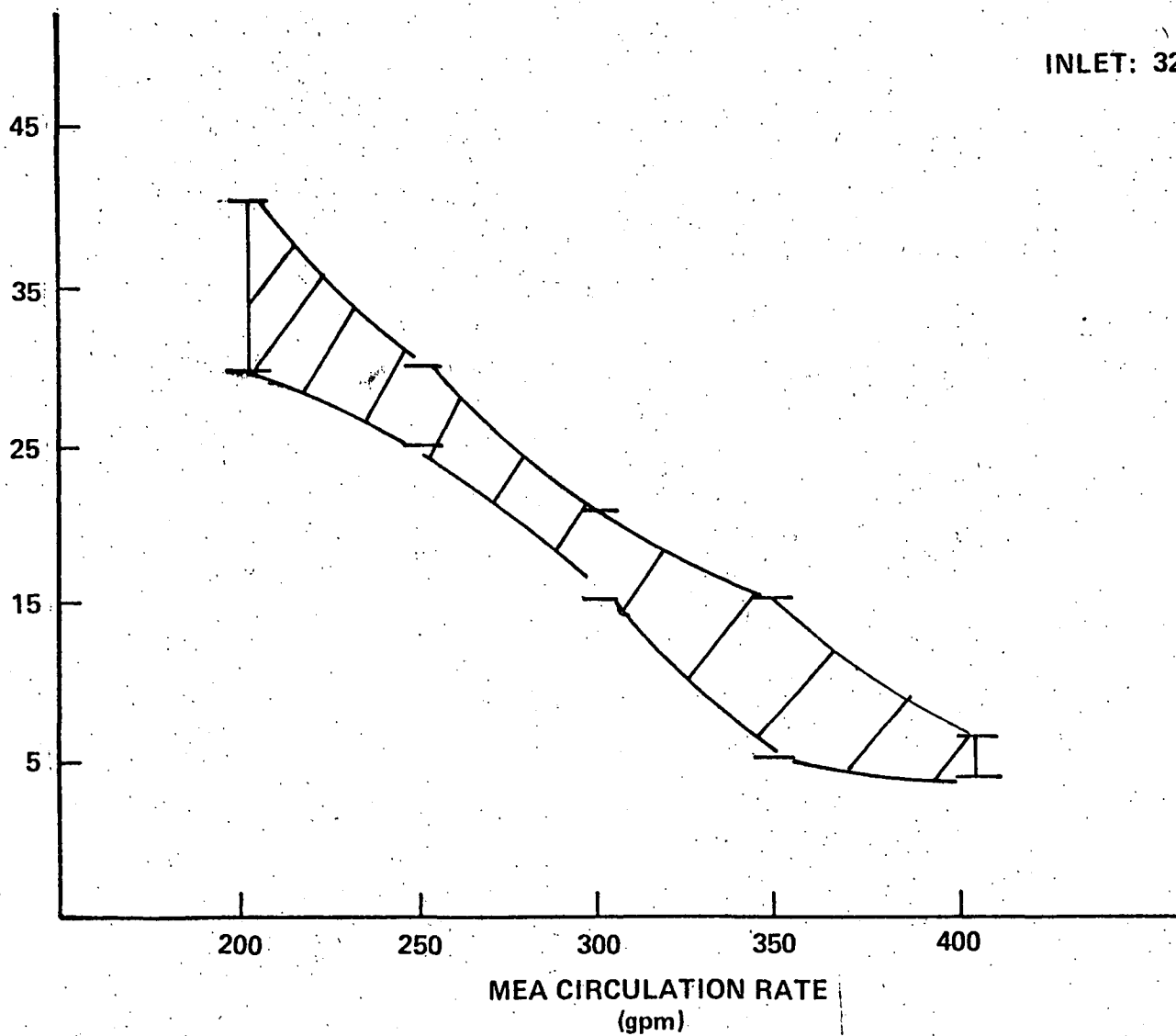
FIG. 4 SULFIBAN PERFORMANCE BSC, BETH.

Table 5.   SULFIBAN PLANTS

PLANT	COKE OVEN GAS CAPACITY	SULFUR RECOVERY
Bethlehem Steel (Bethlehem, PA.)	two, each 60 MMSCFD	3-Stage Claus, HCN Destruct
Jones & Laughlin Steel (Pittsburgh Works)	90 MMSCFD	Single Contact Sulfuric Acid
Shenango Inc. (Pittsburgh, PA.)	32 MMSCFD	3-Stage Claus, HCN Destruct

There are presently commitments for Sulfiban plants at Bethlehem Steel;
Johnstown (two) and Lackawanna.

<u>Bethlehem Steel</u> - <u>Bethlehem, PA.</u>

Started up in August 1975 and operated through March 1976 - Severe corrosion occurred in still column below a stainless-carbon steel weld (the top 16' uses stainless) - Column was entirely replaced with stainless, lined and placed into service in May 1976 - Operated until September 1976 when a mechanical problem in the reboiler (see Process Attachment for explanation of function) occurred - System now in service.

<u>J & L Steel</u> - <u>Pittsburgh Works</u>

System began start-up in October 1975 was partially destroyed by an explosion during welding as the still column - It ran for eight days thereto - Relined, new packing, and scheduled for start-up in March 1977 - Acid plant has not run as of December 31, 1976.

Sulfiban absorption efficiencies have been measured at all three plants as well as at a pilot plant run at Bethlehem's Lackawanna Works. These data are summarized in Figure 4 and Table 6. The important distinction between Sulfiban and other COG desulfurization systems is that the MEA solution removes COS and CS_2 as well H_2S.

The Sulfiban process has been demonstrated to produce 5 gr H_2S per 100 dscf of sweet COG and 2 gr of organic sulfur (as H_2S) per 100 scf of COG[35,10].

3. Carl Still Process

This technology is based upon commercial absorption of H_2S from coke-oven gas, steam stripping of the acid gas, and sulfur recovery by Claus, sulfuric acid or Stretford processes. It was developed by Firma Carl Still of Recklinghausen, West Germany and is marketed in the U.S. by the Dravo Corporation. Two Still/Dravo systems are or have been built in the U.S.

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Table 6.   SULFIBAN PERFORMANCE DATA

PLANT	H₂S* INLET	OUTLET	ORGANIC SULFUR* INLET	OUTLET
Bethlehem (Bethlehem, PA.)	325-375	5 (high MEA) 40 (low MEA)	8	1.2
Jones & Laughlin (Pittsburgh, PA.)	369-416	0.3 - 3	N.D.	N.D.
Shenango (Pittsburgh, PA.)	536-606	8 - 13	N.D.	<100ppm

*Units: gr H_2S/100 dscf

Table 7. STILL/DRAVO PLANTS IN THE UNITED STATES

PLANT	COG CAPACITY	SULFUR RECOVERY
Armco Steel (Middletown, Ohio)	60 MMSCFD	Single Contact Sulfuric Acid
Wheeling-Pittsburgh (Follansbee, West Virginia) (1977 Start-up)	90 MMSCFD	Single Contact Sulfuric Acid
Armco Steel (Ashland, Kentucky)		Proposed to EPA

(see Table 7) and apparently one other is being proposed.

The process flow diagram is shown in Figure 5. Since the process is clearly described in the Still brochure (see Process Attachment) only these additional comments are provided here. NH_3 is the absorbant:

(1) The process is selective for H_2S; it does not remove organic sulfur.

(2) The principal attraction of this process is that it simultaneously treats H_2S in COG and NH_3 waste waters. No additional reagents are needed in this process, for example. Hence new plants particularly may be designed for the Still process.

(3) The basic Still process has many variants. The most important ones are that: (a) The Stretford process can be used to recover sulfur as can a Claus plant. An acid plant is a third option. (b) the process allows for recovery of anhydrous ammonia. While the latter is not of direct interest to the final COG H_2S level, it is useful for the EPA engineer to know that this material is a useful by-product.

(4) Since the Still process description mentions the "USS Phosam" process (ammonium phosphate scrubbing of COG with steam stripping to recover NH_3 and to concentrate NH_3 liquor for H_2S stripping) for recovering anhydrous NH_3, a brief description of this process is provided in the Process Appendix. The Armco-Middletown plant uses Phosam.

Dravo quotes a guaranteed level of 25 gr H_2S/100 scf of COG[11], although Firma Carl Still asserts 10 gr/100 scf is possible[36].

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- all NH3
- 10 – 50 gr/100 scf H2S
- organic   sulfur

H2S, HCN, acid gases
CO2

Sweet COG
½ HCN

NH3 , HCN

CO2

H2S
Abs.

NH3
Abs.

Deacifier

NH3
Still

flush.
liquor

COG.

H2S
CS₂
COS
NH3
Napth.
HCN

Steam

liquor of
NH3
H2S
HCN
CO2
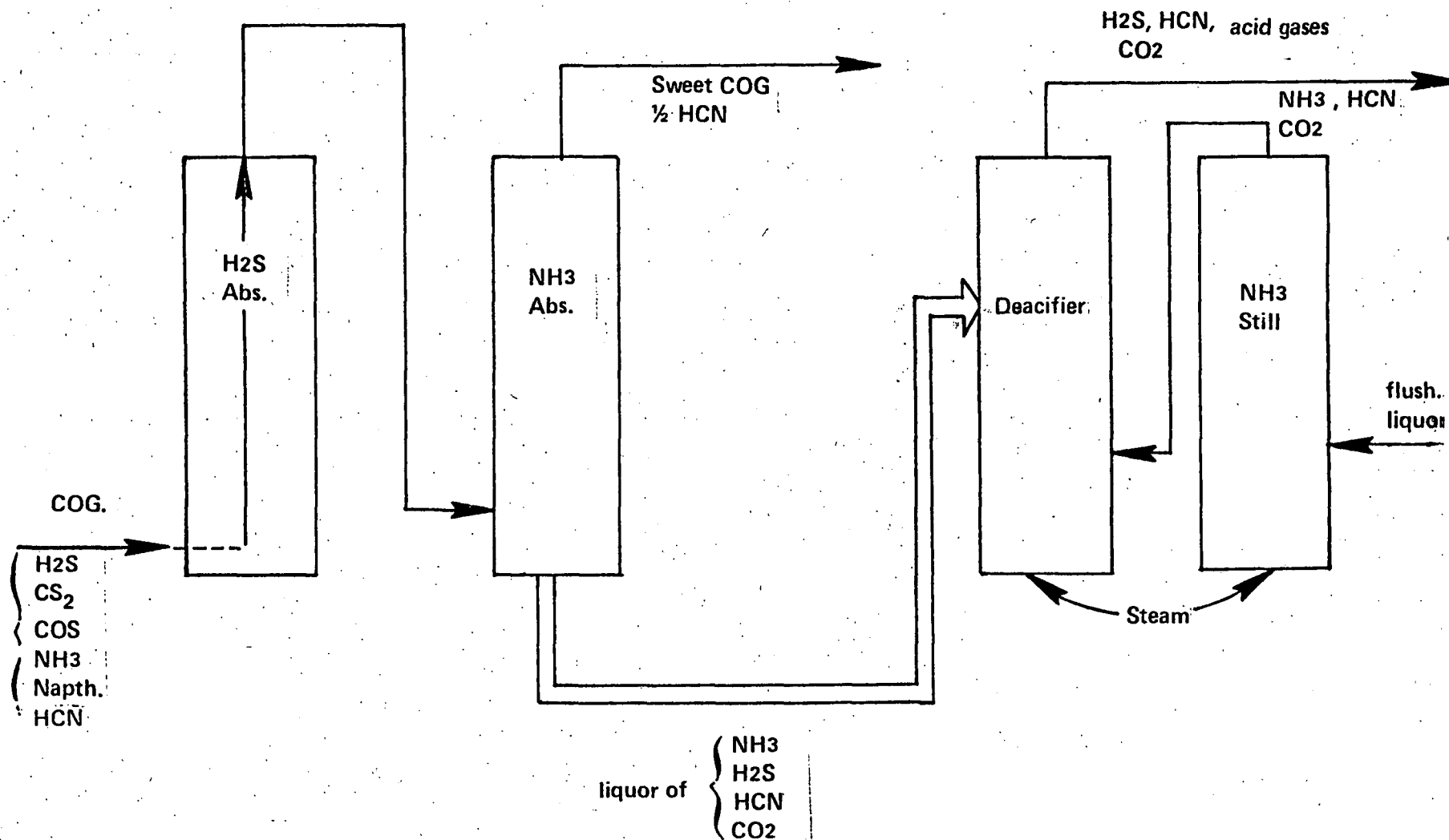
FIGURE 5. STILL—DRAVO PROCESS

The distinction is one of economics not technology[11]. The Armco and Wheeling-Pittsburgh plants are designed to meet an overall 50 gr H_2S/100 scf standard.

(4)   Diamox Process

Diamox is a Japanese developed process (Mitsubishi Chemical Industires, Ltd.). It too is based upon NH_3 absorption of H_2S and liquid regeneration by steam stripping in a still column.

The MCI description in the Process Appendix contains the basic process flowsheet as well as a list of facilities at which the process is operating[12].

MCI published data show H_2S levels in the sweetened COG of less than 10 gr/100 scf[37]. MCI quotes a 97% removal efficiency for a 277 gr/100 scf coke-oven gas[12]. Since, as noted above, absorber efficiency is dependent upon inlet (H_2S) and various process variables, and since we do not have the specifics for the MCI tests (yet) we can only state that Diamox is capable of 10gr H_2S/100 scf.

Diamox will require Claus or acid plant recovery and the comments with respect to these technologies for Sulfiban, Still and Vacuum Carbonate are relevant for Diamox.

B.   SULFUR RECOVERY TECHNOLOGIES

1.   Claus Process for Sulfur Recovery for COG Desulfurization

Claus plants operate on the H_2S rich acid gas produced by the Vacuum Carbonate, Still, Sulfiban, or Diamox absorbers to recovery molten elemental

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sulfur. The process is well known and is described in many articles[20].

A recent EPA publication in support of the proposed refinery Claus NSPS is referenced for a description of Claus technology[13]. The principle difference between Claus plant operation on refinery or natural gas H_2S streams and coke-oven gas acid gas is the presence in the latter of HCN. As stated previously, HCN has created severe Claus plant corrosion problems at Wierton and Burns Harbor. At present, for instance, the Wierton Vacuum Carbonate plant is down due to this effect. Therefore, as previously noted, prior to the acid gas entering the Claus plant.

Two techniques for HCN removal are in use in the U.S. Cold water washing has been employed by Koppers in the 1940's and is utilized by U.S. Steel today at the Clairton Works[14]. Wierton is to install water washing[5,15]. HCN is removed from the gas stream in a tower which takes advantage of the different aqueous solubilities of H_2S and HCN. HCN is then stripped from water solution, along with a small amount of H_2S carry-over. The stripped gases may then be incinerated or recombined with the main clean COG stream. If this latter step is proposed, the sweet underfire COG may have a bit more H_2S than that sampled at the absorber outlet, due to this blending.

A recent development of Bethlehem Steel is the catalytic "HCN destruct reactor." Williams and Homberg and Singleton and Homberg[16] describe this well in the attached articles and further description is not needed here.

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Successful operation has been obtained at the pilot unit at Lackawanna[36] and the full scale units of Shenango and Bethlehem. Scheduled annual downtimes of this catalyst unit are said by the vendor to be in the range 10 days - 2 weeks, which is a serious matter. Parallel cyanide destruct units can avoid this long a downtime by providing an alterate path for the acid gases during catalyst replacement and maintenance periods.

The Dravo Corp. proposes to deal with the Claus-HCN problem by catalytically decomposing the gas in the Claus furnace. According to Hall[18], Dravo's proposal is to completely convert HCN to $N_2 + H_2 + CO$. This broad concept has not yet successfully been implemented at Vacuum Carbonate - Claus installations.

Claus plant sulfur yields determine the sulfur content of the Claus gas emission. Typically, two thirds of sulfur entering the Claus plant burner is recovered as elemental sulfur in the burner stage, with increasingly lesser yields obtained in the subsequent catalytic recovery reactors. As shown in Williams and Homberg, even with four catalytic stages a portion of the incoming sulfur is emitted to the atmosphere as a tail gas. However, practical Claus plant yields are closer to 96%. This was the stated design target of Shenango and Bethlehem for average long term operation. Yields as high as 99$^+$% are quoted for very carefully controlled Claus plant design and operation, but such has yet to be achieved in stable operation[20] and not for COG-derived H_2S feeds. Hence, for practical purposes, 4% of input total reduced sulfur (TRS) should be taken to be the lowest non-treated tail gas performance attainable for standard Claus plants. That is, at most 96% of input sulfur should be considered recoverable as elemental sulfur.

In terms of emissions, this is equivalent to 0.083 lb. SO_2 from the Claus plant incinerator* per pound of sulfur recovered. In terms of concentration, SO_2 is found in the range 5,000-20,000 ppm. The exact concentration is a function of the concentration of H_2S in the Claus plant feed and amount of fuel used by the incinerator. For a plant recovering 95% of input sulfur before the incinerator, for example, a requirement for 500 ppm SO_2 in the Claus tail gas** requires an overall yield of 95% $+\frac{9500}{10,000}$ (5%) = 99.7%.

Claus tail gas emissions can be treated to reduce substantially the amount of SO_2 that is emitted to the atmosphere. Description of these tail gas treatment processes and their performance levels are contained in a standard support document recently published by EPA's OAQPS in support of the Claus sulfur recovery plant proposed standard (F.R. October 4, 1976) for petroleum refinery applications. The reader is referred to this SSEIS[13] for an exposition of details of system chemistry and application.

Briefly, three of these processes are described in the following:

(a) SCOT (Shell Claus Off-Gas Treatment)

The Claus tail gas composition is SO_2, H_2S, and some S vapor. SCOT first hydrogenates this stream to H_2S with H_2 from sweetened COG. H_2S is then concentrated in an amine absorber/stripper system. (See the Process Appendix for more details). The concentrated H_2S is then fed to the main COG absorber or to the Claus plant inlet. SCOT went on-stream at U.S. Steel,

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*At close to optimal yield the tail gas to the incinerator consists of a 2:1 ratio of H_2S:SO_2. A small amount of S vapor also is contained in the incinerator feed. After combustion of course, SO_2 is the dominant species.

**The California SIP requires this at present[21].

Clairton in 1975. Figure 6 shows the Clairton flowsheet relevant to SCOT; note that Claus yields increase from 95% to 99.9%. EPA test data for SCOT (see SSEIS) confirm this capability.

(b) Beavon Process

The Beavon process also converts Claus tail gas to H_2S. SO_2 is hydrogenated, as per SCOT. COS and CS_2 are catalytically hydrolyzed ($CS_2 + 2H_2O \rightarrow 2H_2S + CO_2$; $COS + H_2O \rightarrow H_2O + CO_2$). H_2S is then recovered in a Stretford plant. Beavon is a development of the Ralph M. Parsons Co., Los Angeles, California. Performance levels are discussed in the Claus plant SSEIS.

(c) Institute Francis Petrol (IFP)

Beavon and SCOT are commercially available <u>reduction</u> <u>processes</u>. Other tail gas treatment (TGT) processes, by IFP, are available. TGT-1500 produces a 1500 ppm total sulfur gas stream and is commercially available. TGT-150 (150 ppm) has yet to be commercially proven. The reader is referred to the SSEIS [13] and to the Process Appendix to this document for process descriptions. Note that reduction to 1500 ppm will provide an overall 99.2% recovery in the example cited above.

(d) Wellman-Lord

This is an oxidation process, well known in the FGD field. Wellman-Lord produces SO_2 as an off-gas by means of a sulfite/bisulfite absorber-stripper system. The output from the W-L is an SO_2 stream which can be either combined
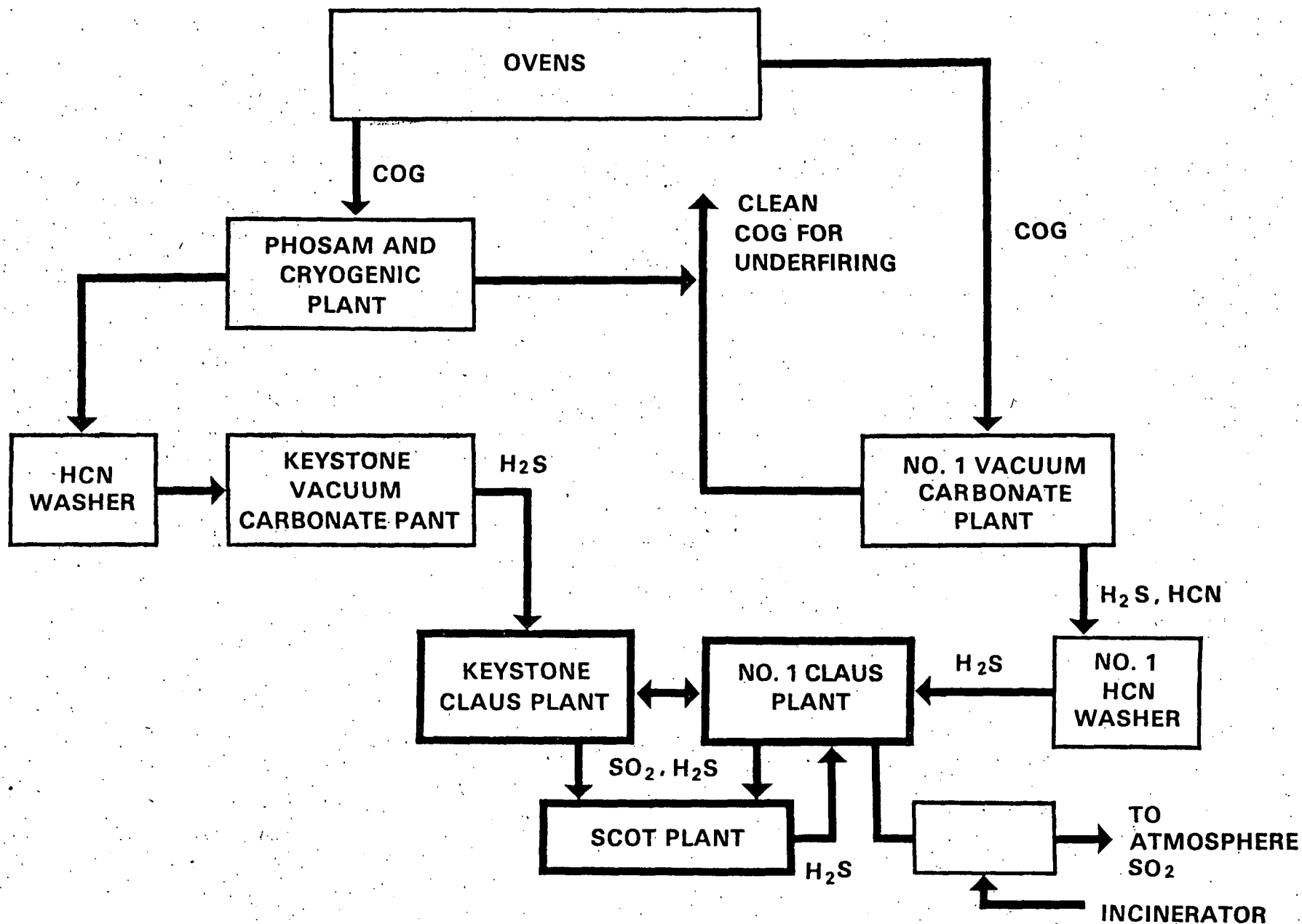
FIGURE 6. U.S. STEEL, CLAIRTON WORKS FLOW SHEET

with the sweetened COG* or recovered as H_2SO_4 in an acid plant.

Since an acid plant probably would not exist at a coke plant using Claus recovery, recycling of the SO_2 to the Claus burner is another option. In the example of the footnote on this page, 2690 lb SO_2/day would be available for a Wellman-Lord tail gas system. The main Claus burner combusts one third of incoming H_2S to SO_2 to initiate the Claus reaction. In this example, (26,890/3) X 2 = 17926 lb SO_2/day are so produced. The Wellman-Lord unit would supply 15% of this need.

Performance levels for Claus tail gas treatment increase Claus yields from 95%-96% to 99.5[+]%. This performance level is documented in the above referenced SSEIS. The October 4, 1976 F.R. proposes this performance level directly for new refinery-based Claus plants. This standard for reduction-based tail gas treatment is 0.025% (250 ppm) SO_2 on a dry no-O_2 basis. This level, implies a 99.9% yield for a straight Claus/96% efficiency plant producing tail gas with a concentration of 10,000 ppm as explained above.

In summary, for tail gas Claus treatment, EPA has found that technology is available to produce tail gases of less than 0.5% of Claus sulfur input.

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*For example, assume that a 50mm scfd, 410 $\frac{gr\ H_2S}{100\ scf}$ COG is desulfurized to 10 gr H_2S in the clean gas, producing $(\frac{400}{7000} \times \frac{50 \times 10^6}{100} \times \frac{32}{34})$ or 26,890 lb S/day Claus recovery. At 95% yield, 25,545 lb/d will be recovered, leaving 1345 lb/day of sulfur as a tail gas. This is equivalent to (1345 x $\frac{34}{32}$ x 7000) or 10 x 10^6 gr/day of H_2S equivalent. Added to the sweet COG, this will increase its equivalent H_2S concnetration from 10 to 10+$(\frac{10 \times 10^6}{50 \times 10^4})$ = 30 gr equivalent H_2S/100 scf of COG produced.

2.   Sulfuric Acid Recovery

The major alternative for sulfur recovery is the production of sulfuric acid.   Tables 4, 5, and 7 indicate this was the process used by Bethlehem Steel, J & L, and Armco for Vacuum Carbonate, Sulfiban and Still stripping.

The reader is referred to other descriptions of the basic contact acid process and its capabilities.[22] The major point is that sulfuric acid production involves a tail gas stream.   Single absorption, single contact acid plants easily produce a 97% recovery of inlet S[22].   Only single absorption has been purchased for COG applications and in fact the new J & L plant is designed for 97% efficiency.   One vendor[11] noted that double contact plants were not being marketed to the steel industry because of competitive forces between liquid absorption and liquid oxidation technologies.

However, the double contact, double absorption process is commercially available for the production of sulfuric acid and offers significantly greater yields and hence lower tail gas emissions of SO_2.   EPA's NSPS, 4 lb SO_2/ton acid, is equivalent to 99.7% sulfur recovery.   A process description of double absorption is contained in the Process Appendix.   Approximately 35 such plants exist in the U.S.[23]

The key technical issue is whether this is attainable on H_2S from COG.   Since no applications have occurred, the direct demonstration has yet to be made.   However, the sole difference for an inlet H_2S stream as compared to S or SO_2 is that water is formed in combustion of the H_2S to SO_2.   This water can be removed in a preliminary drying tower prior to contacting the SO_2.   Alternatively, a "wet" acid plant can be designed to accept this water as

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is done for the production of acid from spent acid feeds which contain hydro-carbons. The technical availability of the double absorption process for coke plant feeds is not an issue for Monsanto, Allied Chemical and other designers[24]. As compared to single absorption plants of the same size (the median American coke plant will produce ∿ 40 tpd acid) capital cost differentials are about 15%-20% or $2.5MM vs. $2.0MM).

Emission rates from double absorption sulfuric acid recovery are at least 99.7% yield or 4 lb SO_2/ton of acid produced as compared to 97% for single absorption. Therefore, double absorption offers as effective a way of reducing tail gas emissions as does Claus plant tail gas treatment technology. The choice of method can be allowed to be one of plant economics and not limited by the inherent emissions effectiveness of Claus + TGT vs. double absorption acid recovery. It is also quite clear that the lowest technically achievable overall SO_2 emission rates will require one or the other process combination for the liquid absorption processes.*

C. LIQUID OXIDATION PROCESSES

These processes differ from the liquid absorption processes described above in that once H_2S is absorbed, it is oxidized to sulfur or ammonium sulfate in the liquid phase. The separate Claus or sulfuric acid steps are avoided and therefore no tail gas problem need be faced. On the other hand, a difficult

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*It is noted that Firma Coal Still suggests that recovery via Stretford is an option. Stretford produces no tail gas.

liquid effluent problem is created in the form of thiosulfate and thiocynate salts, which are not present in the liquid absorption processes to the same degree.

Two processes have been investigated by DSSE, the Stretford Process by the North West Gas Board of the U.K. and the Takahax Process of Nippon Steel Corp. Two other processes, Fumax, a Japanese process, and Giammarco Vetrocoke, a German process involving an arsenic solution, have not been studied due to time pressures. Basic process descriptions of the Stretford and Takahax processes are provided in the Process Appendix.

1. Stretford Process

The Stretford process produces elemental sulfur from H_2S in COG. It does not remove organic sulfur. At present, there is one application in North America, located at the coke plant of Dominion Foundary & Steel Company (Dofasco) of Hamilton, Ontario (42mm scfd). Dofasco is building additional coking capacity (a new No. 6 Battery, 6m wet coal, by Didier) and has ordered a second Stretford plant to handle the extra COG.

The Stretford process absorbs H_2S in a packed tower in a solution of sodium carbonate, sodium ammonium vanadate, and ADA (anthraquinone disulfuric acid). The process flow diagram is shown in Figure 7. In the absorber, HS is oxidized to S and vanadium is reduced from V^{+5} to V^{+4}. The oxidizer system allows V^{+4} to be reoxidized to V^{+5} by the reduction of ADA. In turn, ADA is reoxidized by air pumped into the oxidizer tank. Elemental sulfur is removed and the Stretford liquor is recirculated to the absorber.

PRODUCT
GAS ←

SULPHUR FOAM TO PURIFICATION

FEED
GAS →

AIR
OXIDIZER

H₂S ABSORBER

PUMPING TANK
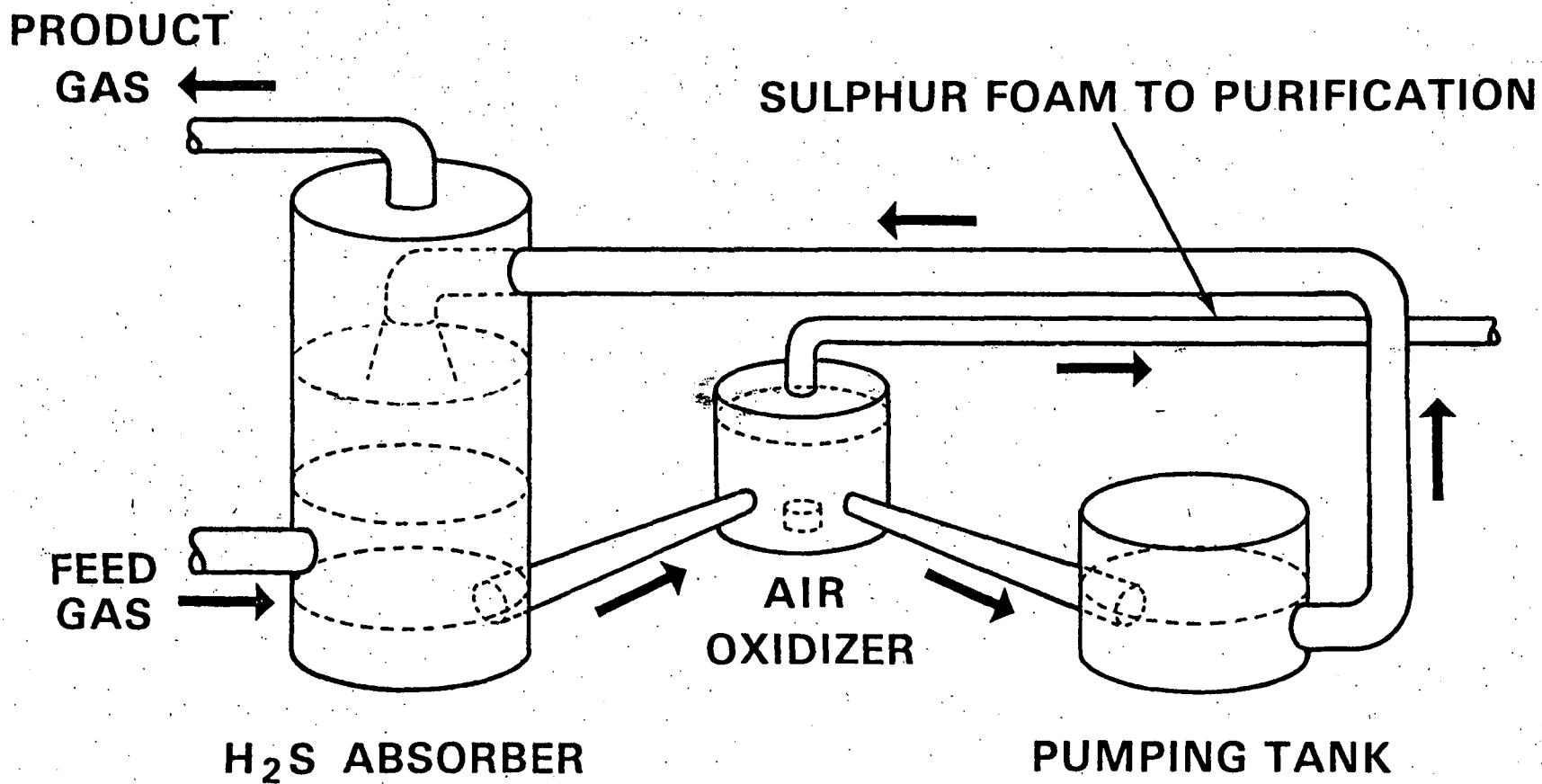
FIGURE 7. STRETFORD PROCESS FLOW DIAGRAM

HCN in foul COG causes the formation of the thiosulfates and thiocyanates. Therefore, removal of HCN ahead of the absorber or of its products in the absorber or removal of its products in Stretford liquor or both is necessary. Removal has been achieved ahead of the Stretford abosrber in an absorbing tower, in which a solution of suspended sulfur and water reacts with the NH_3 in COG to form ammonium thiocyanate and thiosulfate. This is known as the polysulfide treatment process (due to the intermediate formation of ammonium polysulfide). The polysulfide process can remove up to 98% of the HCN from foul COG[25]. In turn, this liquor, containing SCN and S_2O_3 needs treatment before disposal. These same compounds also build up in the Stretford liquor, if allowed, and either spent Stretford liquor or a steady blowdown thereof require treatment for these salts.

Peabody-Holmes of the U.K. has developed and operate a Stretford process waste liquor process (Fixed Salts Recovery) at the Orgreave plant of British Steel Corp (26 MMSCFD of COG). The chemistry and other details of this process are described in the Process Attachment. The essential step is high temperature oxidation in a reducing atmosphere, generated by substoichiometric combustion of COG. SCN and S_2O_3 are converted to $H_2S + CO_2 + N_2$ and are recirculated to the front end of the Stretford tower. A critical question for the Stretford process is whether the Peabody-Holmes waste liquor process is adequately demonstrated. To this end Peabody offers the following[25,26]. After laboratory and pilot scale development, the Orgreave full scale unit was brought on-stream for operation and testing in August 1975. The plant has operated continuously with two exceptions for the past six months. In August 1976 an "incident" involving a COG explosion in a burner, not related to the basic process, brought the plant

down. It had run for five weeks prior to then and ran from November 20 to Christmas 1976 when it was again brought down to provide a holiday for BSC workers. It will be operational in mid-January once more. From this, one sees that the process is considered a development by P-H and BSC operators and that this project is proving successful from a system chemistry perspective. In an attachment, which is seen by EPA staff to be quite confidential, Peabody-Holmes believes they have demonstrated that their combustion process works. In the August 5, 1976 in-house memo, Peabody-Holmes noted that "steady-state" operation was still needed at that time to fully prove the system's chemistry. Two recent judgements by the steel industry reflect the diversity of its views. Dofasco has ordered two Holmes' units; one for its existing Stretford plant and one for the new Stretford plant mentioned above. The first Fixed Salt Recovery (FSR) system is to be on-stream September 1977. Kaiser Steel has just decided[27] to purchase Takahax based in part upon the longer operating times Takahax has experienced. Wilputte Corp., the Peabody-Holmes licensee in the U.S. vigorously maintains the Holmes process is commercially proven[26].

Woodhall-Ducklam, a British engineering firm, has also piloted a Stretford waste liquor facility based on the same basic chemistry as the Holmes process. Woodhall-Ducklam has not yet built a full scale unit although one is under construction at the Redcar plant of British Steel Corp.[28] The reader is also directed to the Nittetsu process (see Takahax for an additional waste liquor treatment alternative).

The Stretford process is very efficient at removing H_2S from COG. Ludberg[1]

quotes concentrations below 1 gr/100 dscf. Wilputte asserts H_2S to 10 ppm (0.6 gr/100 dscf) is well achievable[25,26]. Massey and Dunlop state removal efficiencies "in excess of 99%" are possible[4]. Organic sulfur is not removed, however. Therefore, the lowest sulfur level emission rate for desulfurization by the Stretford process is 1 gr H_2S/100 dscf of COG produced plus organic sulfur in the foul gas.

2. Takahax Process

Takahax was developed and is sold by Nippon Steel Corp. In the U.S., Nippon and Chemico Air Pollution Control Company (of Envirotech) have a working relationship for the marketing of Takahax. Many details of the process chemistry are described in the Appendix and are not redescribed here.

The basic flow diagram for Takahax is shown in Figure 8. H_2S is absorbed from COG in a column, using either a Na or NH_3 based solution. HCN is not removed ahead of the absorber but is allowed to build up as thiocyanate in the absorber. A blowdown is removed for treatment in one of three ways.

The Nittetsu Chemical (NICE) process, like the Holmes process, is based on substoichemitric combustion of S_2O_3 and SCN to H_2S, CO_2, N_2, and Na_2CO_3 (in liquid solution, returned to the absorber) H_2S produced from the NICE process can be either recycled to the absorber or sent to a sulfuric acid plant. Alternatively, complete combustion of the ammonia waste liquor $((NH_4) \ S_2O_3$ and NH_4SCN to $SO_2 + CO_2$, and thence SO_2 to sulfuric acid) is possible. Wet oxidation at very high pressure and temperature to ammonium sulfate, for the NH_3 stripping of H_2S version of Takahax, is a third waste liquor treatment possibility[29].

Since Takahax is available for each of these waste liquor options, "Takahax"
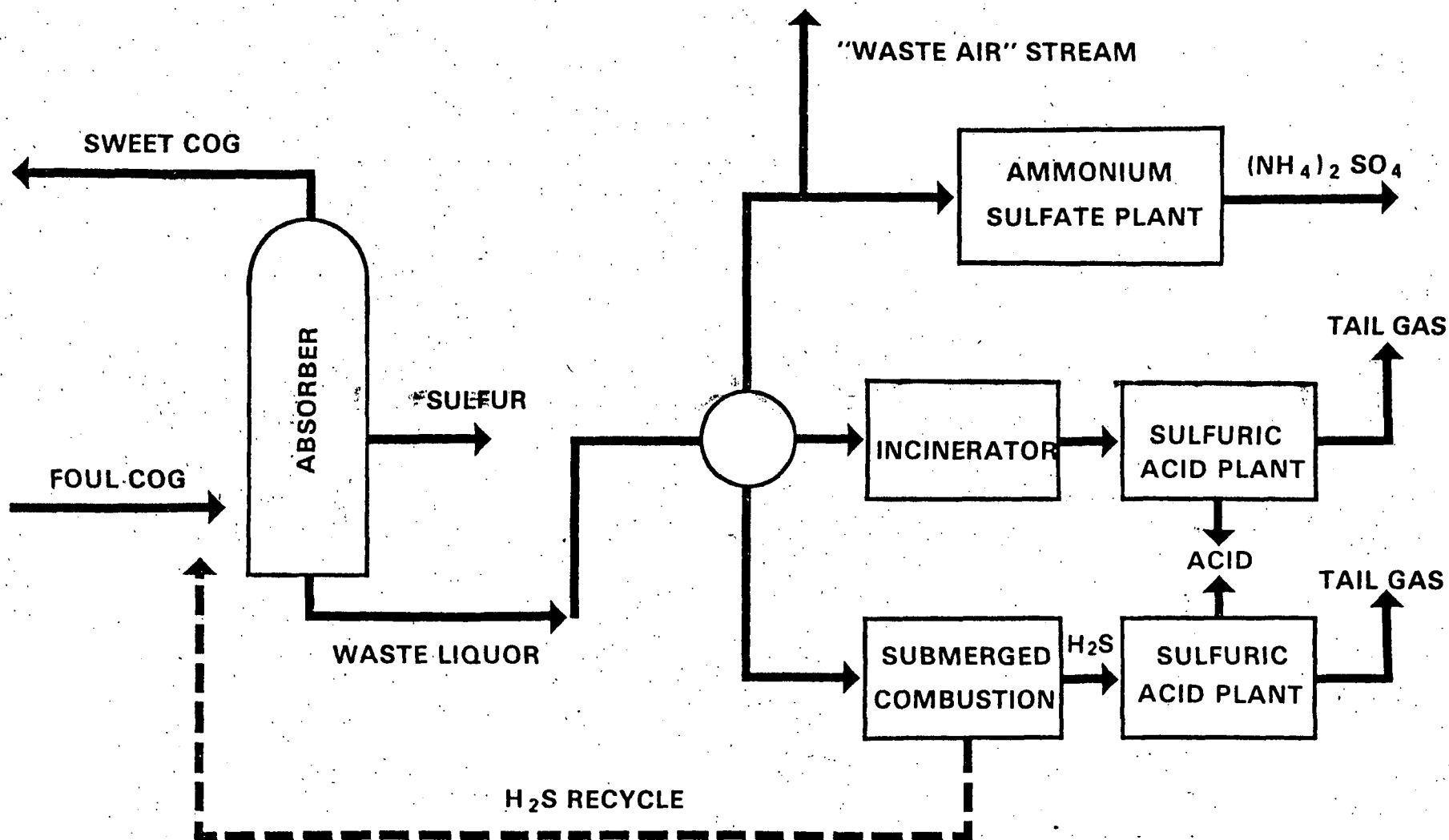
FIGURE 8. TAKAHAX FLOW SHEET

is a generic term. Nippon Steel offers four process options.

"A" - NH_3 absorption + wet oxidation of liquor to recover H_2S in COG as
ammonium sulfate.
This version produces two "waste air" streams containing a small
amount of sulfur both of which need scrubbing before release to
the atmosphere.

"B" - NH_3 absorption + combustion of waste liquor, producing elemental
sulfur and an SO_2 stream from the waste liquor combustion process.
This SO_2 requires recovery as H_2SO_4 with attendant considerations
mentioned in Section IIC, above. Again, a waste air stream from
the absorber section carries some sulfur to the atmosphere.

"C","D" - Na_2CO_2 absorption + NICE waste liquor treatment. H_2S is recovered
as elemental sulfur. The NICE process is used on H_2S off-gas which
Nippon Steel proposes as feed, along with molten sulfur, to an acid
plant. H_2S could also be recycled to the absorber with sulfur the
process output as well. This latter version is termed the "D" type.

Takahax is a commerically demonstrated process. Nine Japanese facilities
exist as shown in Table 8. Kaiser Steel has decided to construct Takahax-A to
comply with an EPA-Kaiser consent decree and has so notified EPA Region IX.
Relative costs are shown in Table 9.

Table 10 provides Takahax performance data[35] for four Nippon Steel
plants. Note that the Nagoya and Yawata plants achieved 4 gr H_2S/100 scf
whereas three other facilities were stated[37] to have been tested at

Table 8.   COKE-OVEN GAS DESULFURIZATION UNITS IN JAPAN (JANUARY 1977 NIPPON STEEL)

NAME	PLACE	GAS VOLUME	DESULFURIZATION	SULFUR TREATMENT
Nippon Steel	Hirohata*	99 MMSCFD	NH_3 - Takahax	Hirohax
Nippon Steel	Muroran*	130	NH_3 - Takahax	Hirohax
Nippon Steel	Oita*	206	NH_3 - Takahax	Hirohax
Nippon Steel	Nagoya	162	N_a - Takahax	Combustion, Sulfuric Acid
Nippon Steel	Nagoya	31	N_a - Takahax	Combustion, Sulfuric Acid
Nippon Steel	Tobata	116*	N_a - Takahax	Combustion, Sulfuric Acid
Nippon Steel's Affiliate	Kimitsu*	227	NH_3 - Fumax	Combustion, Sulfuric Acid
NKK	Fukuyama*	116	NH_3 - Takahax	Combustion, Gypsum
NKK	Ogishima*	90	NH_3 - Takahax	Hirohax
Kawasaki	Chiba*	80	NH_3 - Fumax	Combustion, Sulfuric Acid
Kawasaki	Mizushima	179	Diamox	Claus, IFP
Kawasaki	Mizushima*	90	Diamox	Claus, IFP
Sumitomo	Wakayama	70	N_a - Takahax	
Sumitomo	Wakayama	107	NH_3 - Fumax	Combustion, Sulfuric Acid
Sumitomo	Kashima	72	NH_3 - Fumax	Combustion, Gypsum
Mitsubishi Che.	Sakaide*	215	Diamox	Claus
Mitsubishi Che.	Sakaide	188	Diamox	Claus, Activated Sludge
Mitsubishi Che.	Kurosaki	85	Diamox	Claus, Activated Sludge
Mitsubishi Min.	Hibikinada	107	Bischoff, V.C.	
Amagasaki	Ohama	53	Rodax, Stretford	Combustion, Sulfuric Acid
Amagasaki	Ogimachi	47	Rodax, Stretford	Activated Sludge
Amagasaki	Kakogawa	132	Rodax, Stretford	Combustion, Sulfuric Acid
Tokyo Gas	Tsurumi*	45	NH_3 - Takahax	Hirohax

*Indicates facilities constructed in 1975 and 1976.

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Table 9.   RELATIVE TAKAHAX COSTS

TYPE	RELATIVE COST
A (Hirohax)	100% – $12 million (1975)
B	110%
C	120%
D	130% (producing H_2SO_4)
D	90% (recycling H_2S to absorber)

Notes

1.   Above data based on the Hirohata plant: 99MMSCFD
                                                 200 gr H_2S/100 scf inlet
                                                 10 gr H_2S/100 scf outlet

2.   Includes cost of duel absorption sulfuric acid plant

Table 10. TAKAHAX PERFORMANCE DATA

PLANT	$H_2S^{(a)}$ INLET	$H_2S^{(a)}$ OOUTLET[b]	START-UP DATE	DAYS SINCE START-UP	DAYS IN OPERATION
Hirohata	200	≤10	4/75	630	630
Oita	260	≤10	6/76	204	204
Mororam	240	≤10	3/76	306	306
Nagoya	300	≤ 4	10/73	1126	1111
Yawata	340	≤ 4	3/74	1036	1036

(a) By J.I.S. methodology, gr H_2S/100 scf.

(b) No organic sulfide removal in the Takahax process.

$\leq$ 10 gr/100 scf. Nippon Steel states this to be a reflection of local pre-
fecture regulations and not system capability.

The NH_3-Takahax process also produces a waste air stream which contains
small amounts of H_2S gas. The Takahax liquor is pumped to a liquid/gas
separation bubble tower into which air is pumped. Waste liquor and regen-
erated solution (reoxidized) are separated and a waste air stream containing
H_2S gas is created. This stream is scrubbed in a counter-current packed
tower to remove its NH_3 content with "mother liquor" (3-4% H_2SO_4). H_2S in
the waste stream is of course not absorbed by this acid liquor and is
emitted to the atmosphere. Exactly the same process chemistry gives rise
to the Hirohax waste stream.

Pertinent data for these streams are shown in Table 11. Note that the
quantity of H_2S to the atmosphere is very small, < 0.01 gr/100 scf of COG.
As H_2S is noticeable even at small concentrations in the ambient air, short
term diffusion model calculations were run to calculate these streams' impact.
For the 99 MMSCFD sized plant from which Table 11 derives, worst case 1-hr
concentrations were $\sim$ 0.0015 ppm or about 40 times below the (H_2S) human order
threshold.

Table 11.   TAKAHAX WASTE AIR STREAM FLOWS

	Outlet (H$_2$S)	Volume	ft^3 H$_2$S Per Day	Equivalent gr H$_2$S per 100 dscf of COG
Takahax Regenerator	2.3 ppm	2.7 - 3.2 MMSCFD	6.2 - 7.4	.0042 - .0050
Hirohax Waste Liquor Process	2.0 ppm	2.0 - 2.9	4.0 - 5.8	.0027 - .0039

Stack Parameters

Temperature - 120°F
Height   - 130 ft
Diameter   - 14 in
Velocity   - ∿30 fps

Section III.   ORGANIC SULFUR IN COKE-OVEN GAS

Only one of the six desulfurization technologies removes COS and CS_2 from COG. Yet both compounds produce SO_2 upon combustion by:

$$COS + \frac{3}{2} O_2 \rightarrow SO_2 + CO_2$$
$$CS_2 + 3\ O_2 \rightarrow 2SO_2 + CO_2$$
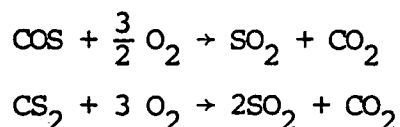
and it is the emission of SO_2 that the technologies are designed to abate.

Organic sulfur has not usually been analyzed with care by coke plant operaters since H_2S predominates the total sulfur level of foul COG. However, after H_2S stripping, uncontrolled organic sulfur may amount to half or more of the total sulfur load in the sweetened COG. For example, typical foul gas may contain 450 gr/100 scf H_2S and 15 gr/100 scf CS_2 + COS. If H_2S is reduced to 10 gr/100 scf then of the 25 gr/100 dscf of total reduced sulfur in the sweet gas, 60% is COS or CS_2. If the stripped acid gas is processed in a 97% acid plant, an H_2S equivalent emission of 12 gr/100 scf will occur. In this case, organic sulfur (O.S.) will still account for 40% of SO_2 emissions.

The best estimates we have for foul gas organic sulfur levels are in the range 5-25gr H_2S equivalent/100scf. (By H_2S equivalent or "H_2S", it is meant that COS or CS_2 volume concentration in ppm is converted to the gravimetric conentration, gr "H_2S"/100 scf, by multiplying by .063). No good empirical or theoretical relationships exist between H_2S and COS or CS_2 levels nor does there appear to be any relationship between sulfur (%) in coal and COS/CS_2 levels in COG. This seems to be the case, despite the H_2S/%S relationship quoted in Section I. One obvious variable affecting (COS) formation is O_2 in COG induced by stage charging. This is an operating variable not subject to predictions based on coal analysis.

Empirical data for organic sulfur levels in actual COG streams exist to some extent. The following data were obtained from various sources.

Table 12. ORGANIC SULFIDE CONCENTRATIONS IN COG

PLANT		FOUL COG ORGANIC SULFUR CONCENTRATION
1.	Jones & Laughlin -Pittsburgh Works	a. 24 gr "H_2S"/100 scf, total of CS_2 + CO_s (Sulfiban design basis)
		b. 5 gr "H_2S"/100 scf - COS 7 gr "H_2S"/100 scf - CS_2 See Table 6
2.	Shenango Inc.	25 gr/100 scf (Sulfiban design basis)
3.	Kaiser Steel	19 gr/100 scf (recent gas analysis used for design)
4.	Bethlehem Steel (Bethlehem, PA.)	3-8 gr/100 scf total O.S. (Williams and Homberg)
5.	Republic Steel	Have stated 10-20 gr/100 scf for design of facilities at Warren, Cleveland, and Youngstown. This is a RSC generic estimate for total O.S.
6.	Crucible Steel	12 gr/100 dscf for COS + CS_2
7.	Bethlehem Steel	
	a. Sparrows Point	14 "
	b. Lackawanna	14 "
	c. Rosedale	10 "
	d. Franklin	10 "

From this list 5-25 gr/100 scf seems to be a reasonable assumption for foul gas O.S. However, as coal sulfur levels and coking practices vary from place to place and with time at any one location direct measurement is encouraged.

Attached is an article by chemists of Jones & Laughlin Steel Corp. who were faced with a foul COG sampling obligation in 1973[30]. J & L had designed a Sulfiban plant based upon a 400 gr H_2S/100 dscf presumption. Because their coal analyses indicated probable higher foul gas H_2S sulfur levels, the Allegheny County Health Department required J & L to develop and operate a TRS* sampling system. Data developed therefrom (see Appendix for an example) can be obtained via Section 114 from J & L Steel Corp.

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*Total reduced sulfur, H_2S/COS/CS_2.

Section IV.   PERFORMANCE LEVELS FOR COG DESULFURIZATION TECHNOLOGY

In this section, are comparisons of the demonstrated technologies described in Section II in terms of their ultimate overall SO_2 emission rates.

Tables 13-15 indicate the H_2S equivalent levels attained by liquid absorption processes and their necessary sulfur recovery adjuncts. Clearly, the highest desulfurization currently achievable is by the high effeciency Sulfiban process operated in conjunction with a high yield Claus or sulfuric acid plant. Also note:

1.   Table 15 indicates the best demonstrated performance levels for other combinations of liquid absorption processes as well. This table was calculated using a total organic sulfur concentration of 15 gr H_2S equivalent per 100 dscf.

2.   Sweet coke-oven gas H_2S levels of 10 gr/100 dscf of COG are obtainable by Diamox, Still, Sulfiban, and perhaps by double stage vacuum carbonate. This only refers to the sweet gas, per se.

3.   Only Sulfiban absorbs COS and CS_2. From Section III, it is clear that COS and CS_2 can each exist in foul COG at levels from 10-25 gr H_2S equivalent/100 dscf. Sulfiban removes these down to a residual 2 gr "H_2S"/100 dscf level.

4.   Standard Claus and single absorption sulfuric acid technology produces a 96%-97% yield.

5.   Claus + tail gas treatment or double absorption sulfuric acid produces a tail gas containing no more than 0.5% of the recovery plant inlet sulfur level. (See Figure 9 for system options).

6. Overall system emissions can be reduced to [(Foul COG Inlet "H_2S" -5) (0.005 + 5] gr "H_2S"/100 dscf of COG produced. At 500 gr "H_2S"/100 dscf, this works out to an overall 9 gr "H_2S"/ 100 dscf of COG. This is the overall lowest level demonstrated for liquid absorption.

For the liquid oxidation process, Table 16 summarizes the analogous performance levels.

The impact of organic sulfur on the overall performance liquid oxidation process is dramatic. Basically, these technologies reduce SO_2 emissions to twice the foul gas organic sulfur gravimetric concentrations, when operated at their maximum H_2S absorption efficiencies. This is so, because virtually all H_2S is removable.

The overall capabilities of the coke oven gas desulfurization technologies discussed in this document are ranked in Table 17. Two rankings are provided, one for H_2S and one for total reduced sulfur. This table provides a direct comparison of all the technology combinations studied in this document's preparation. Since their purpose is SO_2 emissions prevention, the right hand column of this table, in the units lb $SO_2/10^6$ ft^3 COG, is most useful. In this table, the phrase "high S recovery" refers to 99.5% sulfur recovery as shown in Table 14.
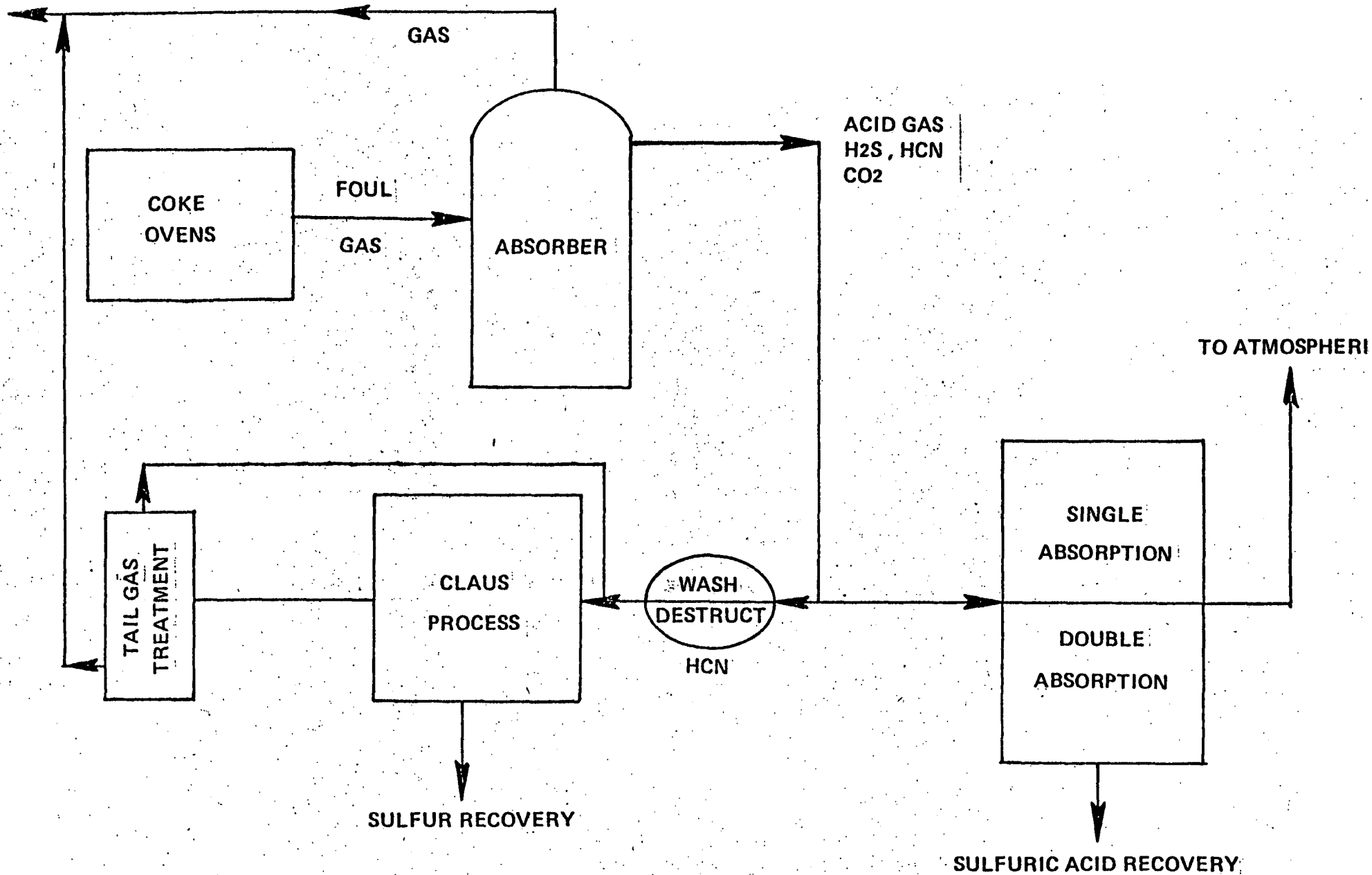
FIGURE 9. LIQUID ABSORPTION OPTIONS

GAS

COKE OVENS

FOUL GAS

ABSORBER

ACID GAS
H2S, HCN
CO2

TO ATMOSPHERE

TAIL GAS TREATMENT

CLAUS PROCESS

WASH DESTRUCT

HCN

SINGLE ABSORPTION

DOUBLE ABSORPTION

SULFUR RECOVERY

SULFURIC ACID RECOVERY

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Table 13. SUMMARY OF LIQUID ABSORPTION TECHNOLOGY PERFORMANCE LEVELS

Best Attainable Outlet Sulfur Concentrations

PROCESS	H_2S	ORGANIC SULFUR	TOTAL REDUCED SULFUR (as H_2S)
Sulfiban	5 gr/100 scf	2	7
Vacuum Carbonate	30**	foul gas level* (FGL)	30 + FGL
Diamox	10		10 + FDL
Carl Still	10	FGL	10 + FGL

*Foul gas levels (see Section III) are usually in the 5-25 gr/100 dscf range.

**Bench scale demonstration of 10 gr/100 scf has been made with a two stage vacuum carbonate process.

Table 14.   SUMMARY OF SULFUR RECOVERY TECHNOLOGY PERFORMANCE LEVELS

PROCESS	SULFUR YIELD (% OF INLET S RECOVERED)	TAIL GAS EMISSION RATE
Claus Process		0.082 lb SO_2 per lb sulfur recovered.
.Three Stage Catalytic Recovery	96%	287 gr H_2S equiv. per lb S recovered.
.With Tail Gas Treatment	99.5%	0.010 lb SO_2/lb S 35 gr H_2S equivalent/lb S
Sulfuric Acid Plant .Single Contact	97%	0.063 lb SO_2/lb S 215 gr H_2S equiv./lb S
.Double Absorption- Double Contact	99.7%	0.0063 lb SO_2/lb S 22 gr H_2S equiv./lb S

Table 15. Best Obtainable Overall Desulfurization Performance
by Liquid Absorption Technology

Sulfur Recovery Process

Removal Process		Three Stage Claus		Single Contact Acid		Claus & TGT		Double Contact Acid		Stret-Ford	
		H_2S / TRS**		H_2S/TRS		H_2S/TRS		H_2S/TRS		H_2S/TRS	
Sulfiban											
	300*	17*	19*	7	9	14	16	6	8	X	
	500*	25	27	8	10	20	22	7	9	X	
Vacuum Carbonate***											
	300*	41	56	31	46	38	53	31	46	X	
	500*	49	64	32	47	44	59	31	46	X	
Diamox											
	300*	22	37	12	27	19	34	11	26	X	
	500*	30	45	13	28	25	40	12	27	X	
Carl Still											
	300*	22	37	12	27	19	34	11	26	10	25
	500*	30	45	13	28	25	40	12	27	10	25

*Total foul gas reduced sulfur concentrations, gr "H_2S" per 100 dscf of COG produced.

**Total reduced sulfur.

***Single stage.

Table 16. BEST OBTAINABLE OVERALL DESULFURIZATION BY LIQUID OXIDATION

| PROCESS | CLEAN COG CONCENTRATION | | OVERALL | |
	H_2S	TRS*	H_2S	TRS**
Stretford	1	16	1	16
Takahax – A	4	19	4	19
Takahax – B	4	19	6**	21
Takahax – C	4	19	6**	21
Takahax – D	4	19	6**	21

*Assumes 15 gr H_2S equivalent/100 scf for organic sulfur in foul coke-oven gas.

**Assumes need for acid plant at 99.5% sulfur yield.

Table 17. Technology for Desulfurization of Coke-Oven Gas

| | H₂S Ranking[a] | | | | TRS RANKING[a] | | | |

Technology	Clean COG	Tail Gas	Total H2S Equivalent	Technology	Clean COG	Tail Gas	Total H2S Equivalent	SO_2[b] Emission Rate
Stretford	1	0	1	Sulfiban-high sulfur recovery	7	2	9	24
Takahax - A	4	0	4	Sulfiban	7	15	22	59
Tahahax - B,C,D	4	2	6	Stretford	6-26	0	6-26	16- 70
Sulfiban - high S recovery	5	2	7	Takahax A	9-29	0	9-29	24- 77
Still- Stretford	10	0	10	Takahax B,C,D	9-29	2	11-31	29- 83
Still - high S recovery	10	2	12	Still - stretford	15-35	0	15-35	41- 95
Diamox - high S recovery	10	2	12	Diamox - high S recovery	15-35	2	17-37	46-100
Sulfiban	5	15	20	Still - high sulfur recovery	15-35	2	17-37	46-100
Diamox	10	15	25	Diamox	15-35	15	30-50	81-135
Still	10	15	25	Still	15-35	15	30-50	81-135
Vacuum Carbonate - single stage	30	14	44	Vacuum Carbonate - single stage	35-45	14	49-63	135-170

(a) All units are gr H₂S or equivalent per 100 dscf of coke oven gas produced.

(b) Unit is lb SO_2 emitted per 10^6 ft³ cf coke-oven gas produced.

COG DESULFURIZATION PERFORMANCE CONCLUSIONS

1. The overall lowest achievable emission rate is achievable with the Sulfiban liquid absorption process operated at high MEA circulation and high MEA regeneration rates, followed by either double absorption sulfuric acid recovery or tail gas treated Claus plant sulfur recovery. This level is 9 gr H_2S per 100 dscf of coke-oven gas produced with all tail gas included as equivalent H_2S. This level corresponds to an SO_2 emission rate of 25 lb SO_2 per 10^6 ft^3 of coke-oven gas produced.

2. The Stretford-Holmes or the Takahax processes may achieve this same or even lower rate of emission. Their lowest equivalent SO_2 emission rates will vary from 16-83 lb SO_2 per 10^6 ft^3 COG, depending upon foul gas organic sulfur levels. Therefore, these two technologies may, at certain plants, be equivalent to the lowest achievable emission rate and may even surpass the rate stated in (1) above. Foul gas organic sulfur levels must be less than 8 gr H_2S equivalent per 100 dscf for this to be possible.

3. When the foul gas organic sulfur concentration is between 9-13gr H_2S equiv. per 100dscf, the two liquid oxidation processes should be characterized as the second lowest emissive technologies. This emission rate will be in the range 24-59 lb SO_2 per 10^6 ft^3 of COG.

4. Above 13gr "H_2S"/100dscf of organic sulfur, the second lowest achievable SO_2 rate is provided by the Sulfiban process operated at high MEA circulation and regeneration rates, with sulfur recovery

by a conventional Claus plant or single contact sulfuric acid plant. This rate is an overall 22 gr "H_2S"/100 dscf or 59 lb SO_2 per 10^6 ft^3 COG produced.

5. Both the Firma Coal Still and Diamox processes can achieve 59 lb SO_2 per 10^6 ft^3 of COG <u>provided</u> <u>organic</u> <u>sulfur</u> <u>levels</u> <u>are</u> <u>below</u> <u>12 gr</u> <u>"H_2S"/100 dscf</u>. Both processes require high efficiency sulfur recovery systems (Claus + TGT, sulfuric acid).

6. Diamox, Still, and Vacuum Carbonate operated <u>with</u> <u>conventional</u> <u>sulfur</u> <u>recovery</u> will not be able to achieve 59 lb $SO_2/10^6$ ft^3 COG because of the combined impact of organic sulfur and the high tail gas emission rate.

7. Organic sulfide levels for the specific COG under consideration should be known.

8. The recommended levels for various EPA regulatory policies are:

   (a) Lowest Achievable Emission Rate: 10 gr/100 dscf of COG produced of total sulfur compounds, expressed as H_2S, including all tail gas sulfur emitted from sulfur recovery equipment.

   (b) Best Available Control Technology (considering cost) for Prevention of Significant Deterioration use: 35 gr/100 dscf of COG produced of total sulfur compounds, expressed as H_2S, including all tail gas sulfur emitted from sulfur recovery equipment.

   (c) Reasonably Available Control Technology: 50 gr/100 dscf of COG produced of total sulfur compounds, expressed as

H_2S, including all tail gas sulfur emitted from sulfur recovery equipment.

Section V.   MEASUREMENT FOR COMPLIANCE

Since reductions in SO_2 emissions from COG combustion require removal of H_2S (and possibly organic sulfides) before combustion and since COG combustion takes place at dozens of separate points, the compliance measurement is for reduced sulfur.

As described in Section IV, it may be possible to achieve compliance with the LAER by means of either liquid absorption or oxidation equipment. Therefore it may be necessary to measure for:

(1) Cswg, concentration of sulfur compounds in the sweetened coke-oven gas.

(2) Ctg, concentration of sulfur compounds in Claus, Takahax, or sulfuric acid tail gas streams.

(3) Vswg, volume flow rate of sweet COG.

(4) Vtg, volume flow rate of tail gas.

(5) Vfg, volume flow rate of foul COG.

The lowest achievable emission rate standard can be written as:

$$\frac{Cswg\ Vswg + 6.63 \times 10^{-4}\ Ctg\ Vtg}{Vfg} \leq \frac{10\ gr\ "H_2S"}{100\ dscf\ of\ COG} \quad \ldots (1)$$

In this relationship the appropriate units are:

[Cswg] = gr "H_2S"/100 dscf

[Vswg] = 100 dscf/hr

[Ctg] = ppmv

[Vtg] = dscf/hr (of tail gas)

[Vfg] = 100 dscf/hr

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Figure 10 is a schematic which indicates the various sampling locations which potentially are needed to determine compliance. The difference between the cleaned and foul COG volumetric flows is the amount of acid gas removed in the absorber. Since the sum of H_2S, HCN, organic sulfides, and CO_2 is typically about 1% of the foul gas flow, it is fair to assume Vswg≈Vfg in computing complinace.* If Vswg is measured in lieu of Vfg this will bias the computed result upwards by about 1%, in the converse case measurement of Vfg will cause an underestimation of the true overall concnetration by 1% (tail gas flux/total flux 1/2%).

Measurement of clean coke-oven gas flow by built-in orifice or venturi flow meters can and should be expected to be part of an operator's process control equipment. Data should be reported to a 24-hour chart located in the sulfur plant control room. Such instrumentation has a tendency to drift from calibration so that before using such equipment in a compliance test, it should be known to be in calibration. Even so, accuracy only to about ± 5% of the true flow should be expected such flow meters tend to change dimension, particularly on the foul gas side, due to tarry COG constituents. Hence even long term averaging will not necessarily insure better accuracy.

Clean coke-oven gas measurements of reduced sulfur compounds concentrations must be sensitive to H_2S, COS, and CS_2. There are two ways of accomplishing this. Direct measurement of each compound by gas chromotography (GC) separation followed by flame photometric or thermal conductivity detection has been

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*Exception: The Clairton Coke Works cryogenic plant or any other synthetic NH_3 producer using H_2 in COG.

FIG 10 COMPLIANCE MONITORING LOCATIONS

COKE OVENS → COAL CHEMICALS PLANT → ① → H₂S ABSORBER → CLAUS SULFURIC ACID OR WASTE LIQUOR PLANT → ③ → INCINERATOR → ③

② → CLEAN COG

FOUL GAS FLOW

SWEET GAS FLOW AND CONCENTRATION

TAIL GAS FLOW AND CONCENTRATION
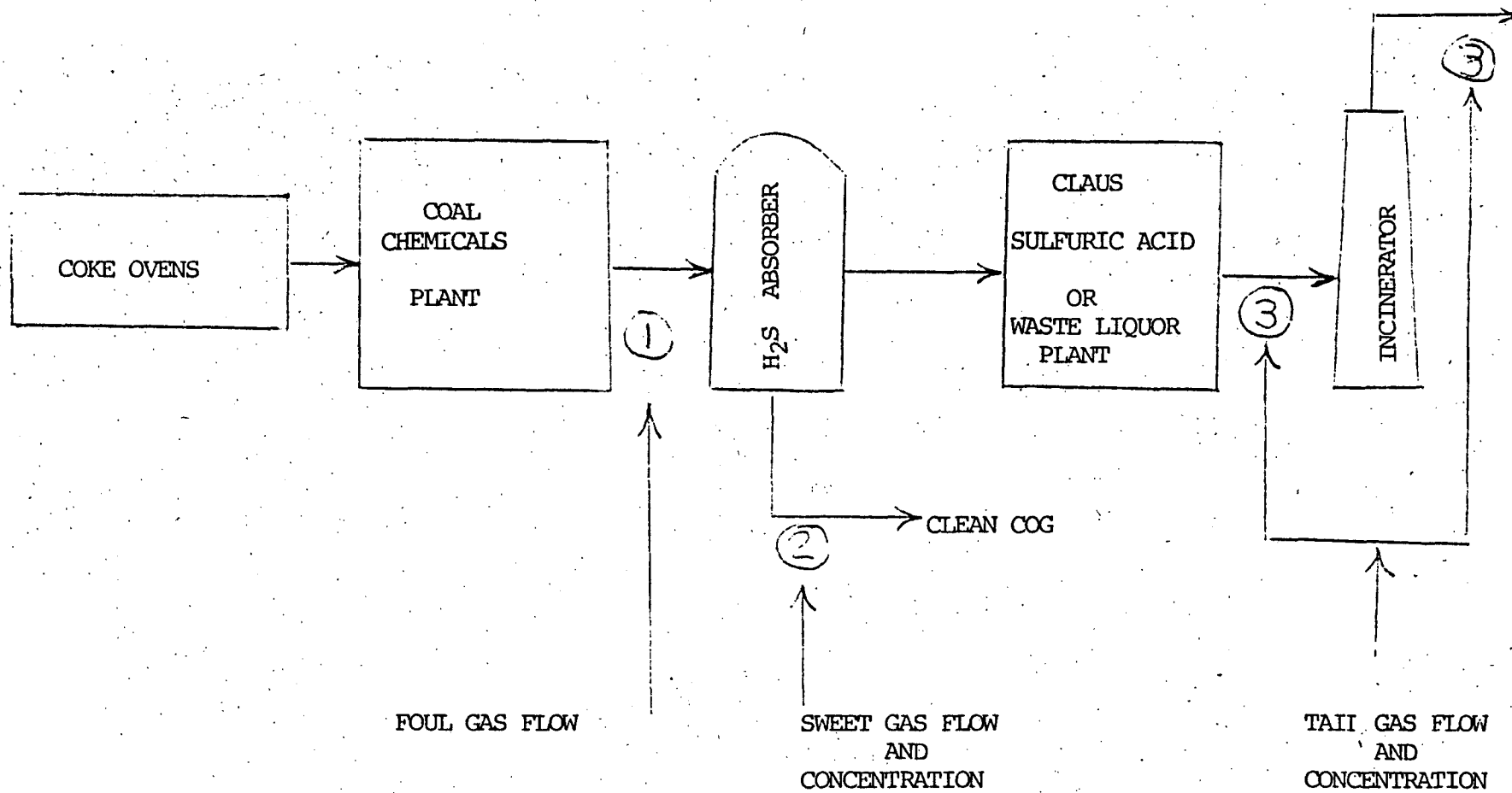
successfully applied. The reader is referred to Manka[30]. The set-up

used by J & L included a _permanent_ connection to the sweet gas line.

The alternative is to acquire periodic gas samples which would then

be returned to a laboratory for GC separation and analysis. This technique

carries the real risk that water condensation in the evacuated sample bottles

will occur, carrying H_2S into solution and hence removal from the sample gas

phase. See the Process Appendix for a discussion of this problem[31]. In

the case of remote sampling and analysis, reheating the sample bottles before

hypodermic needle extraction of the gas sample will be necessary. Reheating

may not completely solve such problems, however. H_2S and HCN may react with

NH_3 to form soluble salts which would thereby falsely remove H_2S from the gas

phase. For these reasons on-site GC analysis is preferred.

The alternative to direct sampling of TRS is to combust the sweet gas

sample to CO_2 and SO_2. Measurement of SO_2 concentrations then can be made

by EPA Methods 6 or 8. This technique assumes complete conversion of all

reduced sulfur compounds to SO_2 and the lack of SO_2 formation. EPA Methods

6 and 8 may therefore provide falsely low readings.

Wet chemistry methods exist for H_2S, COS, and CS_2 concentrations in

coke-oven gas. These are the traditional methods employed by the industry

in routine sampling. The most popular is the Tutweiler titration method

which can be used for either H_2S or TRS. While this method is useful at

foul gas concentrations, the method has been reported to be less valid

at (H_2S) below 10 gr/100 dscf. Patience in carrying out the titration

to the true end point has been indicated as one cause of poor detectability.

with the method[32]. Another range finding device used by the gas process-
ing industry is generally referred to as the "sniffer tube." The only valid
use of these handheld devices is for quick order-of-magnitude determinations.

Tail gas sampling is necessitated in the case of the liquid absorption
processes for both concentration and flowrate, per Eq. (1). For Claus
sulfur recovery plants, with or without tail gas treatment, EPA has pro-
posed Method 15 (F.R., October 6, 1976) for (H_2S), (COS), & (CS_2) deter-
minations. Sulfuric acid plant compliance testing in the formal NSPS is
by Method 6. These methods are recommended for COG tail gas streams.
For Claus plants, however, which pass the tail gas through an incinerator,
a problem particular to the COG occurs. Since it is necessary to determine
the entire second term in the numerator of Eq. (1), Vtg must be measured.
This was not necessary in the case of the refinery Claus plant NSPS because
of the absence of parallel sulfur bearing streams. The incinerator produces
a very hot ($\sim$1500° F) stream which makes flow rate determinations, particularly
continuous determinations, difficult. One company's solution[33] is to sample
for Vtg Ctg at the inlet to the incinerator with a venturi flow meter. A dis-
advantage to be noted, however, is that the inlet to conventional Claus plants
contain sulfur vapors in small amounts, which may condense in the Ctg or Cfg
sampling lines.

Averaging time for compliance testing is another monitoring issue. The
refinery sulfur recovery NSPS proposal requires a four hour testing period.
Each hour, four grab samples are to be acquired from a side stream which runs
to an on-site chromatograph. One test comprises 16 grab samples. The arith-
metic average of three tests is to be used to determine compliance. For

Table 18. COKE-OVEN GAS SAMPLING FIELD SHEET

Plant_____

Battery No. (s)_____

Date_____

$$\text{Level} = \frac{C_{swg}\, V_{swg} + 6.63 \times 10^{-4}\, C_{tg}\, V_{tg}}{V_{swg}}$$

HOUR	SAMPLE NO.	Cswg	Vswg	Ctg	Vtg	LEVEL*
1 Clock Time	1					
	2					
	3					
	4					
2 Clock Time	1					
	2					
	3					
	4					
3 Clock Time	1					
	2					
	3					
	4					
4 Clock Time	1					
	2					
	3					
	4					
Average						Result

coke-oven gas flows are variable from minute to minute due to the inherent

batch operation of coke plants. Since it is necessary to determine both

Cswg Vswg and Ctg Vtg to determine compliance, _it is imperative that Cswg_,

Vswg, Ctg, and Vtg be determined simultaneously.

The suggested monitoring scheme is outlined in Table 18. Compliance

is determined by comparing the appropriate standard to the arithmetic average

of the 16 numbers in the right hand column.

Section VI.   ENERGY AND COST IMPACT OF COKE-OVEN GAS DESULFURIZATION

A.   Cost Impact

A general discussion of economics of coke-oven gas desulfurization

is very difficult to develop because of the large variability of specific

plant factors, the highly competitive and rapidly developing state of

technology, and the variability and uncertainty in by-product prices.

Each U.S. steel company which has installed or is committed to install

desulfurization technology (U.S. Steel, Bethlehem, Armco, J & L, Shenango,

Kaiser, Republic, Inland, Youngstown Sheet and Tube, and others) has of

course performed site specific cost studies. These studies are limited

in their generality* and are not available to EPA. Published cost studies

are limited either by scope or vintage.

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*In one case a vendor was asked to provide in a bid 12 separate paramatiza-
tions of the costs of the same basic process at a given site, for a given
COG.

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Recent cost studies considered in this guidance are:

STUDY	SCOPE
Massey & Dunlap -Spring 1974	Hypothetical parametric case study of Stretford and V.C. and Sulfiban with conventional Claus recovery.
Massey & Dunlap -Spring 1975 [34]	Hypothetical parametric case study of Stretford plus waste liquor and and V.C., Sulfiban, and Still with both conventional Claus and single contact sulfuric acid recovery.
GCA - Spring 1976 (EPA funded) [18]	Vendor provided costs for plants of Republic Steel, Youngstown Sheet and Tube for Stretford and Still & Sulfiban with Claus and sulfuric acid recovery conventional. Done in support of Ohio SO_2 SIP.
EPA - July 1976	Claus plant tail gas treatment study for the refinery NSPS.

From this table it is apparent that the two Japanese processes, Diamox and Takahax, are not reported. As well due to differences in design assumptions these studies are not readily comparable. Nor is there one published overall cost comparison particularly for the lowest achievable emission rate technology paths:

(1) Sulfiban + Claus + Tail Gas Treatment
(2) Sulfiban + Double Contact/Double Absorption Sulfuric Acid

or in the case of $\leq$ 8 gr/100 dscf organic sulfur in foul gas

(3) Stretford + Holmes Waste Liquor
(4) Takahax + Hirohax, Elemental Sulfur, or Sulfuric Acid Recovery

Furthermore the representativeness (note, not the accuracy) of the Massey/Dunlop case studies is uncertain because: (1) they postulate an inlet (H_2S) of 500 grains, which is higher than the bulk of American coke plants (according to the experience of the various EPA Regional Enforcement Divisions and DSSE), and (2) competition in the U.S. is much keener in 1977 because of the positive developments at the Holmes' Orgreave project for Stretford, the three American Sulfiban plants and the entrance of Takahax into the American market than when the Massey/ Dunlop studies of 1971-1975 were developed.

One other difficulty in assessing the cost of achieving the LAER level is the role of organic sulfides. If a given coke-oven gas contains less than 8 gr H_2S equivaliet/100 dscf of COS and CS_2, then it is technologially possible for both Stretford and Takahax to achieve the LAER level This is not true of all coke-oven gases, however (see Section III and IV). Prediction of organic sulfide concentrations is difficult. For new coke batteries, therefore, costing the technology to achieve LAER is difficult. Extrapolation from existing batteries and coal blend data or from special field tests of new coals in existing ovens is one possibility for lessening such uncertainty. However, the fact remains that the cost of achieving the LAER level will be dependant upon the composition

For all of these reasons the validity and representativeness of the existing cost figures for coke-oven gas desulfurization are questionable. Table 19, 20 and 21 extracted from references (18) and (34) provide some baseline cost data. The reader is asked to study the specific references

Table 19. COSTS FOR COG DESULFURIZATION SYSTEMS AT REPUBLIC STEEL - CLEVELAND WORKS, $10³

	Holmes-Stretford			Sulfiban			Dravo-Still		
	Plant No. 1	Plant No. 2	Total	Plant No. 1	Plant No. 2	Total	Plant No. 1	Plant No. 2	Total
Capital requirement									
Battery limits plant, installed (BLP)[a]	7,450.0	5,400.0	12,850.0 (12,100.0)[b]	9,000.0	4,900.0	13,900.0	8,400.0	5,600.0	14,000.0
Site preparation and utilities,[c] 20% of BLP	1,490.0	1,080.0	2,570.0	1,800.0	980.0	2,780.0	1,680.0	1,120.0	2,800.0
Fixed capital investment (FCI)	8,940.0	6,480.0	15,420.0	10,800.0	5,880.0	16,680.0	10,080.0	6,720.0	16,800.0
Working capital,[d] 20% of gross operating cost	295.0	181.8	477.3	359.0	193.9	554.5	276.6	170.9	447.5
Total capital investment	9,235.0	6,661.8	15,897.3 (15,147.3)[b]	11,159.0	6,073.9	17,234.9	10,356.6	6,890.9	17,247.5
Annual operating cost									
Labor[e]	210.0	173.1	383.1	237.9	164.1	402.0	227.1	176.7	403.8
Administrative and general overhead,[d] 60% of labor	126.0	103.9	229.9	142.7	98.5	241.2	136.3	106.0	242.3
Utilities[e]	304.0	186.2	490.1	815.8	396.4	1,212.2	596.0	289.7	885.8
Materials[e]	596.0	270.9	866.9	307.2	161.8	469.0	151.2	100.8	252.0
Local taxes and insurance,[d] 2.7% of FCI	241.4	175.0	416.3	291.6	158.8	450.4	272.2	181.4	453.6
Gross operating cost	1,477.4	909.1	2,386.5	1,795.2	979.6	2,774.8	1,382.8	854.6	2,237.4
Sulfur by-product credit,[f] $40/ton	- 233.4	- 95.4	- 328.8	- 233.4	- 95.4	- 328.8	- 233.4	- 95.4	233.4
Net operating cost	1,244.0	813.7	2,057.7	1,561.8	884.2	2,446.0	1,149.4	759.2	2,004.0
Annualized cost									
Annualized capital cost[g]	940.7	678.5	1,619.2 (1,542.8)[b]	1,136.6	618.8	1,755.4	1,054.8	701.9	1,756.7
Federal income tax[d,h]	165.0	118.5	283.4 (270.5)[b]	199.4	108.6	308.0	184.1	122.2	306.3
Net operating cost	1,244.0	813.7	2,057.7	1,561.8	884.2	2,446.0	1,149.4	759.2	2,004.0
Average annual cost	2,349.7	1,610.7	3,960.3 (3,871.0)	2,897.8	1,611.6	4,509.4	2,388.3	1,583.3	4,067.0
Average annual control cost, $/lb S removed	0.180	0.302	0.215 (0.210)	0.222	0.302	0.245	0.183	0.296	0.221

[a] Vendor estimates, December 1975. Each plant is independent, including sulfur recovery.

[b] Wilpitte Corporation offered a reduced price if a contract was awarded to provide both facilities simultaneously.

[c] Site preparation, utility connections to battery limit plant, and COG connection to battery limit plant based on GCA review of similar costs reported in the literature.

[d] Based on Utility Financing Method as modified by the Panhandle Eastern Pipeline Company and described in Reference 42.

[e] See Tables 16 and 17.

[f] Conservative estimate based on price of $44/long ton received by SOHIO for by-product sulfur.

[g] Capital costs are amortized based on a discounted cash flow of 8 percent over 20 years.

[h] Average federal income tax = 1.731 percent of sum of total capital requirement and working capital

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Table 20. COSTS FOR 60×10^6 scfd COG DESULFURIZATION SYSTEMS AT YS&T 10^3, MAY 1976

	Holmes-Stretford	Sulfiban	Dravo-Still
Capital requirement			
Battery limits plant installed (BLP)[a]	$7,500.0	10,000.0	9,500.0
Site preparation and utilities,[b] 20% of BLP	1,500.0	2,000.0	1,800.0
Fixed capital investment (FCI)	9,000.0	12,000.0	11,300.0
Working capital,[c] 20% of gross operating cost	219.2	326.7	300.9
Total capital investment	9,219.2	12,326.7	11,600.9
Annual operating cost			
Labor[d]	210.9	255.9	245.4
Administrative and general overhead,[c] 60% of labor	126.6	153.6	147.3
Utilities[d]	304.0	595.4	637.4
Materials[d]	211.4	304.8	169.5
Local taxes and insurance,[c] 2.7% of FCI	243.0	324.0	305.1
Gross operating cost	1,095.9	1,633.7	1,504.7
Sulfur byproduct,[e] credit $40/ton	-233.6	-219.0	-219.0
Net operating cost	862.3	1,414.7	1,285.7
Annualized cost			
Annualized capital cost[f]	939.0	1,255.5	1,181.6
Federal income tax[c,g]	163.4	219.0	206.0
Net operating cost	862.3	1,414.7	1,285.7
Average annual cost	1,964.7	2,889.2	2,673.3
Average annual control cost, $/lb S removed	0.150	0.236	0.218

[a] Manufacturer estimates, May 1976.

[b] Site preparation, cost to bring utilities to the battery limit plant, and connect raw COG ducts to battery limit plant based on GCA review of similar costs reported in the literature.

[c] Based on Utility Financing Method as modified by the Panhandle Eastern Pipeline Company and described in Reference 18.

[d] See Tables 5 and 6.

[e] Conservative estimate based on price of $44/ton currently received by SOHIO for byproduct sulfur.

[f] Capital costs are amortized at a discount cash flow rate of 8 percent over 20 years. This method yields an average annual capital cost, including depreciation of 10.18 percent of total capital investment.

[g] Average federal income tax = 1.731 percent of sum of total capital investment and working capital.

Table 21. Desulfurization and Sulfur Recovery Plant Operating Requirements

Basis: 500 grains H_2S/100 SCF at inlet

Item	VACUUM CARBONATE 20MMSCFD 90%n	98%n	60MMSCFD 90%n	98%n	SULFIBAN PLANT 20MMSCFD 90%n	98%n	60MMSCFD 90%n	98%n	FIRMA CARL STILL 20MMSCFD 93%n	60MMSCFD 93%n	STRETFORD W/EFFLUENT TREATMENT 20MMSCFD 99%n	60MMSCFD 99%n
Desulfurization Plant												
Cooling H_2O, gpm[a]	1011	1314	3032	3942	530	1060	1590	3180	1400	4200	~0	~12
Power, KWH/day	1579	2526	4737	7579	1300	1300	4148	4148	4380[d]	11,220[d]	6000	18,000
Chemicals, #/day[c]	177	177	530	530	300	300	900	900	-	-	N.A.	N.A.
Steam, #/hr												
Actifier and/or Ejectors	5421	7179[b]	16,263	21,537[b]	5840	10,914	17,520	32,746	5500	16,000	-	-
Condensate Treatment	1120	1120	3380	3380	-	-	-	-	-	-	-	-
Total	6541	8299	19,643	24,917	5840	10,914	17,520	32,746	5500	16,000	2200	6600
Claus Sulfur Plant												
Steam Credits, #/hr												
High Pressure	558	607	1674	1824	558	607	1674	1824	558	1674	-	-
Low Pressure	282	307	846	922	282	307	846	922	282	846	-	-
Total	840	914	2520	2746	840	914	2520	2746	840	2520	-	-
Net Desulf. + Sulfur Plant Stm. demand, #/hr	5701	7385	17,123	22,171	5000	10,000	15,000	30,000	4660	13,480	-	-
Sulfuric Acid Plant												
Cooling H_2O, gpm[a,c]	230 (1241)	250 (1564)	690 (3722)	751 (4693)	230 (760)	250 (1310)	690 (2280)	751 (3931)	230 (1630)	690 (4890)	-	-
Power, KWH/day	1560 (3139)	1699 (4225)	4440 (9177)	4835 (12,414)	1560 (2860)	1699 (2999)	4440 (8588)	4835 (8983)	1560 (5940)	4440 (15,660)	-	-
Steam Credit (600 psig), #/hr	2220 (4321)	2417 (5882)	6670 (12,973)	7263 (17,654)	2220 (2780)	2417 (7583)	6670 (8330)	7263 (22,737)	2220 (3280)	6670 (9330)	-	-
Net System Manpower Requirements												
(i) Operator, man/shift	1	1	1	1	1	1	1	1	1	1	1	1
(ii) Chemist, hr/day	2	2	2	2	2	2	2	2	2	2	2	2

Footnotes:

(a) Vacuum Carbonate and Sulfiban plants use once-through river cooling water. Firma Carl Still plants employ cooling tower water. Note that costs per thousand gallons are different.

(b) Approximately 16 percent of stated steam rate is required to supply incremental heat to the actifier.

(c) Figures in parentheses represent net requirements for a combination of desulfurization and sulfuric acid plants.

(d) Refrigeration unit assumed operational 4 months out of a year. Power requirements with and without refrigeration unit are 6000 and 2880 KWH/day for 20MMSCFD, and 16,000 and 7200 KWH/day for 60MMSCFD, respectively.

(e) Na_2CO_3 for the Vacuum Carbonate plant, monoethanolamine for the Sulfiban plant. Information not available (NA) for Stretford technology.

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for a statement of assumptions and methods. To these data DSSE has added new supplementary vendor cost estimates.

In order to facilitate comparisons, Table 23 was prepared. The statistics of Tables 19-21 are adjusted in this comparison to place all technologies on a before tax and by-product credit basis. Due to the approximate year difference between the GCA and Dunlap/Massey estimations, the reader may wish to raise Massey/Dunlap costs by about 10% - 15%.

Amortized capitol plus operating costs are: 5.6 - 9.2¢/MCF for Stretford, 6.3 - 10.8¢ MCF for Sulfiban, and 7.1 - 11.3¢ MCF for Vacuum Carbonate. The Sulfiban capital cost estimate range ($7.07 - 10 million) appears to be confirmed by an independent estimate of Sulfiban's costs, shown in Table 22.

Tables 19-23 do not include the necessary cost of tail gas treatment for achievement of an overall 10 gr "H_2S"/100 dscf performance level by the liquid absorption processes. Nor do these tables show the differential costs of operating a liquid absorption tower/still column at the lowest clean COG H_2S concentrations. (Higher steam useage occurs at the lowest H_2S levels.) Table 25 indicates the differential steam demand for Sulfiban between 40 gr/100 scf and 5 gr/100 scf is about 7.9 MMBtu per ft^3 COG. Assuming $2.00/MMBtu* this works out to $506 per day or 1.58¢/MCF of COG. Therefore, the increased Sulfiban efficiency to achieve LAER increases operating and total amortized costs by about 25% and 15% respectively, with respect to the more restructive existing SIP's.

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*Includes fuel and boilerhouse operating costs.

Table 22.   RECENT (JANUARY 1977) VENDOR BID

1.   COG TO BE TREATED

 100,000,000 scfd

 250 gr/100 scf inlet H_2S

  19 gr/100 scf inlet O.S.

 2.2 inlet CO_2

  50 gr/100 dscf overall outlet

2.   DESIGN BASIS

 Sulfiban Plus Single Contact Sulfuric Acid

 In round figures:

  .$13 million total battery limits capital cost
  . $7 million - sulfiban
  . $6 million - acid plant

3.   (a) This capital cost is equivalent to 13¢/scf (Dunlap and Massey(1975))

      - 7.8¢/scf; GCAC (1976)
      - 13.9¢/MCF

     (b) The Sulfiban/acid plant ratio is 1.16 (Dunlap - 1.01)

Table 23. COMPARISON OF COG DESULFURIZATION COSTS

COST	500 gr → 10 gr:COG 95% - CP; 97.5% Acid Plant V.C. - DUNLAP				500 gr → 10 gr: COG 98% CP; 97.5% A.P. SULFIBAN - DUNLAP				SULFIBAN - GCA	500 gr → 10 gr STRETFORD		
	V.C. - Claus		V.C. - Acid		Acid		Claus		Claus	Dunlap	GCA	Wilputte
	20MM	60MM	20MM	60MM	20MM	60MM	20MM	60MM	60MM - Operating (70MM - Peak	60MM	60MM	60MM
Capital ($MM)	2.89	5.14	3.95	7.54	3.75	7.07	2.69	4.67	10.0	4.49	7.5	9.2
Annualized Capital ($/day)	747	1329	1021	950	970	1828	698	1208	2750	1161	2063	2493
Annualized Operating ($/Day)	1220	2985	1236	2964	1407	3491	1468	3743	3586	2178	2337	2986
Net Amortized Cost, Before Taxes												
.$/Day	1967	4304	2257	4914	3775	5319	2116	4951	6336	3339	4400	5479
.¢/MCF	9.84	7.14	11.29	8.19	6.29	8.87	10.83	8.25	10.56	5.57	7.33	9.16
(Before by-product credit)												
Estimate Date	First Quarter, 1975 Cost Estimates								5/76	1st Q. 1975	5/76	2/77

Table 24. COMPARISION OF ALTERNATIVE EMISSION CONTROL SYSTEM COSTS FOR A 10 LTD SULFUR PLANT
(Cost Adjusted to June, 1975)

| Control System | Total Costs | | | Differential Over Preceding Case | | | |
	Investment ($)	Annual Operating Cost ($/yr)	Emission Rate Total Sulfur As SO_2 (Lbs/hr)	Investment ($)	Annual Operating Cost ($/yr)	Emission Rate Total Sulfur As SO_2 (Lbs/hr)	Unit Cost ($/ton)
Base Case	$ 902,000	$133,600	93	-	-	-	18
Alternative I	1,028,000[a]	198,800[a]	19	126,000	65,200	74	210[b]
Alternative II							
Oxidation	1,320,000[a]	352,200[a]	2	292,000	153,400	17	2148[b]
Reduction	1,765,000[a]	442,000[a]	2	737,000	243,200	17	3406[b]

Notes:
(a) Includes costs of base case Claus sulfur recovery plant.
(b) Incremental costs per incremental ton of SO_2 recovered.

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Table 25.   ENERGY DEMANDS FOR COKE-OVEN GAS TECHNOLOGIES

Source	SULFIBAN - CLAUS PROCESS						STRETFORD		
	Massey & Dunlap	GCA (Y.S.& T.)	GCA (RSC-C#1)	GCA (RSC-C#2)	ATC	ATC	Massey & Dunlap	GCA (Y.S.& T.)	Wilputte
COG flow (MMSCFD)	60	60	65	33	32	32	60	60	60
Net Process Steam (lb/day)	720,000	672,000	700,000	308,000	211,300	447,000	158,400	68,900	34,300
Power (kwh/day)	4,148	10,920	13,200	8,880	3,600	3,000	18,000	29,760	21,900
Power (Btu per ft^3 COG)	0.72	1.91	1.31	2.83	1.18	0.98	3.15	5.21	3.84
Steam Energy (Btu/ft^3)	13.2	12.3	11.8	11.8	2.3	15.4	2.7	1.3	0.63
Total Energy Demand (Btu/ft^3)	13.9	14.2	13.1	14.6	8.5	16.4	5.9	6.5	4.47
lb steam/ 1000 ft^3	12.0	11.2	10.8	9.3	6.6	14.0	2.6	1.2	0.6
Basis (gr/ 100 scf) Inlet	500	464	461	381	475	475	500	464	500
Basis (gr/ 100 scf) Outlet	10	25	25	25	40	5	5	10	10

The differential capital and operating costs for high sulfur recovery

for the liquid absorption systems with respect to conventional Claus sulfur

recovery is shown in Table 24, which has been extracted from reference (13),

Page 8-12. The 10 long tons/day example plant cited in Table 24 is the size

of a Claus plant needed to recover sulfur from a 30 MMSCFD COG flow at 500 gr

H_2S/100 scf. This is exactly in the range of the discussion relevant to

Tables 19-22. Table 24 indicates that the increased capital investment

(20 yr, 8%, straight line) for the reduction tail gas systems (e.g., SCOT)

is ∿ 2.8¢ per MCF. The amortized increase for tail gas treatment of Claus

off-gas is ∿ 3.6¢/MCF or 33% over the baseline Sulfiban-Claus system of

Table 23. This last estimate, however, overstates the differential cost of

tail gas technology. Once in place, TGT equipment allows for a less effi-

cient Claus system since its tail gas is then being cleaned. In fact, this

is the process selection made for the Clariton coke works at which the two

Claus plants are only capable of ∿ 92% yield. The SCOT TGT system improves

this to 99.9% yield.

B. Energy Impact

The energy demands of COG desulfurizative technologies capable of

meeting the lowest achievable SO_2 emission rate are shown in Table 25.

Both electrical energy and process steam demands are considered. Elec-

trical energy is rated at 10,500 input Btu per kwh. Steam is assumed

to require 1100 Btu/lb.

Table 26.   RELATIVE ENERGY DEMAND OF COG DESULFURIZATION TECHNOLOGY

(COG FLOW - 20 MMSCFD)

	COG ENERGY DEMAND		
COG Heat Content	Stretford (5-10 gr) H_2S**	Sulfiban[a] (40 gr) TRS*	Sulfiban[b] (10 gr) TRS
16,500 $\frac{MMBtu}{Day}$	180 MMBtu/day 1.1%	255 1.6%	504 2.9%

(a)   Conventional Claus.

(b)   With tail gas treatment.

*Percentage of COG heat content used as process steam or electricty.

**Refers to gr/100 dscf of overall sweet COG plus tail gas emission. Add 5-25 gr organic sulfide (as H_2S) per 100 dscf to compare to Sulfiban.

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The range of total energy demands is 5-16 Btu/ft^3 COG processed. Liquid oxidation requires the least overall power because process steam demands are lower than for the liquid absorption processes. The energy cost per ft^3 COG rises sharply as the absorption processes are operated at higher H_2S removal efficiencies.

For example, to desulfurize to the lowest achieved level Sulfiban, 5 gr/100 scf, an additional 8 lb of steam per ft^3 of COG, a doubling from the 40 gr/100 scf level, is required.

The energy demand for COG desulfurization is expressed as a fraction of the energy content of COG produced in Table 26. COG is assessed at 550 Btu/ft^3. The energy demand, relative to the heat content of COG for conventional moderate sulfur recovery efficiency H_2S removal, and the highest efficiency case are shown in this table. An additional equivalent 1.3% of available COG heat value is needed to achieve the LAER value over the base case of an overall 40 gr "H_2S"/100 dscf, if Sulfiban is chosen. Note that the Stretford process is able to produce a high desulfurization efficiency (at least for H_2S) with lower energy requirements than for the Sulfiban process.

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2. Wilson and Wells, Coal, Coke and Coal Chemicals, first edition, McGraw-Hill, 1950, p. 240.

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4. Dunlap, R. W. and M. J. Massey, JAPCA 25(10) 1019-1027 (1975).

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6. Massey, M. J., "Comments on the Technology and Economies of Coke-Oven Gas Desulfurization," a 1971 working paper of the Allegheny County Air Pollution Control Advisory Committee, 301 39th Street, Pittsburgh, PA.

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Appendix A -- VENDORS OF COG TECHNOLOGY

PROCESS	VENDORS
Vacuum Carbonate	Frank Vedja Koppers Co. Coke Plant Project Department Engineerings & Contraction Division Chamber of Commerce Building Pittsburgh, PA. 15219 (412) 391-3300
Carl Still	J. Gordon Price Dravo Corp. 1 Oliver Plaza Pittsburgh, PA. 15272 (412) 566-3264
Sulfiban	Mark Peters Applied Technology Corp. 4242 Southwest Freeway Houston, TX. 77072 (713) 626-8000
Diamox	Mitsubish Chemical Ind., Ltd. 277 Park Avenue New York, NY. (212) 922-3771
Takahax	Mr. Yamasaki Nippon Steel Corp. 345 Park Avenue New York, New York (212) 486-7150
Stretford	Walter Carbone 12 Floral Park Avenue Murray Hill, NJ. (201) 464-5900

Appendix A - VENDORS OF COG TECHNOLOGY (cont'd)

PROCESS   VENDORS

Sulfuric Acid   Don Pogue
                                  Enviro Chem Division
                                  Lindberg Road
                                  Monsanto Chemical
                                  St. Louis, Missouri

APPENDIX B – J&L Field DATA BY Honeywell GC

Date	Time	Avg. COS, ppm	Avg. CS₂, ppm	No. Analyses	H₂S Equivalent, gr/scf COS	H₂S Equivalent, gr/scf CS₂
Jan 7, 1974	812-1607	55	82	39	3.5	9.05
	1607-2402	60	85	38	3.8	10.7
Jan 15	933-1613	35	54	33	2.2	6.7
	1613-2408	40.5	53	38	2.6	6.7
July 10	840-1615	98	139	42	6.16	17.7
	1615-2400	104	139	42	6.55	17.7
July 11	2400-807	100	139	39	6.3	17.7
	807-1603	99	139	42	6.2	7
	1603-2400	94	118	44	5.9	14.7
July 12	2400-806	106	95	42	6.6	12.0
	806-1602	90	89.5	42	5.7	11.3
	1602-2409	84	64	43	5.3	8.0
July 13	2409-805	93	62	42	5.85	7.8
	805-1601	51	56	42	3.2	7.0
	1601-2408	77	52	43	4.9	6.5
July 14	2408-804	76	51	42	4.9	6.4
	804-1600	67	52	42	4.2	6.5
	1600-2408	74	64	43	4.7	8.1
July 15	847-1600	79	70	39	5.0	8.8
	1600-2407	77	64	42	4.9	8.0
July 25	842-1600	97	136	40	6.1	17.0

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