

Session III: CONTROL TECHNOLOGY DEVELOPMENT

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SELECTION OF ACID GAS TREATING PROCESSES FOR COAL CONVERTER OUTPUTS

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Abstract

Many factors must be evaluated in the selection of acid gas removal processes for coal-derived converter output gases. Some of these considerations, among others, include the gasification process, the sulfur content of the coal, the presence of other contaminants and their effects, the end use of the product, and the multitude of clean-up processes and their economics. While the limited scope of this paper will not permit an in-depth examination of such a complex subject, some generalization will be discussed and applied to some typical cases. One aspect to be discussed is the influence of the sulfur content of coal on the selection process for different converter systems. Typical situations to be examined include a high pressure (1000 psi) case for SNG, an intermediate pressure (400 psi) case for turbins fuel, and a low pressure (atmospheric pressure or slightly above) for industrial fuel.

Generalization for the selection of acid gas treating processes on coal converter output gases is not easily made. Many different factors must be evaluated in order to select from an expanding list of available acid gas removal processes. It will only be possible to examine a few of these aspects within the limited scope of this paper.

One of the most important factors, the sulfur content of coal, provides a starting point for this discussion. Sulfur reports to the output gas primarily as H_2S almost proportionately to its content in coal. The particular process used for gasification of the coal has a relatively minor influence.

In contrast, the carbon dioxide content of gas is greatly dependent on the gasification system. A generalized gasifier performance chart illustrating the carbon dioxide fraction of

carbonaceous product gases as a function of H_2/CO ratio is given in Figure 1. In some cases, reactions like the water gas reaction, combustion and methanation proceed further and contribute to variation in product composition.

The difference in the way that sulfur and carbon report is significant because the H_2S/CO_2 ratio and the carbon dioxide partial pressure in the converter output gas is relevant to acid gas removal process selection. Solution oxidation processes such as Stretford or Takahax, which remove H_2S and convert it directly to sulfur, require a high pH in the absorbent solution. High CO_2 concentration lowers the solution pH, and in turn, the rate of H_2S mass transfer in the Stretford solution. As a result, many Stretford process absorbers have ended up being extremely large towers to compensate for low mass transfer rates. The Holmes version of the Stretford process uses an improved gas-solution contacting technique, but even so, high CO_2 concentrations must still be considered carefully when using this process.

The general practice of industry for bulk acid gas clean-up has been to absorb the acid gas from the product gas, convert the H_2S to sulfur by the Claus process and now, to meet environmental demands, clean-up the Claus tail gas with a third process. To become the favored method for bulk acid gas clean up, the selected step-wise approach was undoubtedly governed by economics, and the effect of the gas on solution pH certainly was a contributing factor. Because the Claus process has been so important in most acid gas removal schemes, the influence of sulfur in coal and converter output on the Claus process must be factored into the selection of acid gas removal processes.

Let's look at some typical converter output gas compositions in Table 1. A general, but perhaps not all inclusive, range of gas compositions from low to high CO_2 contents are shown for both oxygen and air blown converters. The data is presented on a dry and sulfur-free basis. Bi-Gas and Wilputte data have been included for later use.

A stoichiometric conversion of sulfur in coal to H_2S in the output gas may be used to develop an equation for an H_2S/CO_2 ratio in the raw product gas as a function of percent sulfur

LEGEND

- △ Riley-Morgan
- ⊕ Wilputte
- Winkler
- Woodall-Duckham/Gas Integrale
- ▲ Wellman-Galusha
- Koppers-Totzek
- ⊖ Lurgi
- Fixed Bed Generator (Anthracite)
- ⊙ Morgantown, W. Va. Data

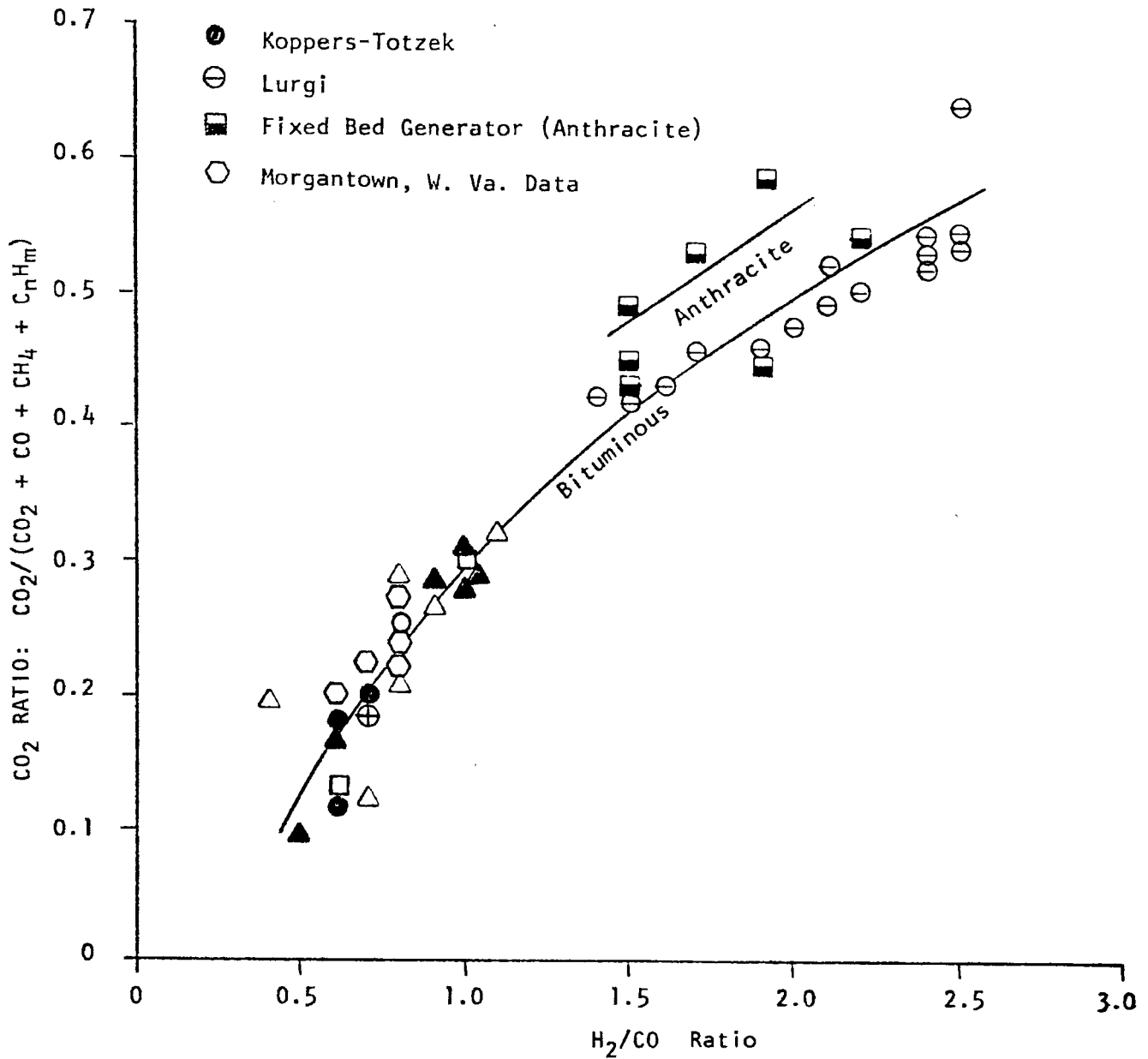


Figure 1. Generalized performance of gasifiers.

TABLE 1
TYPICAL CONVERTER OUTPUT GAS COMPOSITIONS

DATA SOURCE	OXYGEN BLOWN PROCESSES			AIR BLOWN PROCESS		
	KOPPERS -TOTZEK	BI-GAS	LURGI	WELLMAN- GALUSHA	WILPUTTE	LURGI
	LOW		HIGH	LOW		HIGH
CO ₂ CONTENT COMPONENTS, VOL. %						
CO ₂	7	22	32	3	6	15
CO	57	29	17	29	23	15
H ₂	35	32	40	15	17	24
N ₂	1	1	1	50	50	40
CH ₄	--	16	10	3	4	6

BASIS: DRY AND SULFUR-FREE GAS

in coal. This ratio designated by the letter Y in Table 2 will later be used to provide a guide for determining the need for selective H₂S removal. To correct for losses to other sulfur outlets such as tar or ash, a correction factor, S_r, has been applied. The conversion efficiency, E, used by the equation is the percent of output gas Btu content divided by the Btu content of the process coal. For simplicity, the sulfur recovery and efficiency factors have been arbitrarily set at values of 100 and 75 in the remaining discussion. A sample calculation for a 5 percent sulfur coal is also shown in Table 2.

In Figure 2, a plot of the H₂S ratio versus percent sulfur in coal has been made using points calculated from the H₂S/CO₂ ratio equation as boundary lines. Data taken from actual gasifier operation have been plotted to support the theoretical analysis. Note that the Koppers-Totzek points fall just about on the upper line. The other data points fall within the general area of these arbitrary boundaries to form a typical area of operation.

Two horizontal lines equivalent to 10 and 15 percent H₂S in acid gas have been incorporated on the H₂S ratio graph in Figure 3. These values¹ were chosen because the economic use of the Claus process probably becomes marginal at about this range. One point evident from this chart is that selective absorption of H₂S will, in many cases, be necessary when using the Claus process. Physical solvents are well known for their selective absorption capabilities, and will, consequently, find appropriate applications in coal gasification. Some chemical solvents do have some selective absorption capability and this aspect will have to be taken carefully into account in coal gasification applications.

Now let's take a few coal gasification cases and examine what might be considered in the selection of acid gas removal processes. As might be expected, it will not be possible to present a cookbook approach to an undisputed choice for acid gas removal, but some points to be taken into account will be covered including selections using a recently published guideline.² The cases which were made to represent typical future situations are:

I. Coal gasification at the 1000 psi level for

SNG manufacture and shown in Tables 3 and 4.

- II. Coal gasification at the 400 psi level for turbine fuel and shown in Tables 5 and 6.
- III. Coal gasification just above atmospheric pressure for industrial fuels and shown in Tables 7 and 8.

Process recommendations which were illustrated in Tables 4, 6, and 8 were physical solvent acid removal processes for the two high pressure cases and a chemical conversion process for the low pressure application. The major missing ingredient in this discussion is comparative economics. The reason is that this information is so difficult to obtain and has such a fragile nature when available. It depends so much on the specifics of the particular application, the environmental constraints, the periods of time and even individual discretion in process and cost estimation. However, some guidelines have been demonstrated and, in particular, a look at the estimated acid gas composition from coal and its impact on process selection has been illustrated by examples.

REFERENCES

1. R. F. Robards, et al., Evaluation of H₂S Removal Process for Desulfurization of Coal Gas, Fourth Energy Resource Conference, January 7-8, 1976, University of Kentucky, Lexington, Kentucky.
2. R. N. Tennyson and R. P. Schaaf, "Guidelines Can Help Choose Proper Process for Gas-Treating Plants," *Oil and Gas Journal*, January 10, 1977.
3. B. S. Lee, "Hygas Pilot Plant Yields Operating Data," *Oil and Gas Journal*, February 11, 1974.
4. J. F. Farnsworth, et al., "Coal Gasification System Could Ease Energy Supply Pinch," *33 Magazine/The Magazine of Metal Producing*, August 1973.
5. L. L. Newman, "Oxygen In the Production of Hydrogen or Synthesis Gas," *Industrial and Engineering Chemistry*, Vol. 40, No. 4, April, 1948.
6. HRI Files on Lurgi data collected in technical mission to Europe after World War II. (Hydrocarbon Research, Inc. is a wholly owned subsidiary of Dynalectron

TABLE 2
SULFUR RATIO IN CONVERTER OUTPUT GAS

AN EQUATION FOR THE RATIO OF HYDROGEN SULFIDE TO
CARBON DIOXIDE IN CONVERTER OUTPUT GAS IS:

$$Y = 11.82 \left(\frac{S_c}{C} \frac{S_r}{E} \frac{H_g}{H_c} \right)$$

WHERE:

- Y = H₂S TO CO₂ RATIO IN RAW OUTPUT GAS
- S_c = PERCENT BY WEIGHT SULFUR IN COAL
- S_r = PERCENT SULFUR REPORTING TO OUTPUT GAS
- H_g = HIGH HEATING VALUE OF THE OUTPUT GAS
- C = PERCENT BY VOLUME CO₂ IN OUTPUT GAS
- E = COAL TO GAS PERCENT EFFICIENCY
- H_c = HIGH HEATING VALUE OF THE COAL

ASSUMPTION: ALL SULFUR IN OUTPUT GAS AS H₂S

EXAMPLE CALCULATION:

$$Y = 11.82 \left(\frac{5.0}{7} \times \frac{100}{75} \times \frac{300}{12,000} \right) = 0.281$$

H₂S/CO₂ Ratio

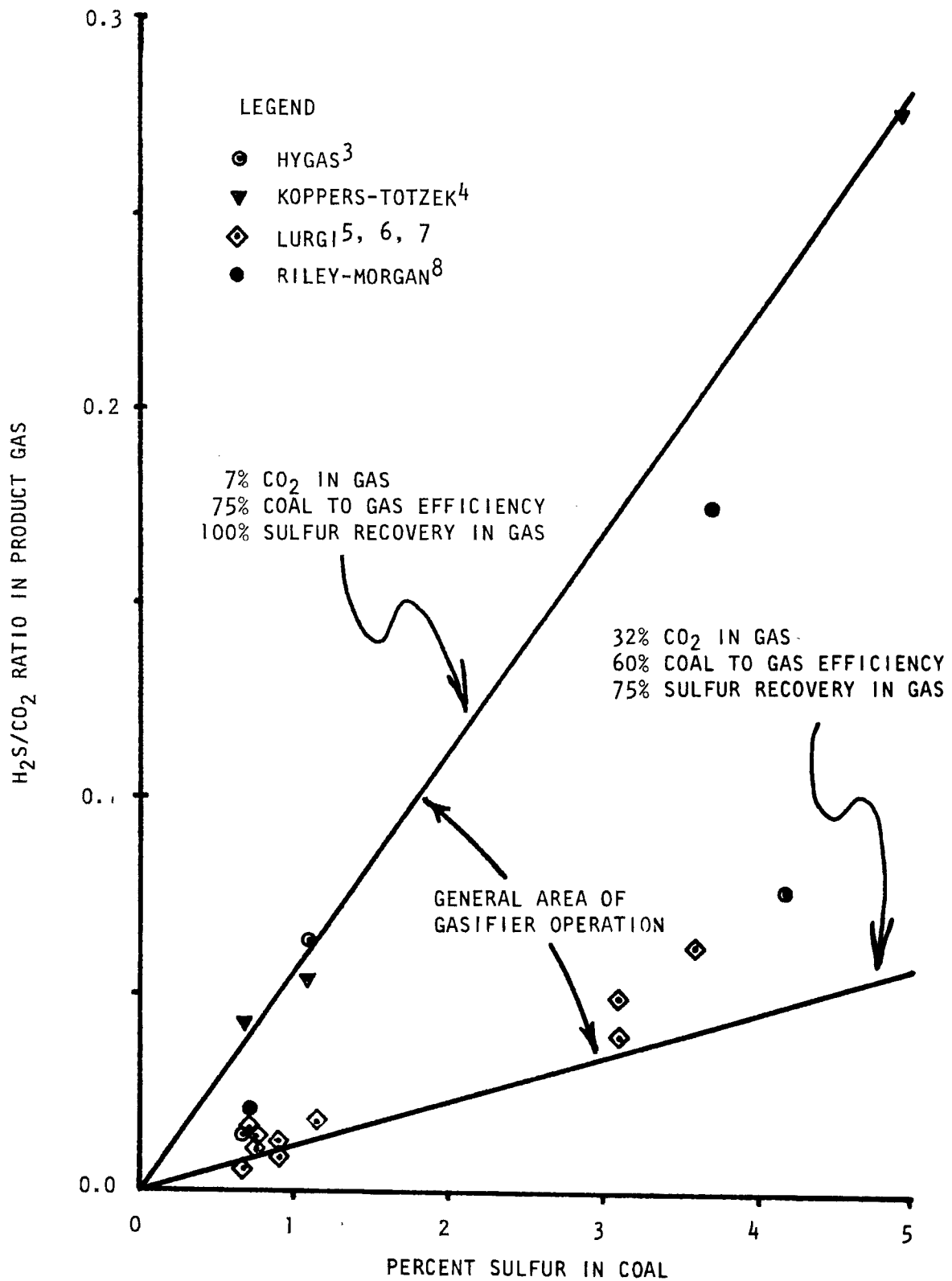


Figure 2. Sulfur transfer to gas in coal gasification.

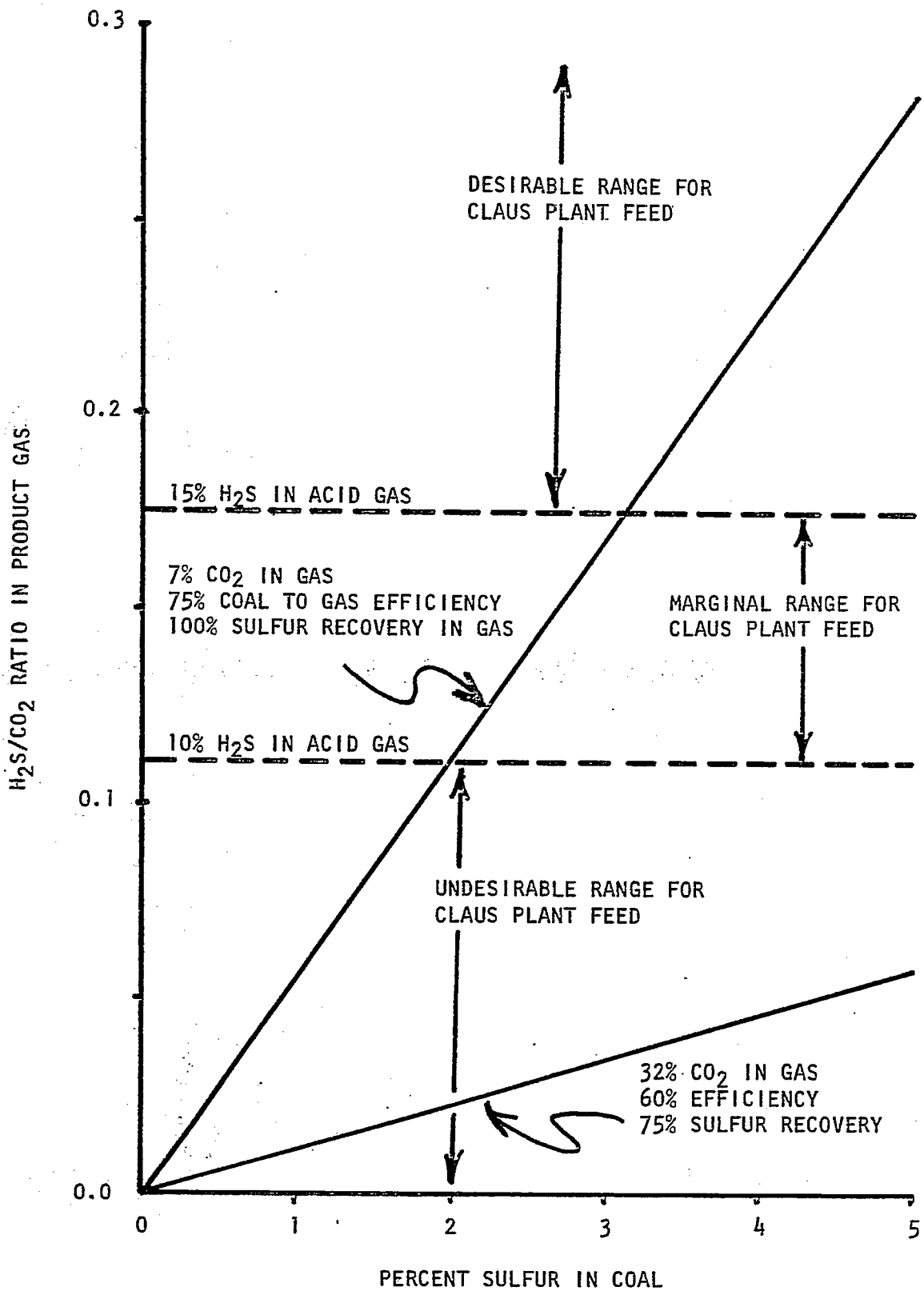


Figure 3. Sulfur transfer to gas in coal gasification.

TABLE 3
EXAMPLE I – GAS REMOVAL SELECTION FACTORS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	BI-GAS	~1000 PSI	4%	SNG

GENERAL CONSIDERATIONS

- ° LOW LEVELS OF H₂S AND CO₂ ARE REQUIRED
- ° CONSERVATION OF GAS HEAT CONTENT IS DESIRABLE

STRETFORD PROCESS CONSIDERATIONS

- ° CONVERTER OUTPUT CO₂ IS 22% OR ~200 PSI PARTIAL PRESSURE
- ° CO₂ PARTIAL PRESSURE IS TOO HIGH

CLAUS PROCESS CONSIDERATIONS

$$Y = 11.82 \left(\frac{S_c}{C} \frac{S_r}{E} \frac{H_g}{H_c} \right) = \frac{11.82 \times 4 \times 100 \times 360}{22 \times 75 \times 12,000} = 0.086$$

- ° H₂S PARTIAL PRESSURE IN PRODUCT GAS = ~20 PSI
- ° H₂S PERCENT OF TOTAL ACID GAS = 8%
- ° SELECTIVE ABSORPTION IS REQUIRED FOR CLAUS ECONOMY

TABLE 4

EXAMPLE I - ACID REMOVAL PROCESS RECOMMENDATIONS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	BI-GAS	~1000 PSI	4%	SNG

GUIDELINE² CHOICES

- ° SIMULTANEOUS REMOVAL OF H₂S AND CO₂
 ABOVE 75 PSI ACID GAS PRESSURE IN FEED AND BELOW 1 PSI ACID GAS PRESSURE IN PRODUCT - ECONOMINE, HIGH LOADING DEA OR SELEXOL
- ° SELECTIVE H₂S REMOVAL IN PRESENCE OF CO₂
 3 TO 60 PSI H₂S PRESSURE - ADIP
 ABOVE 60 PSI H₂S PRESSURE - RECTISOL OR SELEXOL
- ° COMMENT: USE SELECTIVE ABSORPTION TO IMPROVE CLAUS FEED

SPECIAL CONSIDERATIONS (COAL DERIVED GAS PROCESSED TO SNG)

- ° ADIP - PARTICULATES, TARS AND OILS CAN CAUSE FOAMING
 - CS₂, MERCAPTANS, COS CAUSE SOLVENT LOSSES
- ° RECTISOL - APPLIED AT SASOL PLANT
 - REMOVES COS, CS₂ AND HCN
 - REFRIGERATION: EXPENSIVE AND HEAT LOSSES
- ° SELEXOL - SOLVENT NOT DEGRADED BY IMPURITIES
 - REMOVES SOME COS, CS₂, NH₃ AND HCN

RECOMMENDATIONS

- ° SELEXOL WOULD BE A GOOD SELECTION AND IT HAS BEEN CHOSEN FOR BI-GAS PILOT PLANT AT HOMER CITY
- ° FINAL DECIDING FACTOR DEPENDS ON ECONOMICS AND TEST RESULTS

TABLE 5

EXAMPLE II - ACID GAS REMOVAL SELECTION FACTORS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	AIR BLOWN LURGI	~400 PSI	4%	TURBINE FUEL

GENERAL CONSIDERATIONS

- ° SULFUR REMOVAL REQUIREMENTS LESS STRINGENT THAN FOR SNG
- ° CONSERVATION OF GAS HEAT CONTENT IS DESIRABLE
- ° CO₂ REMOVAL IS UNDESIRABLE

STRETFORD PROCESS CONSIDERATIONS

- ° CONVERTER OUTPUT CO₂ IS 15% OR ~60 PSI PARTIAL PRESSURE
- ° CO₂ PARTIAL PRESSURE IS PROBABLY TOO HIGH
- ° LOWER HEAT EFFICIENCY THAN HIGH TEMPERATURE PROCESSES

HIGH TEMPERATURE PROCESS CONSIDERATIONS

- ° FRODINGHAM AND OTHER DRY IRON OXIDE PROCESSES
 - UNDER DEVELOPMENT OR NOT YET PROVEN
 - SO₂ BY-PRODUCT
- ° HOT CARBONATE PROCESS
 - ALKALI METAL CARRY-OVER IS VERY DAMAGING TO TURBINE
 - BEING TESTED FOR THIS APPLICATION AT POWERTON PLANT IN ILLINOIS

CLAUS PROCESS CONSIDERATIONS

$$Y = 11.82 \left(\frac{S_c}{C} \frac{S_r}{E} \frac{H_g}{H_c} \right) = \frac{11.82 \times 4 \times 100 \times 180}{15 \times 75 \times 12,000} = 0.063$$

- ° H₂S PARTIAL PRESSURE IN PRODUCT GAS = ~4 PSI
- ° H₂S PERCENT OF TOTAL ACID GAS = 6%

TABLE 6

EXAMPLE II - ACID GAS REMOVAL PROCESS RECOMMENDATIONS

STUDY BASIS:	CONVERTER AIR BLOWN LURGI	PRESSURE ~ 400 PSI	SULFUR IN COAL 4%	END USE TURBINE FUEL
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GUIDELINE² CHOICES

° SELECTIVE H₂S REMOVAL IN PRESENCE OF CO₂

3 TO 60 PSI H₂S PRESSURE - ADIP

BELOW 3 PSI H₂S PRESSURE - STRETFORD, VETROCOKE OR ADIP

SPECIAL CONSIDERATIONS (COAL-DERIVED GAS PROCESSED TO TURBINE FUEL)

- ° ADIP
 - PARTICULATES, TARS AND OILS CAN CAUSE FOAMING
 - CS₂, MERCAPTANS, COS CAUSE SOLVENT LOSSES
- ° VETROCOKE
 - CONTAINS ARSENIC AND ALKALI SALTS
- ° FRODINGHAM
 - NOT ESTABLISHED AND SO₂ PRODUCT
- ° HOT CARBONATE
 - POTENTIAL PROBLEM WITH ALKALI SALT

RECOMMENDATIONS

- ° PHYSICAL SOLVENT PROCESS
- ° FINAL DECIDING FACTOR WOULD PROBABLY DEPEND ON ECONOMICS

TABLE 7
EXAMPLE III — ACID GAS REMOVAL SELECTION FACTORS

STUDY BASIS:	CONVERTER WILPUTTE	PRESSURE ABOVE ATMOSPHERIC	SULFUR IN COAL 4%	END USE INDUSTRIAL FUEL
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GENERAL CONSIDERATIONS

- ° SPECIFIC END USE WILL BE INFLUENTIAL
- ° SULFUR REMOVAL REQUIREMENTS LESS STRINGENT THAN FOR SNG
- ° CO₂ REMOVAL PROBABLY NOT NECESSARY

STRETFORD PROCESS CONSIDERATIONS

- ° SATISFACTORY FOR LOW H₂S PARTIAL PRESSURES
- ° SELECTIVELY REMOVES H₂S
- ° LOW CO₂ PARTIAL PRESSURE IS AVAILABLE

CLAUS PLANT CONSIDERATIONS

$$Y = 11.82 \left(\frac{S_c}{C} \frac{S_r}{E} \frac{H_g}{H_c} \right) = \frac{11.82 \times 4 \times 100 \times 160}{6 \times 75 \times 12,000} = 0.141$$

- ° H₂S PARTIAL PRESSURE IN PRODUCT GAS = ~ 0.2 PSI
- ° H₂S PERCENT OF TOTAL ACID GAS = 12%
- ° SELECTIVE ABSORPTION SUGGESTED FOR CLAUS ECONOMY

TABLE 8

EXAMPLE III - ACID GAS REMOVAL PROCESS RECOMMENDATIONS

STUDY BASIS:	CONVERTER	PRESSURE	SULFUR IN COAL	END USE
	WILPUTTE	ABOVE ATMOSPHERIC	4%	INDUSTRIAL FUEL

GUIDELINE² CHOICES

- ° SELECTIVE H₂S REMOVAL IN PRESENCE OF CO₂
BELOW 3 PSI H₂S PARTIAL PRESSURE - STRETFORD, VETROCOKE OR ADIP

SPECIAL CONSIDERATIONS (COAL-DERIVED GAS TO INDUSTRIAL FUEL)

- ° ADIP
 - PARTICULATES, TARS AND OILS CAN CAUSE FOAMING
 - CS₂, MERCAPTANS, COS CAUSE SOLVENT LOSSES
- ° VETROCOKE - CONTAINS ARSENIC
- ° STRETFORD: ADDITIONAL POINTS FOR THE APPLICATION
 - PREVIOUSLY APPLIED TO COAL DERIVED GASES
 - NITROGEN COMPOUNDS, IF TOO HIGH TO BE TOLERATED, CAN BE REMOVED BY PRETREATMENT
 - MAKES ELEMENTAL SULFUR

RECOMMENDATION

- ° SOLUTION OXIDATION PROCESS SUCH AS STRETFORD

Corporation.)
7. R. E. Morgan, et al., Lurgi-Gasifier Tests of Pennsylvania Anthracite, Bureau of Mines, Report of Investigations 5420, 1958.

8. A. H. Rawdon, et al., NO_x Formation in Low and Intermediate Btu Coal Gas Turbulent-Diffusion Flames, Proceedings NO_x Control Technology Seminar, EPRI, San Francisco, February 1976.