Chemical Removal of Pyritic Sulfur from Coal

J. W. Hamersma, M. L. Kraft, E. P. Koutsoukos, and R. A. Meyers

TRW Systems Group, One Space Park
Redondo Beach, California 90278

INTRODUCTION

The Meyers Process for the chemical removal of pyritic sulfur from coal is a TRW proprietary process (1) which is currently in a bench scale development phase under the sponsorship of the Demonstration Projects Branch of the Environmental Protection Agency. Laboratory results, which preceded the current bench scale activities, are presented here. These results show that 40-75% of the total sulfur content, corresponding to near 100% of the pyritic sulfur can be removed from all coals tested utilizing a mild aqueous extraction. The background for the process concept and a summary of the results of over one hundred coal extractions are presented below.

BACKGROUND

The concept of chemically removing pyrites from coal has not heretofore been advanced as a solution to the sulfur oxide air pollution problem as it is known that iron pyrites are insoluble in any known liquids. For example, the acids hydrochloric, hydrofluoric, sulfuric or combinations of these, which dissolve many inorganic salts have little or no effect on iron pyrites. On the other hand, it is well known that pyrites may be oxidatively converted to sulfates, soluble in strong acid, by strong oxidizing agents such as nitric acid or hydrogen peroxide. In fact, they have long been used for the analysis of the pyritic sulfur content of coal. However, these reagents have never seriously been advanced as a method for lowering the sulfur content of coal, because even though they are strong enough to dissolve pyrite, they also oxidize (in the case of nitric acid, nitrate) the coal matrix. Thus, it was not thought possible to devise a process for chemically removing or dissolving the pyritic sulfur content of coal.

In order to provide an economically viable process for the chemical removal of pyrites from coal, it would be necessary to utilize an oxidizing agent (most likely aqueous) which is a) selective to pyrite, b) regenerable, and c) highly soluble in both oxidizing and reduced form. It was discovered

that either ferric sulfate or ferric chloride meets the above combination of requirements, and these reagents form the basis of the process chemistry which is described in this paper.

CHEMISTRY

In the Meyers Process, aqueous ferric sulfate or chloride (mild but effective oxidizing agents) selectively oxidize the pyritic sulfur content (2) (3) of coal to form free sulfur and sulfate which dissolves into the aqueous solution. The free sulfur may then be removed from the coal matrix by steam or vacuum vaporization or solvent extraction (4) and the oxidizing agent may be regenerated and recycled. The chemistry is outlined in eqs 1-4 below.

$$2\ Fe^{+3} + FeS_2 \longrightarrow 3\ Fe^{+2} + 2S \qquad (1)$$

$$14\ Fe^{+3} + 8\ H_2O + FeS_2 \longrightarrow 15\ Fe^{+2} + 2\ SO_4^{=} + 16H^+ \qquad (2)$$

$$S \cdot Coal \longrightarrow S + Coal \qquad (3)$$

$$3\ Fe^{+2} + 3/2\ [O] \longrightarrow 3\ Fe^{+3} + 3/2\ [O=] \qquad (4)$$

The aqueous extract solution which contains iron in both the ferrous and ferric state, may be regenerated, in any number of ways, including air oxidation of the ferrous ion to ferric (eq 4) (5). Another fortunate aspect of this process lies in the fact that "iron is used to remove iron", so that on regeneration it is not necessary to separate the iron which is extracted from the coal from a metal oxidizing agent.

The experimental method is quite simple, involving treatment of coal with aqueous ferric chloride or sulfate solution at approximately 100°C to convert the pyritic sulfur content to elemental sulfur and sulfate. The aqueous solution is separated from the coal and the coal is washed to remove residual ferric salt. The elemental sulfur which is dispersed in the coal matrix is then removed by vacuum distillation or extraction with a solvent such as toluene or kerosene. The resulting coal is basically pyrite free and may be used as low sulfur fuel.

RESULTS

Four coals were selected for process evaluation whose sulfur form distribution is typical of coals east of the Mississippi River and which represent major United States coal beds: Pittsburgh, Lower Kittanning, Illinois #5 and Herrin #6. The Pittsburgh bed has been described as the most valuable individual mineral deposit in the United States and perhaps in the world. Its production accounts for approximately 35% of the total cumulative production of the Appalachian bituminous coal basin to January 1, 1965, and 21% of the total cumulative production of the United States to that date (6). The Lower Kittanning bed together with its correlative beds contains even larger reserves than the Pittsburgh seam. The No. 5 bed is the most widespread and commercially valuable coal bed in the Eastern interior coal basin. The Herrin No. 6 bed is second in commercial importance only to the No. 5 bed.

Analysis fo the four coal samples that were used for this study are shown in Table 1. The indicated tolerances are the standard deviations. Five or more coal samples were used for sulfur, ash and heat content analyses while three or more samples were used for sulfur forms analysis (7).

Table 1

Dry Analyses of Coals

	Lower Kittanning	Illinois #5	Pittsburgh	Herrin #6
Pyritic Sulfur	3.58 ± .08	1.57 ± .03	1.20 ± .07	1.65 ± .04
Sulfate Sulfur	0.04 ± .01	0.05 ± .01	0.01 ± .01	0.05 ± .01
Organic Sulfur	0.67 ± .10	1.86 ± .04	0.68 ± .16	2.10 ± .06
Total Sulfur	4.29 ± .06	3.48 ± .03	1.88 ± .07	3.80 ± .04
Ash	20.77 ± .59	10.96 ± .26	22.73 ± .48	10.31 ± .28
Btu	12,140 ± 55	12,801 ± 58	11,493 ± 60	12,684 ± 55
Rank	Medium Volatile Bituminous	High Volatile B Bituminous	High Volatile A Bituminous	High Volatile B Bituminous

Both ferric chloride and ferric sulfate have been used in this study with good results. However, from a process standpoint, ferric sulfate has the following advantages: a) it is less corrosive, b) regeneration is less complicated and expensive in that the iron sulfate formed (equation 2) does not have to be separated from iron chloride, and c) the removal of residual leach solution is easier and therefore more economical.

It has been found that the extent of the reaction indicated by equation 2 relative to that of equation 1 or the sulfate to sulfur ratio to be 2.4 $\pm$ .2 when rock pyrite is used and 1.4 $\pm$ .4 for sedementary pyrite found in the coals used in this work. Although both materials are FeS_2 of the same crystal structure, differences in reactivity have been documented which have been attributed to impurities and crystal defects peculiar to the various possible modes of formation (3a). In the case of coal, no significant variation in this ratio was found with ferric ion concentration, acid concentration, coal or reaction time. The results for each coal are found in Table 2.

Table 2

Sulfate to Sulfur Ratio for Extraction of Coal and Mineral Pyrite with Ferric Chloride Solution

Substrate	Sulfate to Sulfur Ratio (Average All Runs)
Mineral Pyrite	2.4 $\pm$ .2[a]
Lower Kittanning	1.4 $\pm$ .3
Illinois #5	1.6 $\pm$ .4
Pittsburgh	1.3 $\pm$ .3
Herrin #6	1.4 $\pm$ .3

[a]Standard deviation

A systematic parametric study was made in order to determine the effect of acid concentration, coal particle size, ferrous and sulfate ion concentration, and reaction time, on pyrite removal. These parameters were studied using conditions (see Experimental) that give 40-70% pyritic sulfur removal

so that the effects of parameter variations are clear and not be so small as to be masked by experimental error as when removal is greater than 85-90%. In addition, studies were performed to demonstrate 90-100% pyritic sulfur removal with both ferric chloride and sulfate as well as a set of experiments that were designed point up differences between ferric sulfate and ferric chloride.

The effect of added hydrochloric acid concentration was studied in order to determine whether or not the acid had any effect on pyrite and ash removal, sulfate/sulfur ratio, final heat content and whether high HCl concentrations chlorinated the coal. Since coal has many basic ash constituents, increased ash removal was expected as well as some suppression of the sulfate to sulfur ratio since the reaction that results in sulfate formation also yields eight moles of hydrogen ion per mole of sulfate (common ion effect). Added acid was studied in the range of 0.0 to 1.2M using concentrations of 0.0, 0.1, 0.3 and 1.2M hydrochloric acid in 0.9M ferric chloride. Duplicate runs were made at each concentration with all four coals for a total of 32 runs. The results showed no clear cut trends even (except one-*vide infra*) when the data was smoothed via computer regression analysis. Apparently, the concentration range was not broad enough to have any substantial effect on the production of sulfate or to cause the removal of additional ash over that which is removed by the pH of 1M ferric chloride ($\sim$pH 2).

An important consideration in any chemical process is the selectivity for the desired reaction. In the case of oxidative leaching of pyrite by ferric ion, the extent of the reaction of the reagent with the coal matrix has a major effect on the process economics. We have found that the extent of this reaction varies from small to substantial depending on the acid concentration, coal, and ferric anion. In order to define this effect quantitatively, the ratio of actual mmoles of ferrous ion produced to the mmoles of ferrous ion necessary to produce the sulfate and elemental sulfur that was recovered was calculated for each run (see equations 1 and 2). This ratio, Fe(II)[Experimental]/Fe(II)[Calculated], has a value of one for 100% selectivity and a higher value for less than 100% selectivity. The data, for ferric chloride, in Table 3 were smoothed by linear regression

analysis using the values generated in the acid matrix while the ferric sulfate values are the average of triplicate runs.

Table 3

Variation of Ferric Ion Consumption with Acid Concentration and Ferric Anion

Coal	Fe(II)(Expt)/Fe(II)(Calc)		
	0.9N $FeCl_3$		0.4N $Fe_2(SO_4)_3$
	0.0M HCl	1.2M HCl	0.0M H_2SO_4
Lower Kittanning	1.2	1.4	1.2
Illinois No. 5	3.8	6.6	1.6
Pittsburgh	2.2	3.4	1.5
Herrin No. 6	3.7	6.4	2.4

It is readily apparent that the higher ranked Appalachian (Lower Kittanning and Pittsburgh) coals react to a lesser extent with ferric ion under all experimental conditions than the lower ranked Eastern interior (Illinois #5 and Herrin #6) coals. In addition, the ferric chloride runs show that a very substantial acid catalyzed reaction occurs in this system which is most evident for the Illinois #5 and Herrin #6 coals. In these coals, a reduction of about 42% in ferric ion consumption is observed when the starting HCl concentration is reduced from 1.2M to 0.0M. The corresponding reductions for Pittsburgh and Lower Kittanning coals are 35% and 14% respectively. When ferric sulfate is used, further reductions in ferric ion consumption ranging from 3% for Lower Kittanning coal to 63% for Illinois #5 coal are observed. From these early data, it appears that ferric sulfate is the preferred form of ferric ion in order to increase selectivity.

The data listed in Table 4 illustrate the effect of top mesh size on pyritic sulfur removal. The coal samples were prepared by the same comminution techniques and consequently, the size distribution of the samples should be

Table 4

Effect of Top Mesh Size on Pyritic Sulfur Removal

Coal	Sulfur Removed[a]		
	-1/4	-14	-100
Lower Kittanning	35	60	65
Illinois No. 5	45	35	50
Pittsburgh	--	45	60
Herrin No. 6	--	70	50

[a]Values rounded to nearest 5%

similar for each coal (8). In general, a increase of pyrite removal is observed for smaller top sizes as expected due to exposure of pyrite encapsulated within the coal matrix. The Illinois #5 and Herrin #6 coals deserve special comment because reaction of the ferric ion with the coal matrix resulted in greater than 75% depletion of the reagent. For the #5 coal, this effect was approximately the same for all three sizes and the resulting depletion of the reagent may have had a leveling effect on the results. In the case of the #6 coal, substantially less ferric ion was consumed by the -14 mesh coal (68 vs. >95%) which is probably the reason for the increased removal. Thus, while the use of a larger coal top size reduces pyrite removal, it is not a strong function of mesh size. It is expected that the internal surface and permeability of the coal to aqueous media are important factors along with the surface exposure of pyrite caused by grinding. In addition, the top mesh size may have an effect on the ultimate amount of pyrite removal, and further research is necessary to clarify the exact nature of these effects.

An examination of equations 1 and 2 shows that both ferrous ion and sulfate ion could have a retarding effect on pyrite extraction. It could also be expected that the rate is dependent on the ferric ion concentration.

Because a commercial process may require the use of various ferric-ferrous ion concentration mixtures, these are important parameters. Work with mineral pyrite has indicated that there is no significant rate difference with ferric ion concentration between 0.5 and 3.0M as long as enough ferric ion is present to dissolve all the material. Results with -100 and -14 mesh Lower Kittanning coal using both ferric sulfate and ferric chloride indicate virtually (±2%) the same removal when the leach is 1.0, 2.0 or 2.5M in ferric ion. The use of 0.5M ferric chloride seems to increase pyrite removal by more than 10%. In addition, a series of experiments were performed with a starting ferrous ion concentration of 0.5M and a ferric ion concentration of 1.0M. Under the conditions used, a reduction of pyrite removal of 7-8% from a baseline of 62% was observed. Thus, the effect of ferrous ion, when present, is small.

Since the use of ferric sulfate in a process has several advantages over ferric chloride, a test matrix was performed, summarized in Table 5,

Table 5

Comparison of Ferric Sulfate and Chloride for Pyrite Removal[a]

Coal	Pyritic Sulfur Removed % w/w				Ferric Sulfate Treated Coal ($0.4N\ Fe^{+++}$) % w/w Sulfate		Removal Correction[b]
	$0.4N\ Fe^{+++}$		$0.9N\ Fe^{+++}$				
	Cl	SO_4	Cl	SO_4	Initial	Final	abs %
Lower Kittanning	43	38	43	54	0.07	0.17	+3
Illinois #5	48	43	50	50	0.05	0.17	+8
Pittsburgh	50	33	58	--	0.01	0.08	+7
Herrin #6	35	33	52	64	0.05	0.20	+9

[a]Conditions: 600 ml 0.4 and 0.9N Fe^{+3} solution, 100 g -100 mesh top size coal, refluxed at 100°C for 2 hrs.

[b]Increase ferric sulfate extraction values by this % to correct for retained sulfate.

to compare the ability of ferric sulfate to remove pyritic sulfur from all four coals. Utilizing solutions 0.4N in ferric ion, it was found that slightly less sulfur was removed by ferric sulfate than was indicated with ferric chloride. However, when a solution of 0.9N in ferric ion was used, it was found that ferric sulfate removed an equal or greater amount of sulfur than ferric chloride. Analysis of the coals also showed that a small amount of sulfate remains with the coal after a simple washing procedure. Preliminary results show that this can be reduced to starting values using more rigorous washing procedures. If we assure that all the sulfate can be removed, then the values for sulfur removal by ferric sulfate extraction can be raised 3 to 9% depending on the coal.

Attempts to increase pyrite removal by increasing the reaction time met with limited success under our standard conditions due to the fact that reaction of the ferric ion with the coal matrix depleted the ferric ion needed for extraction of the pyrite. Thus, for example, increasing the coal reaction time from 2 to 12 hours only increased pyritic sulfur removal from 60 to 80 percent for Pittsburgh coal. Similar results were obtained for the other three coals. The only alternatives were to increase the amount of leach solution or use a continuous or semi-continuous (multiple batch) reactor. A multiple batch mode was chosen because it was a simple laboratory procedure and at the same time could approximate conditions encountered in a commercial plant. A 1 hr per batch leach time was used because our 2 hr results indicated that in the early stages of removal the rate begins to tail off after 1 hr and six leaches (or batches) per run were used in order to assure that any pyrite that could be removed in a reasonable amount of time was removed. The progress of removal was monitored by analyzing the sulfate content in each spent leach solution, while elemental sulfur was not removed until all the leaches were completed. Table 6 shows pyrite extraction as a function of successive leaches as followed by sulfate analysis of the leach solution. Note that the major portion of pyritic sulfur is removed in the first two leaches or two hours, followed by lesser amounts in the third and fourth leaches and only small amounts in the final two leaches.

Table 6

Pyrite Extraction as a Function of Successive Leaches

	Lower Kittanning	Pittsburgh	Illinois #5	Herrin #6
Initial Pyritic Sulfur, mmol	102	37.5	43.4	49.7
Extracted Pyritic Sulfur as Sulfate[a] mmol 1	31.2	13.5	11.4	12.5
2	12.4	6.0	5.5	6.3
3	9.2	4.6	3.6	5.0
4	4.8	2.1	1.8	2.1
5	0.4	0.6	0.7	1.0
6	0.3	0.3	0.5	0.6

[a]A nominal 40% of the pyritic sulfur remains with the coal as elemental sulfur. All indications are that the sulfur to sulfate ratio is constant.

The results in terms of final sulfur values and pyrite removal are given in Table 7. Note that pyritic removal computed from either sulfur forms analyses or the difference in total sulfur between processed and untreated coal (Eschka analysis) resulted in essentially identical values of 93 - 100%. This corresponds to total sulfur removal of 40-70% depending on the organic sulfur content of the coal. The observation of greater than 100% removal is due cumulative error in analysis and the removal of small amounts of sulfate (0.02-0.04%). Presently, these experiments are being duplicated using ferric sulfate, and preliminary analysis indicates the same results.

Table 7. Pyritic Sulfur Removal Data[a]

Coal	Total Sulfur Analysis				Pyritic Sulfur Analysis[c]		
	Start, %	Finish, %	Total S[b] Removal, %	Pyritic S Removal, %	Start, %	Finish, %	Pyritic S[b] Removal, %
Lower Kittanning	4.32	0.93	78	95	3.58	0.06	98
Pittsburgh	1.88	0.75	60	95	1.20	0.09	93
Illinois No. 5	3.48	1.88	46	102	1.57	0.10	94
Herrin No. 6	3.80	2.04	46	107	1.65	0.05	97

[a]6 1-hr leaches with fresh 1M $FeCl_3$ (0.1M HCl).

[b]Assuming total sulfur removal = $\frac{S_o - S_f}{S_o}$ 100 where S_o = percent sulfur content at start and S_f = percent sulfur content after extraction

[c]Based on sulfur forms analysis.

CONCLUSION

The use of ferric chloride or sulfate to remove pyritic sulfur from coal has been demonstrated to be a feasible process to remove pyritic sulfur from coal with high selectivity. In addition, it has been shown that this removal is not affected to any great extent by the presence of ferrous, sulfate, or hydrogen ions, or coal mesh size. The use of six 1 hr leaches gives 93-100% pyritic sulfur removal.

EXPERIMENTAL

Sampling. A determined effort was made to obtain samples with uniform composition. The cleaned coal samples were taken by the U.S. Bureau of Mines (Lower Kittanning and Pittsburgh) and the Illinois Geological Survey (Illinois #5 and Herrin #6). Each gross sample (-1/4 x 0) was coned and quartered or riffled to smaller samples and ground to the desired mesh sizes by the appropriate ASTM method. The analysis in Table 1 are an average of determinations on five or more samples representing both -14 and -100 mesh samples taken or ground on several different occasions.

Standard Runs. Coal, 100 g, of the desired mesh (-14 x 0 or -100 x 0) was added to a 1-l. resin kettle equipped with a stirrer and reflux condenser together with 600 ml ferric chloride or ferric sulfate 1M in ferric ion. The solution was brought to reflux (102°C) for the desired time (usually 2 hrs), filtered and washed thoroughly on the filter funnel. This washing procedure was sufficient for runs using ferric sulfate, but a much more thorough washing procedure is necessary in the ferric chloride runs to reduce the chloride content to usable levels. After removal of the iron salts, the coal was refluxed with 400 ml toluene for 1 hour to remove the sulfur from the coal, then the coal was dried at 150°C under vacuum. All calculations are based upon the dry weight of the coal.

Multiple Pass Runs were performed in the same way except that the ferric chloride was changed every hour for total reaction time of 6 hours and the ferric sulfate was changed at 1, 2.5, 4.5 hrs with a total reaction time of 8.5 hrs. After the final filtration and wash, the sulfur was removed by toluene extraction and the coal dried in the normal manner.

Coal analyses were performed by Commercial Testing and Engineering Co., Chicago, Illinois. Data handling and curve fitting were done on the TRW Timeshare/CDC 6500 computer system.

REFERENCES AND NOTES

1. Patent pending.

2. Oxidation of pyrite and copper sulfide ores by ferric salts is known (3) but the scope and selectivity of the reaction have not been investigated. In Reference 3b), however, the authors state (without direct proof) that iron pyrite in copper ore concentrates is not attacked in a period of hours at 100°C. Contrastingly, we have found that treatment of -200 mesh top size iron pyrite mineral with 1M aqueous ferric chloride solution at 100°C results in 49% dissolution after 2 hrs, 96% in 8 hr and 99.5% in 16 hr.

3. a) J. W. Mellors, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. XIV, John Wiley and Sons, New York, 1961, p.221-232

   b) F. P. Haver and M. M. Wong, J. Met., 25 February 1971.

4. It was not obvious at the start of our work that elemental sulfur could be removed from the coal matrix, as previous reports had indicated that coal heated with elemental sulfur resulted in recombination and elimination of hydrogen sulfide (e.g., B. K. Mazumdor, Fuel, 41, 121 (1962).

5. E. J. Sercombe and J. K. Gary, Brit. Pat. 1,143,139 (1969). V. V. Emilov, Y. P. Romanteev and Yu. A. Shchurouskii, Tr. Inst. Met. Obogashch., Akad. Nauk K9z, SSR, 30, 55-64 (1969); L. Liepna and B. Macejevskis, Dokl. Akad. Nauk SSR, 173 (6), 1336-8 (1967).

6. P. Averitt, "Coal Resources of the U.S.", U. S. Geological Survey Bull. 1257, January 1, 1967.

7. All analysis and sampling were done according to ASTM procedures; cf. "Annual Book of ASTM Standards", Part 19, Gaseous Fuels; Coal and Coke", American Society for Testing and Materials, Philadelphia, 1971.

8. P. Rosin, and E. Rammler, Jour. Inst. Fuel., vol 7, October 1933, p 29-36; J. G. Bennett, Jour. Inst. Fuel, vol 10, October 1936, pp 22-39; M. R. geer and H. F. Yancy, Trans. A.I.M.E., vol 130, 1938, pp 250-269. A. S. Scott, Bureau of Mines Rept. of Investigations 3732, 1943, 9 pp; Bertrand A. Landry, Bureau of Mines Bull. 454, 1944, 127 pp.

ACKNOWLEDGEMENT

The authors wish to acknowledge the support of the Environmental Protection Agency (after initial feasibility demonstration) under Contract EHSD 71-7, and the encouragement of Messrs. T. K. Janes and L. Lorenzi of that agency and J. Blumenthal, E. R. Boller, E. A. Burns, B. Dubrow, W. Krawitz, A. A. Lee, C. A. Flegal, and L. J. Van Nice of TRW Systems, and the technical assistance of Messrs. J. M. Hom, D. R. Moore and D. B. Kilday.

ENGINEERING, ECONOMIC, AND POLLUTION CONTROL ASSESSMENT OF THE MEYERS' PROCESS FOR REMOVAL OF PYRITIC SULFUR FROM COAL

L. Lorenzi, Jr.

Control Systems Division
Environmental Protection Agency
Research Triangle Park, North Carolina 27711

J. S. Land, L. J. VanNice, and R. A. Meyers

TRW Systems Group, One Space Park
Redondo Beach, California 90278

INTRODUCTION

Combustion of coal for heat, steam, and electrical power generation is by far the largest single source of atmospheric sulfur dioxide pollution in the United States; it currently accounts for about two-thirds of the total sulfur oxide emissions. The Federal government has established Standards of Performance for New Stationary Sources (1). These standards limit the discharge of sulfur dioxide into the atmosphere to 1.2 pounds per million Btu's of heat input for solid fossil fuel combustion operations generating more than 250 million Btu's per hour. This emission limit corresponds to a maximum sulfur content restriction of 0.6 - 0.8% for most Eastern coals. However, coal for utility consumption averages about 2.5 - 3.0% sulfur. The Meyers' Process presents a new and potentially low cost approach to meeting a significant portion of the requirement for low sulfur coal.

The Meyers' Process, initially developed by TRW, Inc., utilizes a simple chemical leaching method to remove iron pyrite from the coal matrix. The process is presently at a bench-scale development phase, under sponsorship of the Control Systems Division, Office of Research and Monitoring, Environmental Protection Agency, with an objective of obtaining all data necessary for the design and operation of a pilot or, eventually, a demonstration plant.

This paper presents the results of preliminary commercial scale process engineering and economic assessments of the Meyers' Process and describes the potential of the process for converting current steam coal production to a sulfur level consistent with Federal regulations for controlling sulfur dioxide emissions from stationary sources.

GENERAL PROCESS CHEMISTRY

The basis for the Meyers' Process for the removal of inorganic (pyritic) sulfur from coal involves contacting the iron pyrite in the coal with an aqueous ferric sulfate solution and oxidizing the pyritic sulfur to elemental sulfur. The free sulfur can then be removed from the coal matrix by solvent extraction or various other processing methods (e.g., steam or vacuum vaporization), and the oxidizing agent can be regenerated (e.g., by air oxidation) and recycled.

The chemistry associated with the process can be illustrated for the individual process operations as follows:

Leacher: $2\ Fe^{+3} + FeS_2 \cdot Coal \rightarrow 3\ Fe^{+2} + 2\ S \cdot Coal$ (1)

Sulfur Recovery: $S \cdot Coal \rightarrow S\ (elemental) + Coal$ (2)

Regeneration: $3\ Fe^{+2} + 3/4\ O_2 \rightarrow 3\ Fe^{+3} + 3/2\ [O=]$ (3)

In addition, about 60 percent of the pyritic sulfur content of the coal has been found to oxidize to sulfate which dissolves in the aqueous leaching solution. The postulated chemistry for sulfate formation during the pyrite leaching is:

$$FeS_2 + 14\ Fe^{+3} + 8\ H_2O \rightarrow 15\ Fe^{+2} + 2\ SO_4^{=} + 16\ H^+ \quad (4)$$

The unique aspect of this process is that iron is used to remove iron. Also, the utilization of an iron sulfate leaching system eliminates the possibility of depositing extraneous chemicals on the coal (both iron and sulfate are present in raw coal). Since the leaching solution can be regenerated, the process, when viewed as a unit, removes iron pyrite from coal by utilizing air (or oxygen) as a raw material and produces elemental sulfur and iron sulfates and/or iron oxides as products.

PROCESS ENGINEERING

The proposed process design is based mainly on the results of laboratory and bench-scale experimentation studies dealing with Lower Kittanning coal. The base case processing rate was selected at 100 tons of coal per hour (equivalent to a 250 MW utility output) with approximately 3.2 tons per hour of pyritic sulfur removed from the coal.

A block diagram showing the processing steps currently envisioned for the removal of pyritic sulfur from coal is presented in Figure 1. The process contains four main sections.

- Pyrite leaching with ferric sulfate solution.
- Regeneration of the ferric sulfate leach solution.
- Coal washing with water.
- Sulfur recovery by solvent extraction and coal drying.

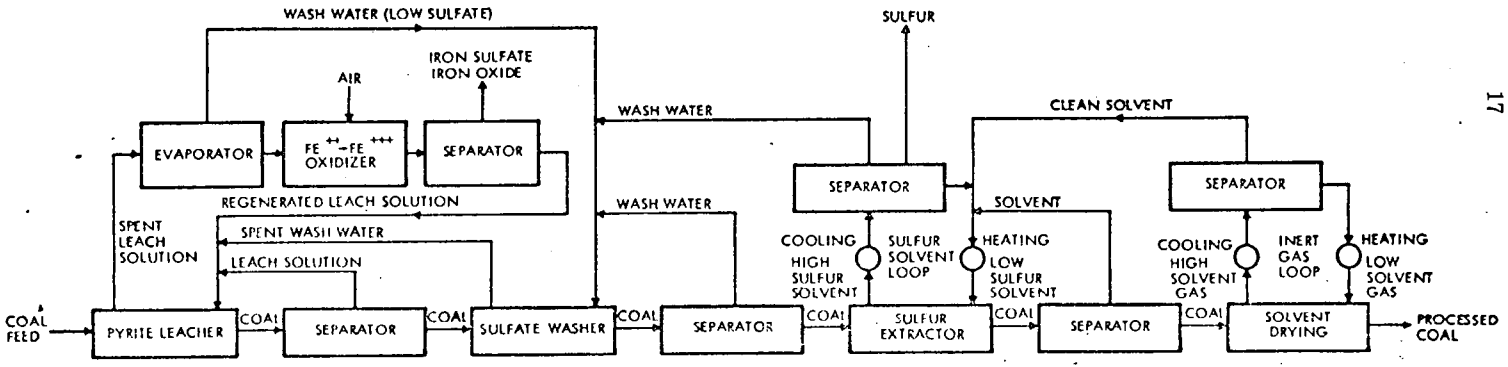


Figure 1. Pyritic sulfur removal process block diagram.

Pyrite Leaching

Based on experimental results, a countercurrent leach step appears desirable; freshly regenerated ferric ion is first contacted with coal nearly depleted in pyrite. Preliminary experimental results indicate that neither ferrous ion nor sulfate ion buildup has a significantly adverse effect on the reaction; thus, the nearly spent leach solution should still be actively attacking pyrite on the freshly introduced coal stream. With fresh coal introduced at the beginning of the leach, there is probably sufficient pyrite near the surface of the coal particle so that no effect on the rate of etching of the pyrite surface is produced by the high ferrous ion concentration. It is believed that toward the end of the leach step, the rate of reaction is controlled mainly by counterdiffusion of ferric ion into and ferrous ion out of the pores in the coal particles; the rate is thereby benefited by high ferric and low ferrous ion concentrations in the leach solution. If this model of the leach step is correct, then the leacher requires little bulk mixing. Equipment which slowly moves coal countercurrently through a slowly flowing stream of leach solution will be highly effective as a leach reactor.

Three coal particle sizes (-1/4 inch, -14 mesh, and -100 mesh) have been studied during the present experimental work. The results indicate that pyritic sulfur removal is possible with all of the above coal particle sizes. The process design provides for a coal leach residence time of four hours. The leacher design temperature is at or near the atmospheric boiling point of the solution (about 100°C) and the design pressure is atmospheric.

It is anticipated from current experimental results that the reaction of ferric ion with pyrite in coal will yield a $SO_4^{=}/S$ reaction product ratio of about 1.5/1. A leach solution of approximately 7500 GPM of 0.5 M ferric ion concentration (100% excess of ferric ion required for complete reaction) with little ferrous ion content or acidity is the nominal design feed to the leacher.

The coal discharging from the pyrite leacher is separated from the bulk of the leach solution and conveyed to a water wash system. It is probable that the separation can be accomplished with simple moving-belt screen filters since surface fluids are readily removed during the next processing step. (Even if powerful centrifuges were employed, fluids would not be driven from one-half of the coal pores which are oriented toward or into the induced centrifugal force field.) The leach solution recovered in the separator is recycled back to the pyrite leacher.

Regeneration of the Pyrite Leach Solution

Spent leach solution from the pyrite reactor will contain unreacted ferric ion, ferrous ion, by-product and recycled sulfate ion, recycled and spent wash water, acid produced by the sulfur and sulfate reactions, numerous minor elements, and possibly some water soluble organic compounds leached from the coal. Regeneration of the leach solution includes the separation of a low ion content wash water for return to the wash section, the air oxidation of ferrous ion to ferric ion, and the separation of ferrous or ferric sulfate and iron oxide in the quantities produced during the leach step.

Regeneration of ferric ion from an aqueous solution of acidic ferrous ion is readily accomplished by oxidation with air. As shown in Figure 1, the regeneration may be carried out in equipment separate from the pyrite leach reactor. This arrangement offers the greatest opportunity for using technology developed independently of the coal leaching. (Regeneration of coal leach solution has much in common with treatment of spent pickle solutions from descaling of iron or steel. Oxidation of ferrous ion to ferric ion is receiving the greatest attention in hydrochloric acid pickling where oxidation of ferrous chloride to ferric chloride precedes hydrolysis and acid recovery.)

Water Washing

Water washing the coal leaving the pyrite leacher is necessary to remove residual leach solution. (Leach solution not washed from the coal will deposit sulfate on the coal during drying and reduce the extraction efficiency.) From bench scale experience, it has been found that drained Lower Kittanning coal retains about 20% w/w of the ferric sulfate leach solution. (These weights were similar for either the -1/4 inch or the -14 mesh samples.) The removal of leach solution from the pores of the coal particles is probably a diffusion controlled process and, if this is the case, could ideally be carried out in a countercurrent washer with long residence time. It is reasonable to predict that a washing time of 5 to 50% of the leaching time, and wash water requirements in the range of one-half to one pound water per pound of coal would be capable of removing substantially all of the residual leach solution from the coal. The spent wash water is pumped to the pyrite leacher, and the water on the coal discharging from the water washer is drained on a moving-belt screen filter. (Bench scale experience indicates drained Lower Kittanning retains about 15% w/w wash water based on dry coal weight.)

Sulfur Extraction and Coal Drying

The coal exiting the washer still contains elemental sulfur formed from pyrite in the coal particles during the leach reaction. The proposed process shown in Figure 1 uses a dissolvent (e.g., aromatic or aliphatic hydrocarbon) to extract the elemental sulfur from the coal. Residual wash water is also displaced from the coal pores during the sulfur extraction. Toluene has been used for extraction in laboratory and bench scale experimental work, but any low priced, convenient solvent could be substituted.

The hot, sulfur-rich solvent exiting the sulfur extractor is cooled to cause sulfur to precipitate from solution, filtered to recover the sulfur, and separated from any immissible water. The low sulfur content solvent is reheated and recycled to the sulfur extractor.

The coal exiting the sulfur extractor is conveyed to a solvent dryer where any residual sulfur solvent is removed. A heated inert gas is used to evaporate the solvent from the coal and carry it to a condenser where the solvent is condensed, separated from the inert gas, and recycled to the sulfur extractor. The dry processed coal is allowed to cool and is then conveyed to storage.

Several alternative methods for removing and recovering elemental sulfur from coal have been assessed in preliminary evaluations. One method involves heating the wet, water-washed coal to molten sulfur temperature (i.e., 250°F) under pressure (15 to 50 psig) and then rapidly depressurizing the coal to cause steam to be formed in the pores. It is postulated that the steam venting from the pores will drive the liquid sulfur droplets from the pores and into the steam condensation equipment. If such a process step is found to be operable, the solvent extraction and solvent drying steps can be eliminated, and steam stripping the sulfur byproduct to remove solvent would be unnecessary.

Other processing methods which have been proposed as alternatives to the sulfur solvent extraction include: 1) melting and displacement of the sulfur in the coal by superheated water (i.e., 50 psig, 300°F) and 2) vaporization of the elemental sulfur by a heated inert carrier gas (e.g., nitrogen), followed by cooling of the carrier gas and condensation and separation of the sulfur.

PROCESS ECONOMICS

Capital and operating costs have been estimated by TRW for a Meyers' processing plant capable of handling 100 tons of coal per hour (sufficient to feed a 250 MW coal fired power plant). Table 1 presents a summary of the capital and processing costs. The estimated overall processing cost for the baseline pyritic sulfur removal process is $1.95 per ton of coal (8¢ per MM Btu). The capital cost for the plant is estimated to be $4 million. As the process is further developed from the bench-scale work these cost figures will change and thus the process economics will be accordingly updated and independently examined.

The coal processing cost is based on 10-year straight line depreciation of the capital plus 10 percent of capital committed annually for maintenance, taxes and insurance. The direct labor costs correspond to 41 operators including shift foreman and plant foreman. A weekly cost per operator was estimated at $200 plus 25 percent payroll burden for fringe benefits. No credit was allowed for the process products: elemental sulfur, iron oxide and iron sulfate. Also no sulfur solvent was assumed retained in the processed coal. (For 0.1% w/w solvent retention in the processed coal, the processing cost increases by approximately 6¢/ton coal.)

The capital cost estimate was developed by estimating major equipment costs and applying installation factors. The capital includes equipment costs for a 25 ft. diameter x 100 ft. long stainless steel-clad kiln-type leach vessel, separators, washer, sulfur extractor, solvent dryer and leach solution regeneration (factored from the leacher cost), heat exchangers (based on calculated surface), pumps and air blower (calculated from estimated horsepower). Each equipment cost was multiplied by a factor to cover field material and labor, engineering, etc.; these installed costs were than added to give the total capital cost.

The costs do not include those for a coal preparation plant because they may already be included in utility operating costs. For instance, if an electric generating facility utilizes a pulverized coal fired boiler, much of the coal preparation requirement may already be in operation. Also if a utility

Table 1

Meyers' Process Economics

Capital Investment	$MM
Pyrite Leach System	1.5
Leach Solution Regeneration System	1.0
Water Wash Unit	0.5
Sulfur Extractor and Coal Dryer	1.0
Total Capital	4.0

Processing Cost	$/Ton Coal
Utilities	0.35
Labor	0.60
Maintenance, Taxes and Insurance	0.50
Depreciation	0.50
Total Processing Cost	1.95

is currently purchasing coal which has been treated in a coal preparation plant to remove rock, etc., additional coal preparation costs may not be necessary, as preliminary experimental results have demonstrated the Meyers' process capable of handling large coal particle sizes (e.g., -1/4 inch).

No provision was included for a return on investment charge for a Meyers' process plant, since the justification for plant installation would be compliance with pollution control regulations and/or the cost incentives associated with utilizing low cost high sulfur coal.

POLLUTION CONTROL

The Meyers' process for the extraction of pyritic sulfur will have essentially 100% application to new and existing coal combustion activities. Since the process produces a cleaned fuel from raw coal, it can be installed at either a combustion site or a mine-mouth location.

The present test work has shown the Meyers' process to be capable of achieving nearly total removal of pyritic sulfur from coal. The pyrite reductions obtained have not indicated any variations due to the rank of the coal, coal region, or coal bed. At an estimated operating cost of $1.95 per ton of coal processed, the pyritic sulfur removal process has excellent economic potential for use either alone or in conjunction with an organic sulfur control technique. The two processes could present a unified overall technique for the total elimination of sulfur dioxide emissions from combustion of the processed coal. Evaluations indicate that use of the pyritic sulfur removal process as the sole SO_2 control technique can result in a considerable impact upon sulfur dioxide emission control.

Coals which typically contain a majority of their sulfur content in a pyritic form are found in the coal mining regions of the Eastern United States (Appalachian Basin). These coal regions are important because the Appalachian Basin contains one-third of the known remaining bituminous coal reserves of the United States and one-half of the estimated total remaining resources east of the Mississippi River, representing a total reserve value of over 280 billion tons of coal (2). The Appalachian Basin also supplies 60% of the total U. S. demand for bituminous coal (3).

The sulfur content of the steam coals in the Eastern coal mining regions has been extensively examined by the U. S. Department of the Interior's Bureau of Mines (4). Consideration of the sulfur content of the Appalachian coals in conjunction with coal bed characteristics from the 1971 edition of the Keystone Coal Industry Manual (3) indicates that less than 10% of the coal mined for utility use in the Appalachian Basin is capable of meeting the sulfur dioxide emission standard of no greater than 1.2 pounds of SO_2 emitted per million Btu's of input energy, as shown in Figure 2. Figure 2 also illustrates that the application of the Meyers' process for pyritic sulfur removal at 95% efficiency can increase the quantity of Appalachian coal capable of meeting the performance standard by a factor of four.

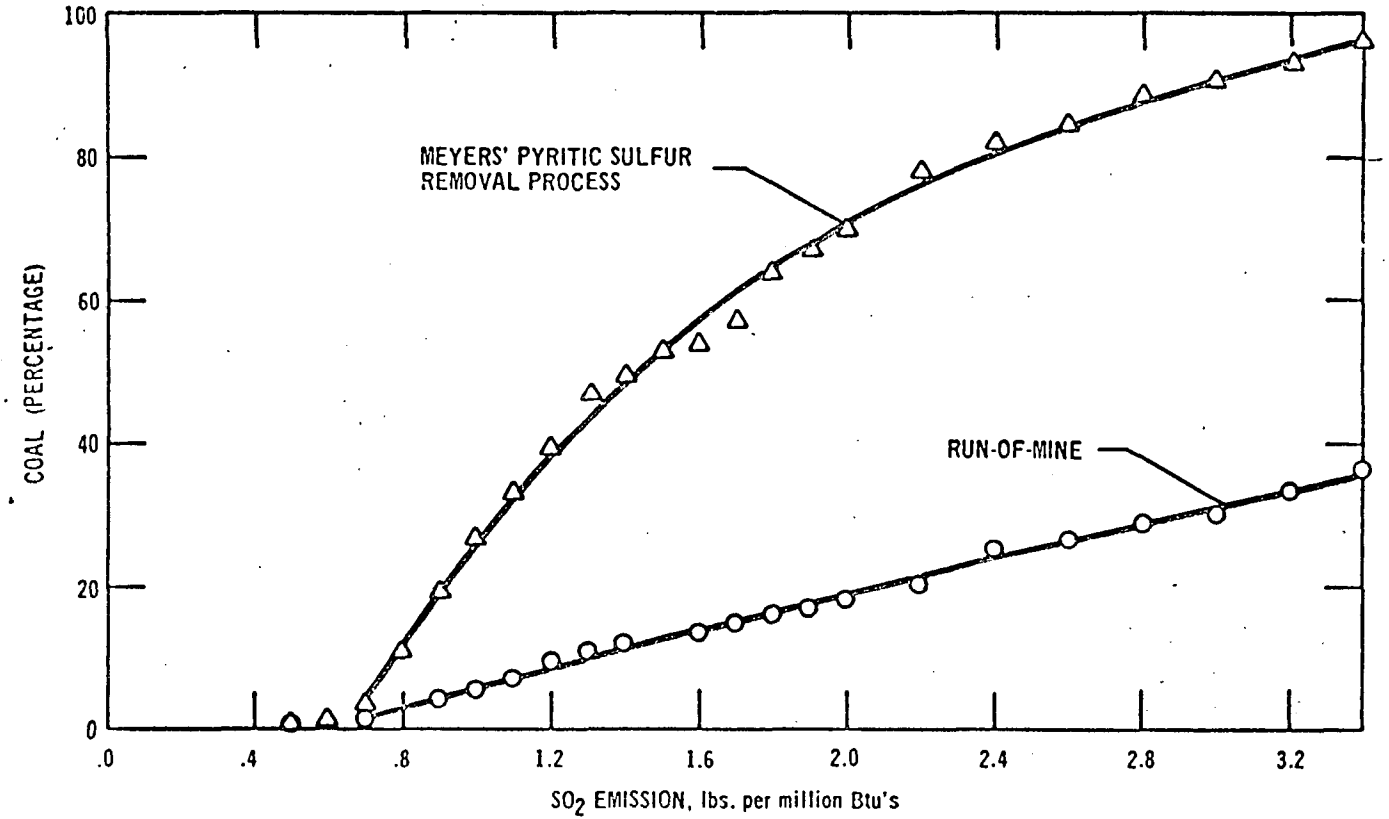


Figure 2. Sulfur Dioxide Emission Characteristics of Appalachian Basin Coal

The impact of the Meyers' process on pollution abatement is even more evident when consideration is given to the utility coals mined in the Pennsylvania bituminous and Maryland state regions. Figure 3 shows that 23% of the as-mined utility coal in Maryland is capable of meeting the new SO_2 emission standards, while 76% of the Maryland coal will be able to meet the standard after application of the pyritic sulfur removal process.

Figure 4 shows that, in Pennsylvania, a ten-fold increase in useable steam coal quantities above the 5% as-mined bituminous coal which meets the New Source Performance Standards is achieved upon application of the Meyers' Process.

CONCLUSION

In active experimentation funded by the Environmental Protection Agency, TRW, Inc., has developed a bench-scale method for leaching pyritic sulfur from coal. In the Meyers' Process, pyritic sulfur is removed by ferric sulfate reaction with the pyrite in coal and recoverable elemental sulfur and dissolved sulfate species are generated. Reaction conditions of 100°C and atmospheric pressure are envisioned, with 95-100% removal of pyritic sulfur a reality. Although the projected operating cost for application of this pyritic sulfur leaching technique may make the process attractive for use in combination with an independent, economically low-cost method for organic sulfur removal, the Meyers' process for pyritic sulfur removal has the potential for widespread production of a clean fuel capable of meeting Standards of Performance for New Stationary Sources.

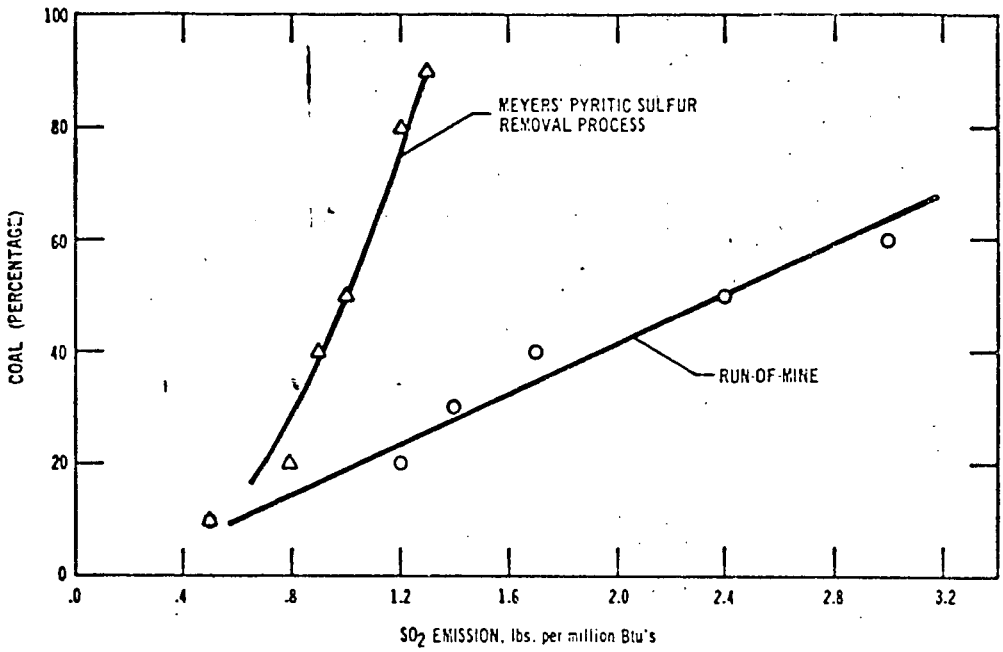


Figure 3. Sulfur Dioxide Emission Characteristics of Maryland Coal.

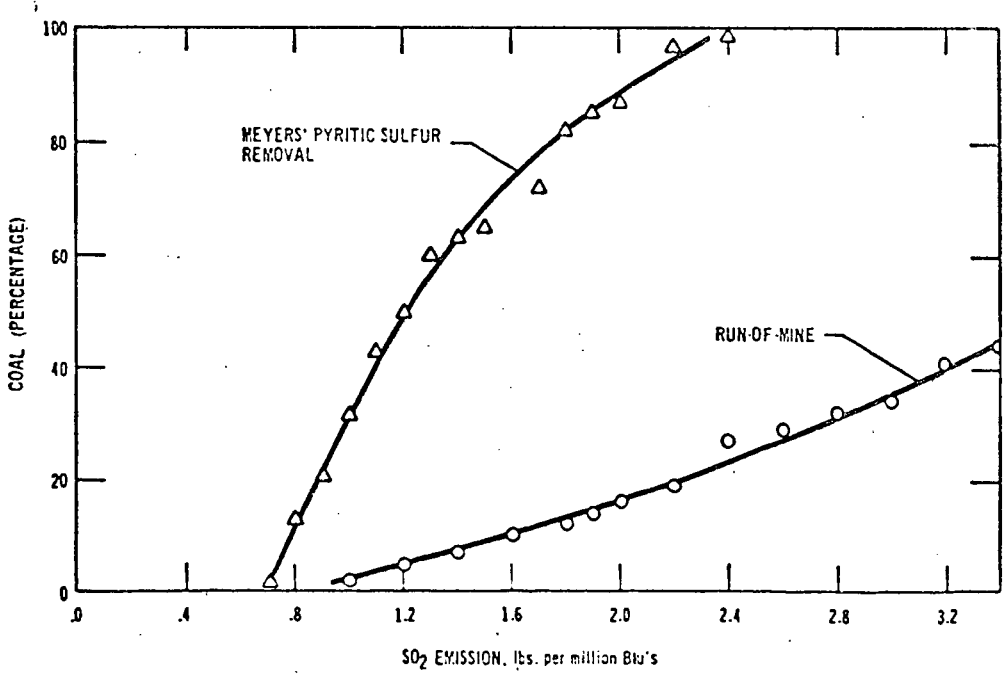


Figure 4. Sulfur Dioxide Emission Characteristics of Pennsylvanian Bituminous Coal.

REFERENCES

1. "Federal Register," December 23, 1971.

2. P. Averitt, "Coal Resources of the United States - January 1, 1967," U. S. Geological Survey Bulletin 1275, U. S. Government Printing Office, Washington, 1969.

3. 1971 Keystone Coal Industry Manual, McGraw-Hill, New York, 1971.

4. A. W. Deurbrouck, "Sulfur Reduction Potential of the Coals of the United States," Report of Investigations 7633, Bureau of Mines, U. S. Department of the Interior, Washington, 1972.

A SOLVENT REFINED COAL PROCESS FOR "CLEAN" UTILITY FUEL

By

Robert G. Shaver

General Technologies Corporation
Subsidiary of Versar Inc.
1821 Michael Faraday Drive
Reston, Virginia 22070

INTRODUCTION

Several processes for conversion of coal to clean fuels are underoing development at various stages. The solvent-refining of coal, o non-catalytic process under development by the Pittsburg and Midway Coal Mining Company far the Office of Coal Research, is an outstandingly advantageous conversion process from the point of view of its potential economics. In comparison to other coal conversion processes it requires less costly equipment ond less severe operating conditions. It consumes less hydrogen and has no need for catalyst(1). The earlier work in hydrogenation of coal was directed toward production of distillate fuels and the use of catalysts was found to be necessary to obtain reasonable yields. Despite improvements in catalysts and in process technology this route of coal conversion is still not economically attractive. In solvent-refining the coal is not converted to distillate fuel, but to a de-ashed, low-sulfur semisolid fuel resembling pitch.

The fuel product of this process has a very consistent heating value of 16,000 Btu per pound regardless of the coal feed stock to the process. This uniformity has been demonstrated in pilot productions from both lignite and bituminous coal(1). The principal variation in the product is in the sulfur content, due to the variation in feed stock sulfur content. This orises from the characteristic of the process to remove all of the mineral sulfur (pyrites) and a part of the organic sulfur ranging above 60%. High ash, high sulfur coals can as readily be brought to a processed fuel of less than 1% sulfur as a lower ash content coal having appreciable organic sulfur content. Typically it can be expected that overall 85% of the sulfur content of the coal can be removed in the processing, a 4% sulfur coal, for exomple, resulting in an 0.8% sulfur solvent refined coal at heating value of 16,000 Btu per pound.

The process in brief is to mix pulverized coal feed stock with a coal-derived solvent oil having a 550-800°F boiling range, passing the mixture with hydrogen through a preheat and reactor, separating excess hydrogen plus the hydrogen sulfide and light hydrocarbons formed, filtering the solution, flash evaporating the solvent and recovering the bottoms as either a hot liquid fuel or a cooled solid product. During the reaction phase, the hydrogen reacts with organic sulfur compounds forming the hydrogen sulfide. The hydrogen also stabilizes the solubilized coal products. The pyritic sulfur leaves the process in the filtration step, as does the ash components.

In this discussion the sole market for solvent refined coal considered is that of the fuel for power-generating utilities, since this market has been shown to be the overwhelming large one for this product[2]. The legislation regarding atmospheric pollution will eventually restrict the sulfur dioxide emissions for the entire nation, and it appears that fuels will be limited to sulfur content less than 1% in general and to less than 0.5% in several highly populated regions. The impact of these restrictions on the direct use of coal as a power-generation fuel will be great, since the supplies of coal of such low sulfur content are quite small compared to the total U.S. coal reserves and they are very inconveniently located relative to the power needs. The use of the solvent refining process, though, allows the coal supply to be used, regardless of its sulfur content. When considered as a clean fuel for power generation, then solvent refined coal not only comes into competition with coal itself in conjunction with stack gas treatments, but also with natural gas, fuel oil and nuclear power.

DISCUSSION OF TECHNOLOGY

The schematic of the recent process technology for the Pittsburg and Midway Solvent Refined Coal process is shown in Figure 1. The salient aspects of the process technology as they affect economics are:

- the delivery of the product as a solid fuel product or as a hot liquid
- the by-products: light liquid hydrocarbon, sulfur, and electrical power
- the fly ash or mineral residue waste
- hydrogen or process fuel feeds to the process.

The distinction between the solid form or liquid form of solvent-refined product is principally one of whether or not the distillation bottoms are cooled below the 300°F solidification point prior to disposition. Probably this issue will depend on whether or not the product is used in an on-site or nearby power plant as apposed to shipping to a distant location. It has been estimated that the additional processing cost to solidify for shipping is 2¢/MMBtu[1].

The liquid hydrocarbon by-product has a high cyclic content and so is useful as a petroleum refinery feed stock or as a source of aromatic organic chemicals. Since a large part of the nitrogen content of the original coal winds up in this by-product, the use as a refinery feed stock would require additional nitrogen removal processing by the refinery.

If the solids from the filtration operation are burned to obtain the heating value, the sulfur dioxide produced can be combined with the hydrogen sulfide from the process to produce elemental sulfur by a Claus-type procedure. This appears to be practical in this case because of the concentrated gas streams encountered. One to 2% of the coal feed weight is the hydrogen requirement for the process. The by-product gas can be used to form all of the required hydrogen by steam reforming. This would eliminate the need for a hydrogen raw material input. The use of a part of the fuel product as process fuel would also eliminate the need for natural gas feed to the process. Whether or not these steps are taken in a given solvent-refining plant depends on local availability of low cost by-product streams of hydrogen and low cost availability of natural gas. It is important to bear in mind that the efficient operation of this process does not require their availability.

Catalytic Conversion of Coal

The most recent catalytic method for converting coal to low-sulfur fuel is the process called the H-Coal Process, also under development by sponsorship of the Office of Coal Research. This process uses a desulfurization catalyst and is very effective in reducing the organic sulfur content to levels of 0.1 to 0.2%. The process, however, is more costly than the solvent refining because of the catalyst and the internal recycle required for its use. The coordinated use of the solvent refining and H-Coal processes for their peculiar individual advantages has been suggested[1] and this may be the most economical way to achieve very low (less than 0.5%) sulfur contents in the fuel when required.

Coal Gasification

Although the costs for producing synthetic gas from coal would be higher than the production of heavy fuel from coal by solvent refining, several of such coal gasification processes are now being developed. The hydrogen requirements are greater and the processing conditions more severe for these. The gas fuel product from such a process will very likely compete as a premium fuel with natural gas and will not be in primary contentation for the bulk of the power generation fuel needs.

Degree of Sulfur Reduction

The present state of development of the solvent refining process allows for about 85% of the sulfur in the feed coal to be removed. All of the pyritic sulfur and some 60-70% of the organic sulfur is removed. On the type of coal that is very common in which the sulfur is roughly 50-50 in these two forms, the final product sulfur content is well below 1%, of the order of 0.8%. Further reduction of the organic sulfur content by utilizing greater quantities of hydrogen than in the present design is believed possible[3], although in the extreme this merges with the catalytic processes such as the H-Coal.

PROJECTED ECONOMICS

Solvent-refined coal as a low sulfur fuel for power generation would compete primarily with such other energy sources as fuel oil, gas and nuclear power, as well as with coal itself fired in boilers served by stack gas treatment processes. The latter, a much studied method of combating pollution from combustion of coal, is an awkward expedient to permit the extended use of high sulfur coals. The principal reason for this is that the electric power companies should not be nor do they desire to be in the chemical production and marketing business, which is the natural outcome of using a stack gas treatment process on a coal-fired boiler and having to dispose of the wastes and by-products. It makes far more sense for the chemical processing industry to provide low sulfur fuel from efficient, optimally-located, and optimally-sized coal conversion plants.

There are two obvious strategies for carrying out this processing-distribution sequence. One is the location of a solvent-refining plants at minehead sites more or less centrally located to the principal marketing areas, to which the product is shipped as a solid fuel. The other is to have consolidated minehead processing plants and power generating facilities in regions where both the coal supplies and the power requirements are in reasonable conjunction. The latter type of facility could, of course, also furnish solid fuel for shipment.

Projection of Demand for Fossil Fuel for Power Generation

Projections of electric power generation anticipate growth in fossil fuel consumption through the next two decades[3]. As shown in Table I, the total expected use of fossil fuels should grow from 13.6×10^{15} Btu in 1970 to 19.5×10^{15} Btu in 1980 and to 25×10^{15} Btu in 1990, nearly a doubling in two decades.

Table I. Fossil Fuel Projection for Electric Power Generation

Year	1970	1980	1990
Coal, 10^{15} Btu	8.1	12.5	16
Oil, 10^{15} Btu	2.1	4.0	5
Gas, 10^{15} Btu	3.4	3.0	4
Total, 10^{15} Btu	13.6	19.5	25

Growth is expected in both coal and oil, but not in gas. In fact an actual decline in gas use is projected between 1975 and 1980, and the whole rate of growth of gas use will fall off dramatically after the vigorous growth prior to 1970.

The Federally mandated emission standard for new and modified fossil solid fuel-fired steam generators with capacity exceeding about 25 megawatts (equivalent) for construction commenced after August 17, 1971 is 1.2 pounds of sulfur per million Btu. This corresponds to roughly 0.8% sulfur in a high heat content coal and about 0.4% for lignite. Even the vast Western coals of markedly low sulfur content are unsuitable for this without further control efforts. Thus essentially all of the coal market for power generation is potentially available to a sulfur-reduced coal product such as solvent refined coal at some not too distant time in the future. Looking at the fossil fuel market for its potential in regard to solvent refined coal production leads to the possibilities shown in Figure 2. In view of the recent cost studies of solvent refined coal[2,4] a sales price range of 50 to 100 cents per million Btu seems to be within a reasonable range. The projections of market potential through 1990 at prices in this range are shown on two assumptions: the limiting one in which all the fossel fuel market for power generation is captured and the more reasonable one which sizes the market at that estimated for coal. A vast sales market ranging between about 4 and 25 billions of dollars is potentially available to the investors in such a process.

Oil Prices for Power Generation

A feasible range of price for solvent refined coal can be inferred by examining the price range of competitive low sulfur fuels for power generation. Low sulfur fuel oils are currently in great demand for power generation in highly populated areas and the demand should, if anything, intensify in upcoming years. Recent quotations of oil prices in several locations[5] have been put on a consistent fuel basis of cents per million Btu in Table II.

Table II. Current Price Variation in Oil for Power Generation

Location	% Sulfur	Price, ¢/MMBtu
New York	0.3 max.	73
	0.5 max.	69
	1.0 max.	61
	Bunker C	53

Table II. Current Price Variation in Oil for Power Generation (Cont.)

Location	% Sulfur	Price, ¢/MMBtu
Chicago	1.0 max.	75
	1.25 max.	73
	1.5 max.	71
Oklahoma	over 1, under 2	40-42

It is well to note the effect of supply and demand in the prices in Table II. In Oklahoma, the demand for oil for power generation is nil because gas is used for all power plants. Residual oil from Substitute Natural Gas plants has been valued at 57-60 ¢/MMBtu at the plant. Based on these facts, very low sulfur residual oil can be valued at 66-69 ¢/MMBtu currently at the ports. Delivery costs are superimposed on these.

The effect on future prices of processing to desulfurize residual oils can be estimated by using processing data for the hydrodesulfurization process[6]. Operating cost data vary between 7 to 19 ¢/MMBtu to reduce to the 1% sulfur level on the type of residual oil feed stock, with vacuum residual oils consuming the most hydrogen and hence having the highest operating costs. The above figures do not include a return on investment. Nevertheless we could expect a desulfurized residual oil product at about the 1% sulfur level to be no less than 50 ¢/MMBtu at a low demand location like Oklahoma and to be at least 65 ¢/MMBtu at a high demand seacoast location like New York. With increased legislative pressure on low sulfur fuels in the future the price at the power plant that most of the major utilities burning fuel oil will face seems to certainly be in the 70-100 ¢/MMBtu range at current dollar values. This helps to define a competitive price range for solvent refined coal product for such use.

Impact of the By-Product Sulfur From Processing of Coal

The supplies of natural low-sulfur fuel will clearly not be equal to the demands upon them in the upcoming decades. The desulfurization of oil and coal by one or another means must make up the deficit. If we look at the recent experience in coal use with regard to sulfur content as shown in Figure 3, we see that the amounts of sulfur to be removed will be considerable. The weight-averaged sulfur content of all the coal fired to power generation in 1969 was 2.6%[3] and we can assume that the coal mined in the future if an economically feasible desulfurization process is being used will not be lower than this experience. If the overall sulfur content allowed in solid fuels is reduced to an average of 0.6% of the weight of coal used in 1990, the by-product sulfur generated by desulfurization of coal will rise in the vicinity of 12-13 million tons in 1990. This figure is sufficiently high to make the recovery of significant economic value by sale of sulfur improbable on the whole. The sulfuric acid market, the principal use of sulfur, recently consumed about 9 million tons of sulfur, so the existence of by-product sulfur of the quantities possible are certain to cause them to be stockpiled and not sold in any significant quantities at current price levels. So it would seem that no credits for sale of sulfur by-product should be taken in realistic projection.

Elements of Cost Pertaining to Solvent Refined Coal Price

The estimation of selling price of solvent-refined coal product has been undertaken for a minehead plant in the Ohio-Illinois-Kentucky area on a 10,000 ton per day basis[1, 4]. The most recent price estimates range from 41 ¢/MMBtu where all by-products are sold, to 47 ¢/MMBtu

where none are sold. In the latter case the light liquid by-product is combined with the solvent refined coal for sale in the power plant fuel product. These prices do include a return an investment but no transportation charges. The annual sulfur by-product sale at $10 per ton we believe to be unrealistic for the long run in which the sulfur market is glutted with pollution control induced sulfur. Reducing the credit for by-products by this amount increases the necessary FOB plant selling price for the optimistic case to 42 ¢/MMBtu. The elements of cost that these estimates cover are: mining, solvent refining, and return on investment.

The transportation of product to the user is a widely variable cost element. A power plant located at the minehead-processing plant site would have effectively no transportation cost. Rail transport of solid product would probably experience the same costs as coal itself[2]. This can be estimated in lieu of specific foreknowledge of rail rate schedules through 1990 as 1 ¢ per ton-mile. As an extreme but nonetheless typical example of current costs to ship coal, low sulfur western coal is currently being shipped to New Jersey at a cost of $22 per ton, which corresponds closely to 1 ¢ per ton-mile.

In a system of well-located processing plants, shipping in excess of 500 miles probably would not be necessary in most cases. The users remotely located from the processing plant would then pay an additional 3-17 ¢/MMBtu for the solid product delivered to the power plant, which includes a cost to solidify the product for shipment. This raises the total estimated price for solid product from 44 ¢/MMBtu at the plant to 45-64 ¢/MMBtu delivered.

Versus low sulfur oil as a competitive fuel, the local delivered price situation would determine the competitive balance. For example in the Chicago area where low sulfur fuel oils are selling for 71-75 ¢/MMBtu, the solvent refined coal could be furnished from the aforementioned hypothetical plant for 53-57 ¢/MMBtu.

However on seacoast locations such as New York, the Gulf Coast and the west coast, low sulfur fuel oil could be currently obtained in the 61-73 ¢/MMBtu region. For the east coast, a mine-processing plant complex in West Virginia could deliver solvent refined coal for 53-65 ¢/MMBtu at most population and industrial centers, which is certainly competitive. However the longer transportation distances between a plant in the Wyoming area and the west coast areas would probably be less attractive in comparisan to delivered fuel oil.

Coal Costs

One cost element in the production of solvent refined coal that is likely to increase noticeably in the future is the cost of mined coal. This is due to several factors including increased labor cost and increased investment for mine safety. A minehead selling price for coal of $6 per ton seems realistic for the near future, which is about 24 ¢/MMBtu for a good quality coal. Adjusting the estimated solvent refined coal prices for this raw material cost would raise the price about 15 ¢/MMBtu. Adjustment for this higher coal cost would bring the estimated selling price of a solvent refined coal utility fuel to 56-63 ¢/MMBtu at the plant location, and to 59-94 ¢/MMBtu delivered, still well within a competitive range for low sulfur fuels even under present day price experience.

When selling in competition with coal itself in conjunction with stack gas treatment, the cost of the raw material coal in solvent refined coal is essentially irrelevant[2]. The principal considerations are the lower transportation cost per MMBtu and the reduced investment and maintenance at the power plant with the SRC. In a similar way, the relative position between SRC and other coal-derived fuels would not shift principally due ta coal cost.

Projected Market for Solvent Refined Coal

By considering efficient solvent refined coal plants at four U. S. locations; West Virginia, southern Illinois, Wyoming, and New Mexico, and examining the projected competitive price per million Btu for the several fossil fuels and derivative fuels in low sulfur emission power plant use, we projected the fractions of the potential market shown in Figure 2 that could be obtained by SRC by virtue of price. These market projections are given in Figure 4 over a range of SRC selling prices at the processing plants from 50 to 100 ¢/MMBtu. The mid-range selling price of 75 ¢/MMBtu should yield a market of about 300 million tons in 1980 and 550 million tons in 1990. This selling price also seems to be the optimum in 1990 for sales dollar volume.

CONCLUSION

The continued wide use of coal in the United States as a fossil-fuel source of energy for power generation is inescapable in the upcoming decade and beyond. Of the several developing processes for producing clean fuels from coal, solvent refining is the most simple and economical. SRC can be used as either a solid or a liquid fuel and has been estimated to capture a very large market in direct competition with other low sulfur forms of fossil fuels in power generation.

REFERENCES

(1) Schmidt, B. K. and Bull, W. C., "Production of Ashless, Low-Sulfur Boiler Fuels from Coal," Preprints, Division ofFuel Chemistry, ACS, Vol. 15, No. 2, pp. 38-49, Sept. 1971.

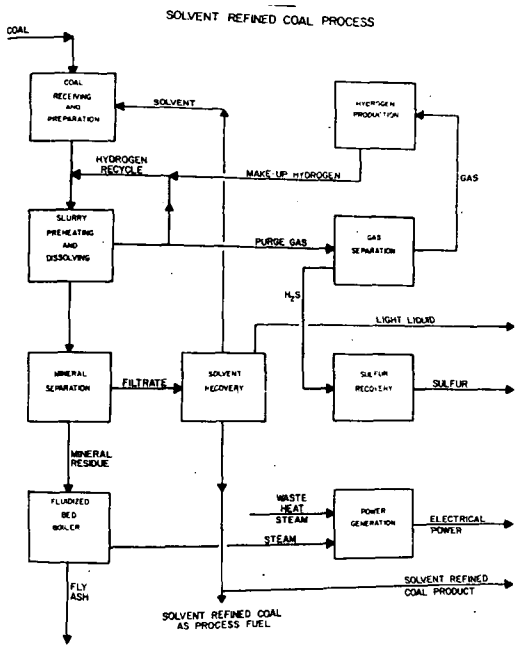
(2) Shaver, R. G., "Study of Cost of Sulfur Oxide and Particulate Control Using Solvent Refined Coal," Final Report Contract No. CPA 22-69-82, Nat. Air Pollution Control Admin., Dept. of HEW, April 1970.

(3) Jimeson, R. M. and Grant, J. M., "Solvent Refined Coal: Its Merits and Market Potential," Presented at Annual Meeting of American Institute of Mining, Metallurgical and Petroleum Engineers, Washington, D. C., Feb. 16-20, 1969.

(4) "Economic Evaluation of a Process to Produce Ashless, Low-Sulfur Fuel from Coal," R&D Report No. 53, Interim Report No. 1, Contract No. 14-01-0001-496, Office of Coal Research, June 1970.

(5) Platt's Oil-Gram, June 1972

(6) Gregoli, A.A. and Hartos, G. R., "Hydrodesulfurization of Residuals with H-Oil," AICHE, Washington, D. C., 1971.



(SOURCE REF. 1)

FIGURE 1

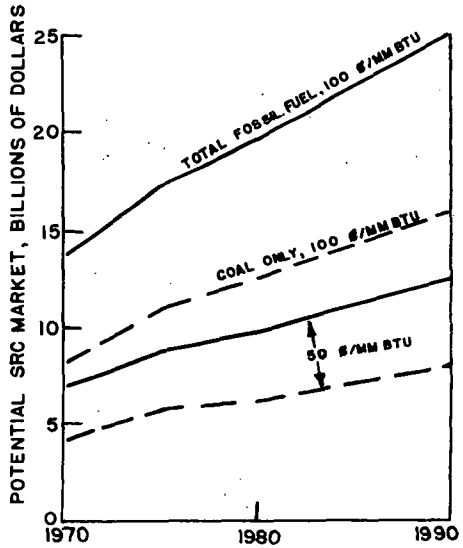


FIGURE 2

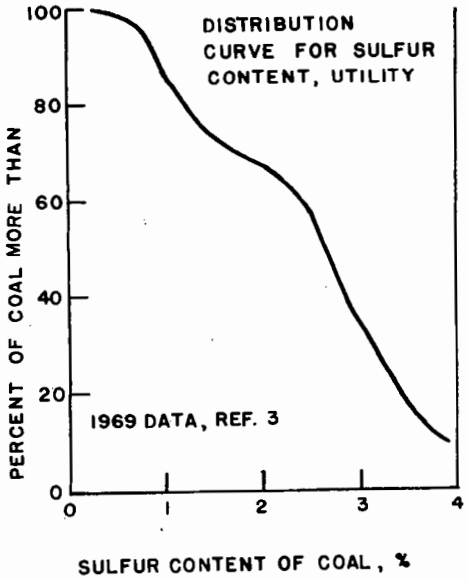
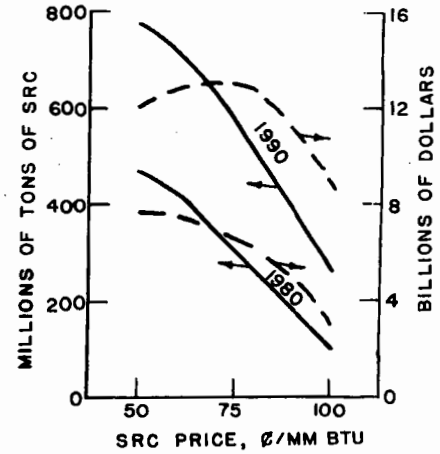


FIGURE 3



PROJECTED SRC MARKET

FIGURE 4

FUEL PROCESSING TAILORED TO ENVIRONMENTAL NEEDS. David H. Archer, Westinghouse Research Laboratory, E. Pittsburgh Works, Churchill Borough, Pittsburgh, Pennsylvania 15325

Projected needs for electric energy will triple the usage of fossil fuels in U.S. power plants over next 20 to 30 years. Advanced techniques for power production are required to minimize emissions of SO_2, NOx and particulates, thermal discharges, capital requirements for new plants, and overall energy costs. Fluidized bed combustion and gasification coupled with combined cycled generation can meet these requirements. Specific fluidized bed combustion and gasification processes for both coal and oil tailored to power production have been devised; and overall plant concepts, evaluated. Reduced power costs in comparison with conventional steam power plants are predicted.

Production of Low Sulfur Fuel Oils From Utah Coals

S. A. Qader and G. R. Hill

Department of Mining, Metallurgical & Fuels Engineering
University of Utah
Salt Lake City, Utah 84112

Introduction:

Hydrogenation is one of the potential methods of producing fuel oil from coal. Coal can be hydrogenated to fuel oil in the form of a paste[1], in ebulating bed[2] reactors, fixed beds[3] and fluid bed[4] reactor systems. In the present investigation, coal was hydrogenated in batch and dilute phase systems to produce oil. The coal oil was desulfurized in fixed and ebulating bed reactor systems to produce low sulfur fuel oils. The economics of producing fuel oils with 0.5 and 0.25 percent sulfur are presented in this communication.

Experimental

Coal was hydrogenated in batch and semicontinuous[4] systems using Zinc Chloride as catalyst. The coal oil was desulfurized in fixed[5] and ebulating bed[6] reactor systems using a pelleted catalyst containing sulfides of nickel and tungsten supported on alumina. Product evaluations were done by standard methods.

Results and Discussion

The product distributions obtained in the batch work are given in Table I. Hydrogenation was carried out at a temperature of 500°C, initial hydrogen pressure of 2000 psi and reaction times up to 90 minutes. The results show that at a coal conversion of about 80 percent, the ratio of oil to gas yields will be about three and 23 percent of the coal sulfur will show up with oil. The data given in Table II indicate that the sulfur content of the oil remains almost same at different coal conversion levels. The sulfur content of the oil, probably, depends upon the organic sulfur content of the coal. The data given in Tables I and II were obtained from a coal containing about 0.6 to 0.7 percent organic sulfur.

The properties of the oil obtained in the semicontinuous dilute phase hydrogenation system[4] are given in Table III. These oils were prepared from a coal containing about 2.5 percent total sulfur. The data show that the whole oil can be directly used as a fuel oil in places where one percent sulfur is tolerated. A 0.5 percent sulfur oil can be produced by desulfurization of either whole oil or the +300°C fraction. If a fuel oil of less than 0.5 percent sulfur is desired, the whole oil may have to be desulfurized.

The whole oil and +300°C fraction were desulfurized in bench scale fixed and ebulating bed reactor systems and the product distributions obtained are shown in Figures 1 and 2. The data show that fuel oils containing about 0.2 percent sulfur can be made by desulfurization of either the whole oil or the +300°C fraction. As the sulfur content of the product oil decreases, there will be an increase in the yields of low boiling oil, gas and coke. A comparison of the data indicates that the fixed bed system produces more gas and coke when compared to the ebulating bed system irrespective of the type of feed oil used.

A conceptual material balance of a refinery producing 100,000 BBL/day of fuel oil from coal was calculated (Table IV) based on the bench scale data obtained by the authors and the published data available. In this projection, a coal containing

7.5 percent moisture, 10 percent ash and about 2.5 percent total sulfur is used as the feed. The hydrogenation can be carried out in any type of reactor system in the temperature range of 500° - 550°C and a pressure range of 2000-3000 psi. The process conditions will be optimized for a coal conversion of about 80 percent. The hydrocarbon gases produced in the process will be used for making process hydrogen. The residual char will be used as a fuel. Based on the conceptual data, a preliminary economic evaluation of the process for making fuel oils of 0.50 and 0.25 percent sulfur was made (Table V). The calculations were based on approximate energy and material balances and estimated equipment costs. The data indicate that fuel oils can be produced from coal by hydrogenation at a manufacturing cost of about 5-6 dollars per barrel. The data (Figure 3) also show that the cost of reducing the sulfur content of fuel oil from 0.5 to 0.25 percent will be about 30-40 cents per barrel.

Acknowledgment

This work was supported by the Office of Coal Research and the University of Utah.

Literature Cited

1. Gordon, K., Report on the Petroleum and Synthetic Fuel Oil Industry of Germany, Ministry of Fuel and Power, H.M.S.O., London (1947).

2. Alpert, S. B., Johanson, E. S., and Schuman, S. C., Chem. Eng. Progr., 60, 35 (1964).

3. Aktar, S., Friedman, S., and Yavorsky, P. M., Bureau of Mines Technical Progress Report 35, July, 1971.

4. Qader, S. A., Haddadin, R. A., Anderson, L. L., and Hill, G. R., Hydrocarbon Processing, 48, 147 (1969).

5. Qader, S. A., and Hill, G. R., Hydrocarbon Processing, 48, 141 (1969).

6. Qader, S. A., Wiser, W. H., and Hill, G. R., Sonderdruck aus Erdol und Kohle-Erdgas-petrochemie Vereinight mit Brennstoff-Chemie., No. 12, 801 (1970).

Table I. Sulfur Distribution In Products
Sulfur Content of Coal: 1.31%

Coal Conversion, Wt. %	Product Yield, Wt. %			Sulfur Distribution, Wt.%		
	Oil	Gas	Char	Oil	Gas	Char
41	36	5	59	16	9	75
52	43	9	48	18	10	72
61	51	10	39	20	13	67
73	57	16	27	22	16	62
81	61	20	19	23	17	60

Table II. Sulfur Distribution in Oil

Coal Conversion, Wt. %	Sulfur Content of Oil, Wt. %
41	0.53
52	0.54
61	0.52
73	0.51
81	0.52

Table III. Analysis of Coal Oil and Its Fractions
(Sulfur Content of Coal = 2.5%)

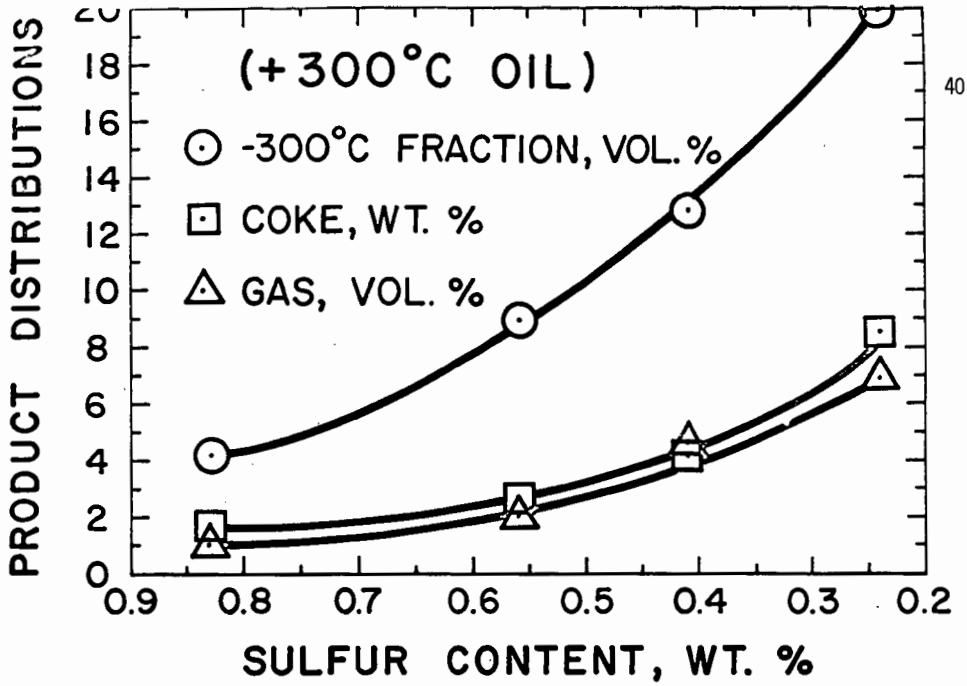
	Whole Oil	-300°C Fraction	+300°C Fraction
Distribution, Vol. %	100.0	42.0	58.0
Sulfur, Wt. %	1.01	0.49	1.53
Nitrogen, Wt. %	1.22	0.65	1.31
Oxygen, Wt. %	5.65	4.54	6.57
H/C (Atomic)	1.09	1.25	0.96
Asphaltene, Vol. %	26.5	10.5	39.6

Table IV. Material Balance
Capacity: 100,000 BBL/Day of Fuel Oil

Sulfur Content of Fuel Oil, Wt. %	0.50	0.25
Raw Materials		
Coal, Tons	39,500	43,500
Hydrogen, MM SCF	1,073	1,275
Catalyst, Tons	732	800
Products		
C_1 - C_4 Gases, MM SCF	271	317
Naphtha, BBL	36,280	49,000
Fuel Oil, BBL	100,000	100,000
Char, Tons	8,052	8,800
Sulfur, Tons	175	175
Ammonia, Tons	350	350
Water, MM Gallons	1.1	1.1

Table V. Economic Summary (MM$)
Capacity: 100,000 BBL/Day of Fuel Oil

Sulfur Content, Wt. %	0.50	0.25
Fixed Capital	312	344
Working Capital	31	34
Total Revenue		
Fuel Oil Price:		
$5/BBL	238	261
$6/BBL	271	294
$7/BBL	304	327
Total Operating Cost	194	224
Rate of Return %		
Fuel Oil Price:		
$5/BBL	6.9	5.4
$6/BBL	12.2	10.2
$7/BBL	17.5	15.0



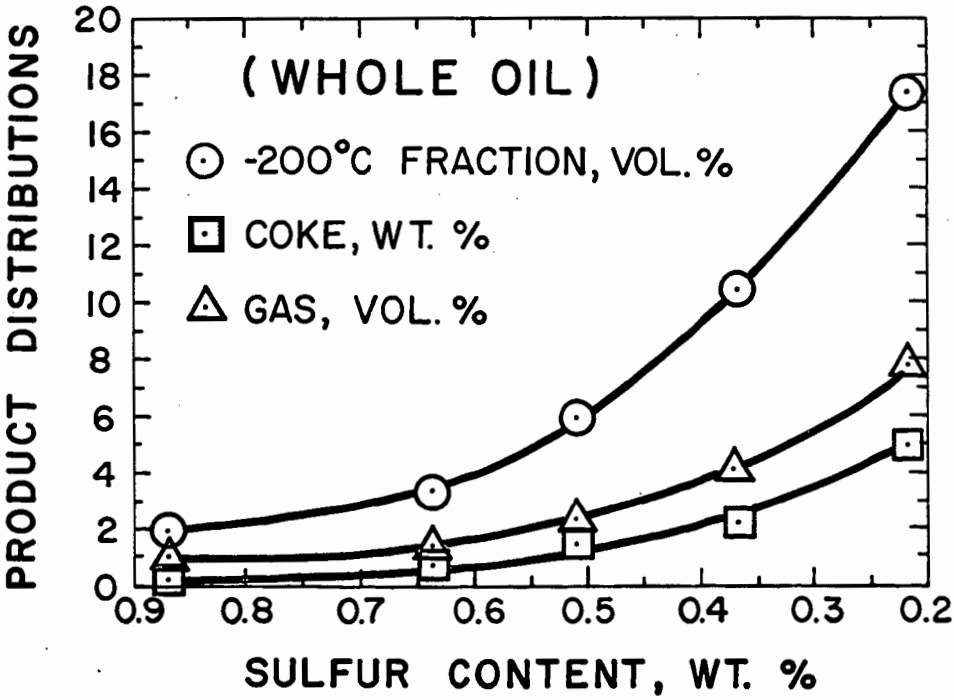
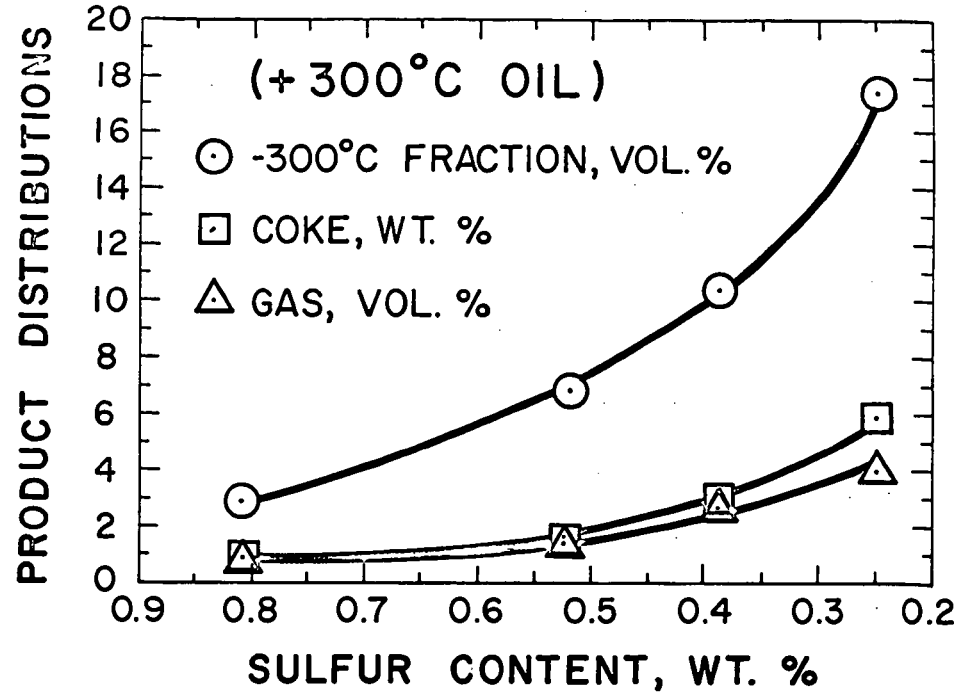


FIGURE 1. INFLUENCE OF DESULFURIZATION ON PRODUCT DISTRIBUTION (FIXED BED)



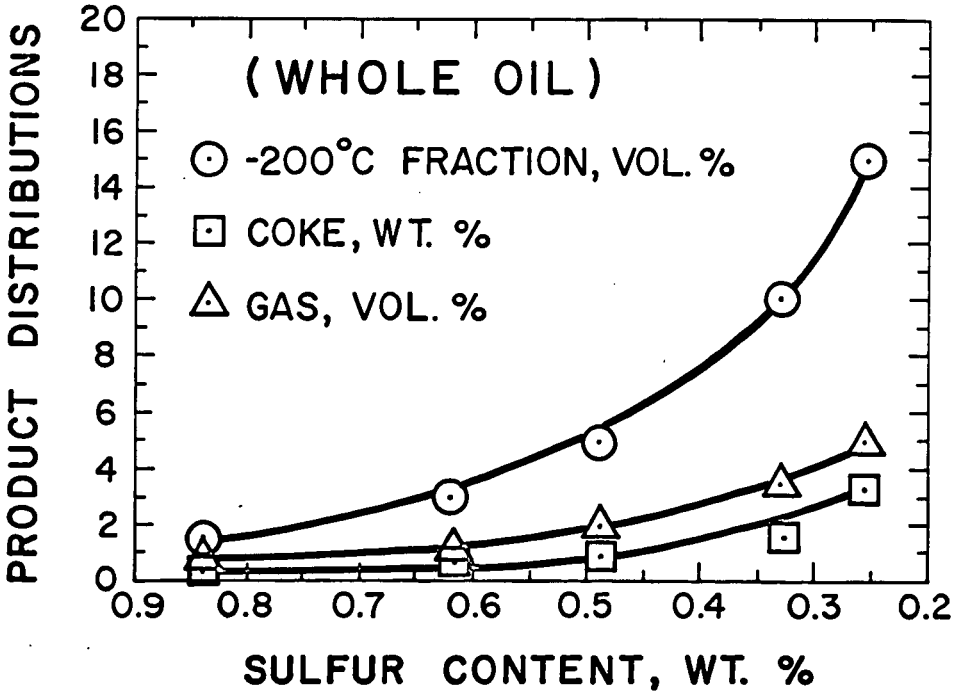


FIGURE 2. INFLUENCE OF DESULFURIZATION ON PRODUCT DISTRIBUTION (EBULATING BED)

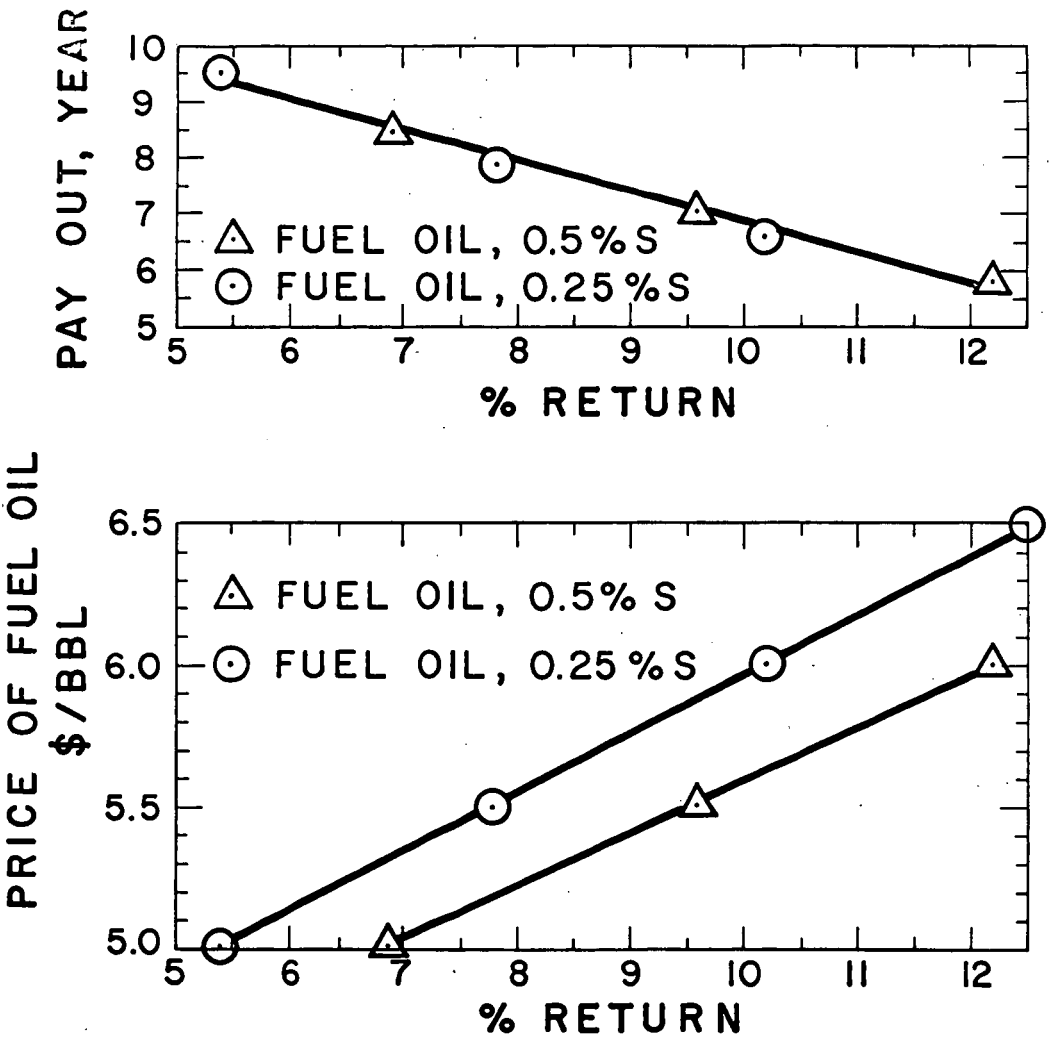


FIGURE 3. VARIATION OF RETURN AND PAYOUT TIME WITH FUEL OIL PRICE

HYDRODESULFURIZATION OF RESIDUALS

A. A. Gregoli and G. R. Hartos

Cities Service Research and Development Company
Cranbury, New Jersey

INTRODUCTION

Since the first commercial H-Oil Unit came on-stream at Lake Charles in 1963, a variety of feedstocks have been processed -- including heavy cycle oils, atmospheric bottoms, vacuum bottoms and cutback propane deasphalter bottoms.

The Unit has operated successfully with both microspheroidal and extrudate catalysts and is being expanded to 6,000 BPD.

Besides the Lake Charles H-Oil Unit, three other commercial units were designed for hydrocracking. The units, though designed for hydrocracking, can be utilized for desulfurization. That is now the primary objective for the Cities Service Lake Charles Unit.

LAKE CHARLES H-OIL EXPERIENCE

The H-Oil Unit was designed to convert 2,500 BPD of West Texas Sour Vacuum Bottoms into lighter products.[1] Later it was found possible to process a heavier lower value feedstock, cutback propane deasphalter bottoms.[2] In late 1966 and early 1967 a commercial demonstration of residual desulfurization was made, feeding West Texas Atmospheric Residuum. The demonstration run was quite successful. Sulfur was reduced from 2.5 to 3.0 weight percent in the feed to 0.3 to 0.5 weight percent in the product. Catalyst usage was approximately 0.05 lbs/bbl.

From 1963 to 1967 a 1/32-inch extrudate catalyst was used. In 1967 relatively minor modifications were made to accommodate a microspheroidal fine catalyst. This eliminated the need for the internal recycle pump previously required to supply the liquid velocity necessary for bed expansion. Operating and performance data have been described previously.[3,4]

From 1967 through 1971 the unit operated with the fine catalyst. During this period the feed was West Texas Sour Vacuum Bottoms cutback with 20% heavy cycle oil. In the last few months of operation with the fine catalyst, conversion of vacuum bottoms to distillate ranged from 55% to 75%, with 75% to 80% sulfur removal. The performance of the microspheroidal or fine catalyst has been demonstrated to be equivalent to the performance of the 1/32-inch extrudate. The unit was expanded from 2,500 BPD capacity to 6,000 BPD. It was necessary to return to the extrudate catalyst at the higher feed rate to avoid excessive expansion of the catalyst bed.

FACTORS AFFECTING DESIGN

A number of design factors must be considered when desulfurizing resids. These are caused by: (1) the complex feedstock characteristics, (2) the tendency to deposite metallic impurities and coke on the catalyst, (3) the required operating severity, (4) the extent and desirability of concurrent reactions, such as hydrocracking, and the relatively high hydrogen consumption and design considerations given to the heat released.

FEEDSTOCK CHARACTERISTICS

Several important feed characteristics considered in H-Oil desulfurization are:

1. The character of the residuum, i.e., whether vacuum, atmospheric, deasphalter bottoms, cracked tars, blends, etc.

2. The asphaltene and metal content.

3. The sulfur level and degree of desulfurization required.

These feed characteristics ultimately influence the selection of operating temperature, hydrogen partial pressure, space velocity, and catalyst type and usage.

CATALYST

Microspheroidal and extrudate catalysts have been used commercially. These catalysts consist of a combination of metals such as cobalt and molybdenum or nickel and molybdenum on an alumina support. An earlier publication reported that a 1/32-inch extrudate performs[3] better than a 1/16-inch extrudate.[5] The most active catalyst is the one with the greatest surface area.[6,7]

Organometallic compounds in the feed are the primary cause of catalyst deactivation. The deactivation rate is influenced by feedstock characteristics, catalyst characteristics and operating severity.

OPERATING CONDITIONS FOR RESIDUUM DESULFURIZATION

Temperature, space velocity, hydrogen partial pressure and catalyst consumption are the essential operating conditions considered in residual desulfurization. These normally range from 700 to 800°F,[6] 0.3 to 3.0 V/Hr/V,[8] and 0.02 to 1.0 lbs/bbl respectively. The ranges do not necessarily represent technical limits but are based on judgment and economic considerations.

DESIGN CONSIDERATIONS

The reaction in residuum desulfurization is exothermic. In the ebullated bed the reactor is isothermal. The temperature is controlled by charging the feed below the reactor temperature.

Solids entering with the feed pass through the expanded catalyst bed without causing a pressure buildup. Catalyst activity and product quality are maintained by adding and withdrawing catalyst while on-stream. Constant catalyst replacement gives the refiner flexibility when changing feedstock.

With the fine catalyst, the velocity required to expand the catalyst is achieved by the flow of the liquid-gas feed mixture passing upward through the reactor.[4] Catalyst inventory and bed expansion are essentially a function of the catalyst particle size and density, liquid viscosity, and liquid and gas velocities. Catalyst is added with the feed and leaves with the product.

The extrudate catalyst requires higher liquid velocities than the fine catalyst to maintain the desired bed expansion. The liquid velocity is provided by recycling a portion of the effluent back to the inlet. The recycle or ebullating pump can be located internal or external to the reactor.

H-OIL DESULFURIZATION COSTS

A wide variety of atmospheric and vacuum residuals can be desulfurized using the H-Oil Process.

Costs for desulfurizing Kuwait Atmospheric, Kuwait Vacuum, Khafji Atmospheric, Khafji Vacuum, Venezuelan Atmospheric and Venezuelan Vacuum Residuals are presented. These feedstocks were selected because they are representative of different types of crudes. The Kuwait Atmospheric and Vacuum Residuals are representative of a high sulfur and low metals crude with moderate gravity and asphaltene content. The Khafji Atmospheric and Vacuum Residuals reflect a high sulfur and moderate metals crude with moderate gravity and high asphaltene content. The Venezuelan Atmospheric and Vacuum Residuals are representative of a low sulfur and high metals crude with moderate gravity and high asphaltene content.

Figure 1 shows 975°F+ conversion and chemical hydrogen consumption varying with sulfur in the 400°F+ fuel oil product. It is apparent from Figure 1 that hydrogen consumption and 975°F+ conversion vary inversely with product sulfur content. In addition, the high metals (or Venezuelan feedstocks) experience the highest increase in conversion and hydrogen consumption when going to lower sulfur levels - followed by Khafji and then Kuwait, respectively. As expected the vacuum residual feeds consume the most hydrogen and represent the highest conversion operations.

Figure 2 is a graphical presentation of the processing costs for the feedstocks considered. The costs represent 1971 dollars and include fuel, power, labor, supervision, overhead, water, catalyst and hydrogen. Figure 2 is intended to show the relative costs for desulfurizing the residual feedstocks considered. The economics, though accurate for this purpose, may not be specific enough for a given company, because the costs do not reflect a return on investment. As is well known an acceptable rate of return on investment differs between companies.

As would be expected, the Kuwait Atmospheric Residual is the least expensive to process of the six stocks. The Venezuelan Vacuum Bottoms are the most expensive followed by Khafji Vacuum, Kuwait Vacuum, Khafji Atmospheric and Venezuelan Atmospheric, respectively. In addition, the Venezuelan stocks show the highest rate of increase in operating costs when going to lower sulfur levels.

SUMMARY

Commercial H-Oil experience using 1/32-inch extrudate and fine catalysts were shown to be equally successful. Important design parameters considered in residual desulfurization include the feed characteristics, catalyst characteristics and operating severity. The range of operating conditions employed for residual desulfurization was presented. Process design considerations using the fine or extrudate catalyst were reviewed. The most attractive system will depend on each application. The cost of desulfurizing Middle East and Venezuelan feedstocks were presented.

The H-Oil Process was developed by Cities Service Research Incorporated. Units have been licensed to the Kuwait National Petroleum Company, Humble Oil and Refining Company, Petroleos Mexicanos and Cities Service Oil Company.

HYDRODESULFURIZATION OF RESIDUALS WITH H-OIL

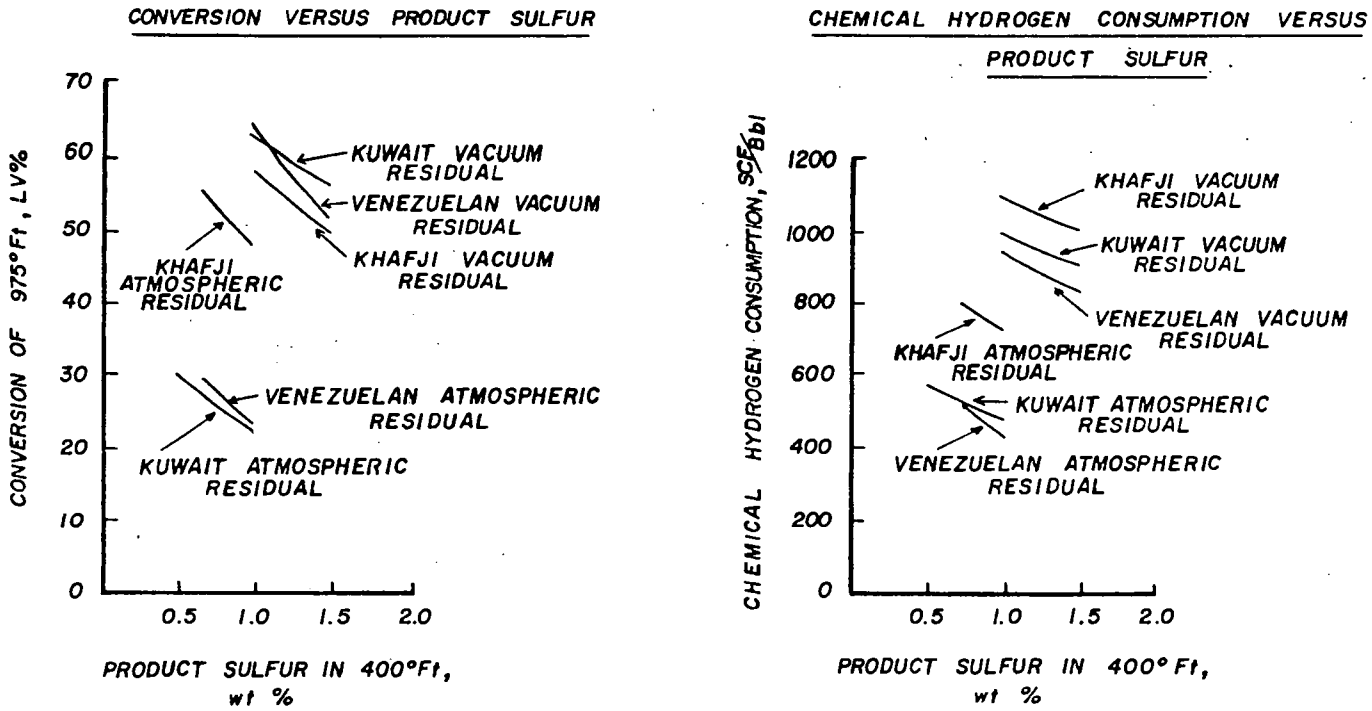
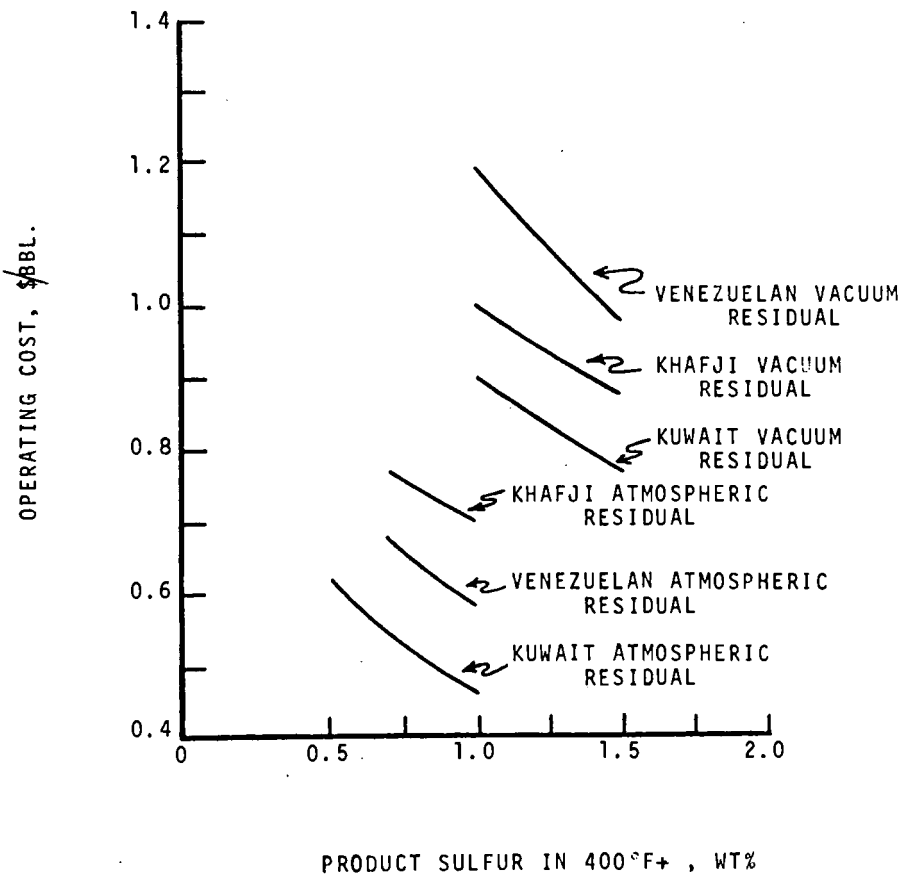


Figure 1

FIGURE 2

HYDRODESULFURIZATION OF RESIDUALS WITH H-OIL

NOTE: THE COSTS REPRESENT 1971 DOLLARS AND ARE FOR GULF COAST CONSTRUCTION. FUEL @ 25¢/MM BTU, POWER @ 1¢/KWH, WATER @ 1¢/M GAL., LABOR @ $5.00/HR., SUPERVISION AND OVERHEAD @ 50% OF LABOR, CATALYST @ 95¢/LB., HYDROGEN @ 35¢/MSCF, AND DEPRECIATION @ 10% OF INVESTMENT. THE ON-STREAM FACTOR IS 0.9.



LIST OF REFERENCES

1. Stewart, N. C., Van Driesen, R. P., "Operation of a 2,500 BPD H-Oil Unit," May 12, 1964, 29th Midyear Meeting of the API's Division of Refining.

2. Griswold, C. R., Van Driesen, R. P., "Commercial Experience with H-Oil," May 11, 1966, 21st Midyear Meeting of the API's Division of Refining.

3. McFatter, W., Meaux, E., Mounce, W., Van Driesen, R. P., "Advanced H-Oil Techniques," May 13, 1969, 34th Midyear Meeting of the API's Division of Refining.

4. Mounce, W., Rubin, R. S., "H-Oil Desulfurization of Residual Oil," February 28, 1971, 68th National Meeting AIChE.

5. Galbreath, R. B., Van Driesen, R. P., Johnson, A. R., Alpert, S.B., "H-Oil as a Tool for Low Sulfur Fuel Oil Production," March 10, 1970, The Japan Petroleum Congress.

6. Galbreath, R. B., Van Driesen, R. P., "Hydrocracking of Residual Petroleum Stocks," Eighth World Petroleum Congress.

7. Alpert, S. B., Chervenak, M. C., Shuman, S. C., Wolk, R. H., "The H-Oil Process: Recent Advances," March 16, 1967, 64th National Meeting of the AIChE.

8. McKinnery, J. D., Stipanovich, J., "Low Sulfur Fuel Oil Production - Gulf Hydrodesulfurization Process," May 13, 1971, 36th Midyear Meeting of the API's Division of Refining.

Catalyst Deactivation due to Pore-plugging by Reaction Products

Esmond Newson

Technical University of Denmark
Instituttet for Kemiteknik
Bygning 229
2800 Lyngby
Denmark

INTRODUCTION

The regulation of sulfur oxide emissions from the combustion of fuels is directed primarily at high sulfur content coal and residual fuel oil [1] . Of the four basic sources of primary energy, heavy fuel oil may be the best hope for meeting sharply increasing energy demands in the near future [2] . The above two factors combined, lead to significant interest in methods of heavy fuel oil desulfurisation. One method for removing sulfur from fuel oil is trickle-bed hydrodesulfurisation. Hydrogen and oil are passed cocurrent downflow over a fixed bed of catalyst at elevated temperatures and pressures. This approach has recently been commercially proven [3] . Hydrotreating of residuum oils in this way has revealed the presence of (undesirable) demetallation reactions taking place in parallel with the desired desulfurisation reactions [4] . Organometallic constituents of the oil, primarily vanadium, nickel and iron, react out of the oil and combine with hydrogen sulfide to produce solid deposits of metal sulfides. The deposition of these reaction products occur both inter and intra-particle. The intra-particle deposits decrease the effective diffusivity of the catalyst particles for desulfurisation, thus causing deactivation by a pore-plugging mechanism [5] . In this earlier paper approximate methods were outlined to predict catalyst life for various feed-stocks at a particular liquid hourly space velocity (LHSV) and desulfurisation conversion. However, predictions were based on pore diffusion theory, initially developed by Thiele [6] , so that no particular pore model was required. This meant that catalysts with different pore size distribution could not be ranked for desulfurisation performance. In addition, pore plugging effects were averaged over the entire reactor length. A better approach would be to look more closely at the top of the reactor where the metals deposition rate is greatest. If pore plugging by metals is considered to be the primary mode of catalyst deactivation, the deactivation wave would probably begin at the top of the bed and then sweep down the reactor.

This paper considers catalyst deactivation in residuum hydrodesulfurisation by a pore-plugging mechanism in combination with coking effects.Simple catalyst pore size distributions are compared in desulfurisation service. Process conditions are varied to show their influence on catalyst lives. Predictions are compared with some available commercial data.

PROPOSED MODEL FOR CATALYST DEACTIVATION

The pore-plugging concept was proposed some years ago by Hiemenz [7] on the basis of gas permeability measurements on fresh and used catalyst pellets.Beuther and Schmid [8] compared the effects of coke deposits on the physical properties of various HDS catalysts. By comparing the surface areas and pore size distributions of fresh and spent catalysts, it was shown that the average pore radius was reduced only slightly

and that the pore size distribution maintained approximately the same percentage distribution in spite of a considerable reduction in surface area. It was observed that the coke content of the catalyst increased sharply to an equilibrium level in a short time, about 40 hours. It was postulated that this was due to a period of uncontrolled hydrocracking. Subsequently, the coke content of the catalyst was observed to remain constant with increasing process time.

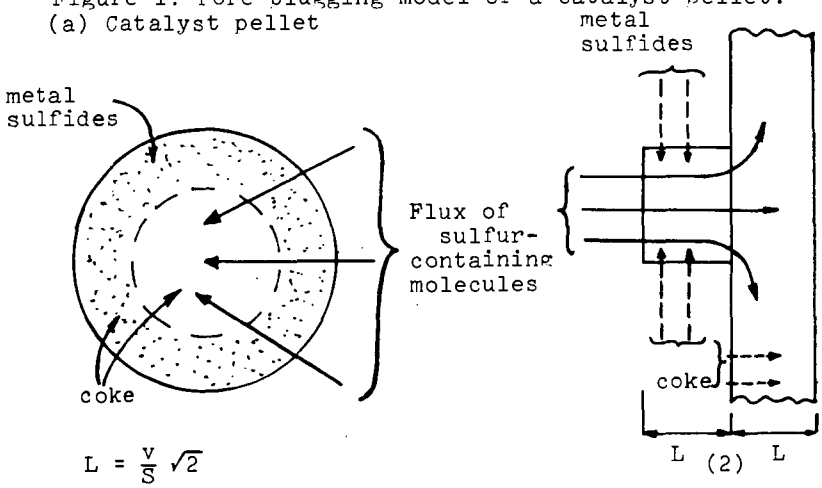
It is therefore proposed that the porosity of the catalyst is made up of three parts.

$$\Theta = \Theta_{c_I} + \Theta_{c_E} + \Theta_{MS} \qquad (1)$$

Rapid, initial coke deposition (Θ_{c_I}) takes up about one-third of the total porosity. Equilibrium coke deposition (Θ_{c_E}) and metal sulfides plugging (Θ_{MS}) then slowly decrease the remainder of the catalyst porosity. This slow utilisation of porosity is incorporated into a pore-plugging model. The latter assumes that only a fraction of the pellet is effective for the demetallation reactions. The flux of sulfur-containing molecules into the pellet is progressively impeded by the deposition of metal sulfides and coke in the catalyst pores. Figure 1(a).

The basis for the pore structure is Wheeler's model [9]. The pellet is approximated as a composite of N pores each of length L. Figure 1(b).

Figure 1: Pore-plugging model of a catalyst pellet.
(a) Catalyst pellet



where $L = \frac{V}{S}\sqrt{2}$

$$N = \frac{S\,\Theta(r)}{\pi r^2\sqrt{2}} = \frac{K_1}{r^2} \qquad (3)$$

The pore wall is not a continuous solid but has many intersections with other pores. The constant K_1 is a catalyst parameter and reflects the size and shape of the pellet together with its pore size distribution. The nature of the pore-plugging model suggests that the number of pores effective for demetallation (N_E) is some fraction of the total given by

$$N_E = \eta N \tag{4}$$

η refers to a time averaged effectiveness factor based typically on electron micro-probe analyses of metals profiles in spent catalyst from one long life test. Other catalysts with different pore size distributions can be compared with the experimental catalyst for potential demetallation capacity by

$$N_{E,B} = \frac{|\Theta(r)|_B}{|\Theta(r)|_A} \cdot N_{E,A} \tag{5}$$

Pore size distributions used in this paper are kept simple and follow Wheeler's approach [9]. For a Maxwellian distribution of pore sizes

$$L_M(r) = A_M \frac{r}{ro} e^{-r/r_o} \tag{6}$$

r_o is the most probable pore radius and is related to average catalyst properties by

$$\bar{r} = 3r_o = 2\frac{V_g}{S_g} \tag{7}$$

The corresponding pore volume distribution is

$$\Theta_M(r) = \int \pi r^2 . L_M(r) . dr \tag{8}$$

The Maxwellian or log normal distributions are considered since the pore size distribution of some hydrodesulfurisation catalysts can be approximated in this way [10]. For a Gaussian distribution of pore sizes

$$L_G(r) = A_G \exp{-\beta^2}(\frac{r}{r_o} -1)^2 \tag{9}$$

$$\bar{r} = r_o|1+\frac{1}{2\beta^2}| = 2\frac{V_g}{S_g} \tag{10}$$

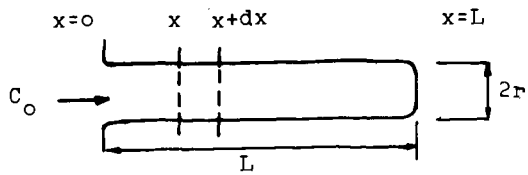
$$\Theta_G(r) = \int \pi r^2 . L_G(r) . dr \tag{11}$$

β is a parameter of sharpness for the distribution. Wheeler showed that many gel type catalysts have this type of pore size distribution [9].

THE DEACTIVATION RATE

Reaction parameters are now considered using an elementary solution for diffusion and reaction in pores which are less than about 50% available to the reaction [9]. This can be justified from preliminary estimates for catalyst life [5].

Figure 2: Diffusion and reaction in a cylindrical pore.



Considering a first order, irreversible reaction in a cylindrical pore and balancing the net influx against the rate of reaction

$$\pi r^2 D \left|\left(\frac{dc}{dx}\right)_x - \left(\frac{dc}{dx}\right)_{x+dx}\right| = 2\pi r dx k c(x) \qquad (12)$$

Dividing through by dx and letting dx→o,

$$\pi r^2 D \frac{d^2C}{dx^2} = 2\pi x r\ k\ c(x) \qquad (13)$$

This is the fundamental differential equation that is usually solved. However, when all the reactant diffusing into the pore is consumed at some distance $x_p \ll L$, then equation (12) can be simplified to

$$\pi r^2 D\left(\frac{dc}{dx}\right)_{x=o} = 2\pi r k \int_o^{x_p} C(x)dx \qquad (14)$$

Now $\left(\frac{dc}{dx}\right)_{x=o}$ can be approximated by $\frac{C_o}{x_p}$ and the exact reaction rate on the pore wall can be approximated by $2\pi r k \frac{C_o}{2}$. Equation (13) is reduced to

$$\pi r^2 D \frac{C_o}{x_p} = 2\pi r x_p k \frac{C_o}{2} \qquad (15)$$

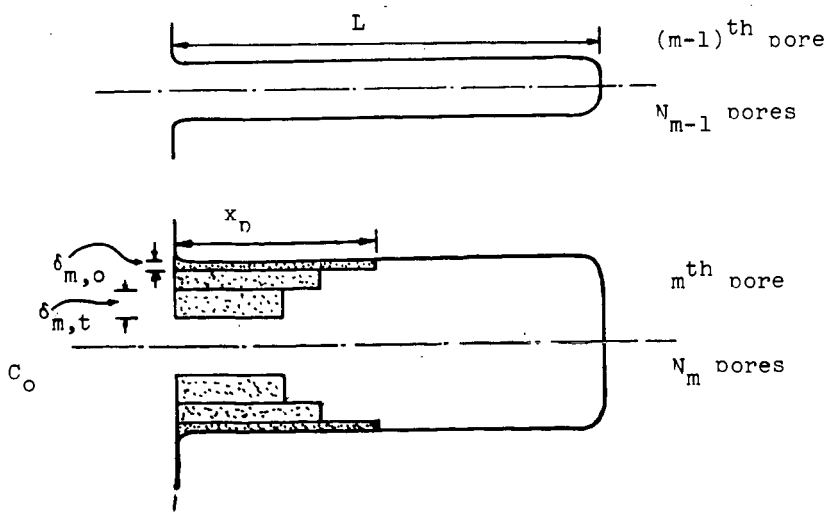
where x_p is the penetration length.

$$x_p = \sqrt{\frac{D}{k} r} = K_2\sqrt{r} \qquad (16)$$

The constant K_2 is dependent on feed type and process conditions both of which determine the demetallation reaction rate.

If the decay of catalyst is slow relative to the oil residence time, a quasi steady state assumption can be made to determine the decrease in pore radii due to deposition of reaction products i.e. coke and metal sulfides. This will then be related to catalyst deactivation.

Figure 3: Deposition of reaction products in catalyst pores.



If the plugging material is spread over all the pores contained in the outer section of the pellet, then the thickness of deposit δ_t for a finite increment of time Δ is given by

$$\delta_t = \frac{(Pl)_T \cdot \Delta}{2\pi \sum_m N_{E,m}\, r_{m,t}\, x_{m,t}} \qquad (17)$$

and

$$N_{E,m} = \frac{S(\Theta-\Theta_{C_T})\eta}{\pi\, r_m^2 \sqrt{2}} \qquad (18)$$

$$r_{m,t} = r_{m,o} - \sum_{o}^{t-\Delta} \delta_t \qquad (19)$$

$$x_{m,t} = K_2 \sqrt{r_{m,t-\Delta}} \qquad (20)$$

Assuming that the demetallation and desulfurisation functions of the catalyst are deactivating at approximately the same rate [11], then demetallation can be used to follow desulfurisation fouling rates. Since the overall demetallation rate equals the flux of metal containing molecules into the pellet,

$$\left[R_{HDM}\right]_t = F_t = \sum_m \frac{N_{E,m}\, r_{m,t}^2}{x_{m,t}} \qquad (21)$$

F_t/F_o is a measure of the decrease in reaction rate due to pore plugging. In constant conversion operation this is usually compensated by raising catalyst temperature. Assuming a power law deactivation function

$$Y \quad \alpha\ R_{HDM}^2 \quad \alpha\ R_{HDS}^2 \qquad (22)$$

then

$$Z = \left[\frac{F_o}{F_t}\right]^2 \qquad (23)$$

represents the number of times the initial deactivation rate is increased. F_o is known from the fresh catalyst properties and specified process conditions. F_t can be calculated at any time onstream so that a curve of deactivation rate ratio versus process time can be constructed. A value of 5-10 for this ratio will probably mean end-of-run under practical conditions.

THE PORE PLUGGING RATE

The rate of deposition of reaction products i.e. coke plus metal sulfides, can be estimated from the kinetics of the respective processes. Demetallation like desulfurisation can be represented by second order kinetics [8], the apparent anomaly being explained by considering the oil as a spectrum of compounds reacting at different rates. The equality of desulfurisation and demetallation selectivities is also well known for a wide range of crude oil sources [12].

For an ideal, plug flow reactor operating at steady state, isothermal operation may be assumed for finite volume element of reactor of length Δl. Considering an irreversible, second order, demetallation reaction taking place in the catalyst pores, a mass balance for reactant i gives

$$\text{In:} \quad (LHSV)\frac{\rho_F}{\rho_B} \frac{C_{F_i}}{1+C_{F_i}\ k_2\ \tau(\frac{l}{L})} \tag{24}$$

$$\text{Out:} \quad (LHSV)\frac{\rho_F}{\rho_B} \frac{C_{F_i}}{1+C_{F_i}\ k_2\ \tau(\frac{l+\Delta l}{L})} \tag{25}$$

At the top of the reactor where $\frac{l}{L}$ = o, the rate of deposition of metal sulfides in the first layer is

$$R_{MS_i} = M_i(LHSV)\frac{\rho_F}{\rho_B}\ C_{F_i}\ \frac{C_{F_i}\ k_2\ \tau(\frac{\Delta l}{L})}{1+C_{F_i}\ k_2\tau(\frac{\Delta l}{L})} \tag{26}$$

The contribution to the pore-plugging rate from the metal sulfides is the sum of all the depositing sulfides divided by a density factor

$$Pl_{MS} = \frac{d}{\rho_{MS}} \sum_{1}^{n} R_{MS_i} \tag{27}$$

n is usually equal to 2 i.e. vanadium and nickel ρ_{MS} was assigned a value of 2 gm/cc based on earlier estimates [5]. A distribution factor d is included to distinguish between metals depositing intra-particle and interparticle. Based on vanadium and nickel concentrations in the asphaltenes and maltenes fraction of oils, this factor is assumed to be 0.8 for a Safaniya atmospheric residuum.

The coke contribution to the pore-plugging rate can be deduced from the observed constancy in coke content of the desulfurisation catalyst during 40-400 hours of operation [8] and 50-1000 hours of operation [13]. At any time on-stream greater than 50 hours, it follows that

$$Q\%\ \text{coke} = \frac{W_c}{W_f + W_c + W_{MS}} = \text{constant} \tag{28}$$

Since the metal sulfides deposition rate is constant in constant conversion operation, the coking rate can be calculated from equation (28) with some modifications

$$\frac{W_{c_1} + \int_{50}^{t} R_C\ dt}{W_f + W_{c_1} + \int_{50}^{t} R_c\ dt + R_{MS}.t} = Q \tag{29}$$

W_c represents the rapid initial coke lay-down already described [8]. For small t ($\not>$ 50 hours), $R_{MS}t \to o$, so that W_f may be found if Q is specified. A typical value for Q would be 10 weight per cent coke. For t > 50 hours, R_c can be written in terms of R_{MS}

$$R_c = (\frac{Q}{1-Q})\ R_{MS} \tag{30}$$

The pore plugging rate due to coke can now be calculated using a coke density (ρ_c) derived from two sets of data [8]. A value of 0.7 gm/cc was calculated.

$$(Pl)_c = \frac{1}{\rho_c} \left(\frac{Q}{1-Q}\right) R_{MS} \qquad (31)$$

The total pore-plugging rate is given by

$$(Pl)_T = (Pl)_c + (Pl)_{MS} \qquad (32)$$

For 10 weight per cent coke on the catalyst, a total pore plugging rate of $\approx 1.3\ R_{MS}$ is calculated.

The total pore-plugging rate is put into equation (17) to determine the reduction in pore radii over the whole pore size distribution, equation (6) for example. The decrease in radius will reduce the flux of metal containing molecules into the pores, equation (21). This flux is compared with the initial value to calculate the catalyst deactivation with time from equation (23).

MAIN ASSUMPTIONS FOR RDS APPLICATIONS

To facilitate catalyst comparisons only one particular oil feedstock is considered, Safaniya (Khafji) atmospheric residuum. Its sulfur content is usually 4 weight per cent with vanadium and nickel contents of about 75 and 25 ppm respectively. Deposited sulfides were assumed to have the formulae V_2S_3 and Ni S.

The desulfurisation performance for various catalysts was compared by coupling their demetallation and desulfurisation functions. For a Safaniya atmospheric residuum at LHSV=1.0 and a desulfurisation conversion of 75%, effective diffusivity values of 6×10^{-8} and 3×10^{-7} cm^2/sec. were estimated for demetallation and desulfurisation respectively [5]. Figure 4 was constructed from the equation [6].

$$\Phi = \frac{R^2}{D_{eff}} (R_{HDM}) \frac{1}{Co} \qquad (33)$$

where

$$D_{eff} = \frac{D(\Theta - \Theta_{C_I})}{2} \qquad (34)$$

From Figure 4, effectiveness factors for demetallation and desulfurisation were found to be 0.1 and 0.45 for a 0.16 cm (1/16 inch) diameter sphere. Subsequent process condition changes leading to temperature changes were made by modifying the intrinsic activation energy using the equation [14].

$$\frac{E_{INT}}{E_{OBS}} = 2 - \eta \qquad (35)$$

Intrinsic activation energies for demetallation and desulfurisation were chosen as 30 and 40 kcals/gram mole. The latter value is realistic based on recent literature [15] when a value of 38 kcals/gram mole was measured. The former value reflects the fact that metal-containing molecules are derived from the heavier portion of the feedstock (550°C+) whereas the sulfur-containing molecules are derived from the whole boiling range (325°C+) of the oil.

At process conditions of LHSV=1.0, 75% conversion and 1500 psig, the coke level on the catalyst was assumed to be 10% by weight [13]. This level was adjusted for temperature changes using the temperature dependence of coke content found by Voorhies [16].

A "standard" catalyst whose properties could be considered suitable for hydrodesulfurisation was selected for the purpose of making catalyst life predictions. Its properties are shown in Table 1 together with properties of two other catalyst which were also considered.

Table 1

Catalyst	"Standard"	Macropores	$\bar{r}$ - shift
$\bar{r}$ (Ångstroms)	40	40	65
V_g(micropores	0.5	0.425	0.7
S_g m^2/gm	250	212	215
R cm	0.08	0.08	0.08
ρ_B	0.7	0.59	0.57
ρ_P	1.2	1.02	0.97
shape	sphere	sphere	sphere
β	5	5	5
% macropores (> 600 Å)	0	15	0

The above catalyst properties were inter-related by the equation

$$\frac{1}{\rho_P} - \frac{1}{\rho_s} = V_g \qquad (36)$$

Pore volume distributions of the catalysts considered subsequently are shown in Figure 5.

DISCUSSION OF MODEL PREDICTIONS

The effect of changing process conditions on catalyst life is shown in Figure 6. The deactivation rate ratio is plotted versus hours on-stream. At an LHSV = 1.0 and 75% conversion, a catalyst life of 1000 hours is predicted. This compares with about 3300 hours (z=5) when the conversion is dropped to 63%. Another curve, LHSV = 0.7 and 75% conversion is shown in Figure 6. These conditions were chosen for comparison with data from the Gulf Tokyo paper [4], Figure 4 and Table 6. From these data the conversion of 75% was given but only a "fixed" space velocity is mentioned. This has been assumed to be 0.7. With this assumption, the pore-plugging model suggests a life of 4000 hours compared to 4500-5000 hours from the Gulf Tokyo paper. Obviously more information on catalyst properties and process conditions is required when commercial data is published. However, the pore-plugging model and the initial assumptions give good order-of-magnitude comparisons.

The effects of changing the pore size distribution of the "standard" catalyst and $\bar{r}$-shift are shown in Figure 7. For a fixed average pore diameter, changing pore size distribution has little effect on catalyst life. The log normal or Maxwellian distribution may have been predicted to give an increased life because of the "tail" in the distribution but since the most probable pore radius is only 15Å(=r_o), the advantage of the broader distribution is lost. If the peak radii, normal versus log normal were both the same, then the broader distribution could be more effective. With a normal distribution, increasing the average pore radius has a big effect on catalyst life. A value of 2000 hours is predicted for the $\bar{r}$-shift catalyst in Table 1. This order of magnitude effect has been observed for this feedstock at these conditions [17] but complete data is not available.

Putting macropores into the catalyst or decreasing pellet diameter also increases catalyst life. The net effect in both cases is to substantially increase the number of pores available for metal sulfides deposition. In Table 1, 15% macropores have been substituted for micropore volume and it is assumed that an increase in effective diffusivity of (x3) is obtained. In Figure 8, a catalyst life of 2000 hours is predicted compared to 1000 hours for the zero-macropores "standard" catalyst. Particle size effects are greater since the increase in number of available pores is effective on the unchanged "standard" catalyst micro-

porosity (=0.6). A life of 3000 hours is predicted i.e. an increase of (x3) when pellet diameter is reduced by (x2). If reactor pressure drop problems are likely, then macropores must be considered first for increasing catalyst life. The approach is limited however by the decreasing strength of the pellet as porosity is increased. Alternatively, changing reactor design, radial flow instead of axial flow [18], would allow smaller particles to be used, about 0.5 mm diameter. Catalyst life would then be substantially increased.

Catalyst changes have previously been physical in nature i.e. macropores, r-shift and particle size. The chemical composition of the catalyst was not changed. The role of coke in pore-plugging does suggest that increasing the hydrogenation function of the catalyst may increase catalyst life e.g. nickel as a "kicker". If nickel was substituted for part of the cobalt then some desulfurisation activity might be lost since the optimum cobalt/molybdenum ratio has been changed [19]. The net effect would be to lose some initial activity but more micro-porosity would be available due to a lower equilibrium coke level on the catalyst. This is the basis for Figure 9 when the coke level of the "standard" catalyst was assumed to be reduced from 10% to 7% due to increasing the hydrogenation function of the catalyst. The catalyst life is seen to be increased from 1000 to 1500 hours(z=5).

The effect of changing process pressure also illustrates the coke contribution to the pore plugging deactivation model. Figure 9 shows that reducing pressure from 1500 psig to 800 psig decreases catalyst life by (x2). An obvious way to compensate is by decreasing LHSV e.g. from 0.7 to 0.5, a ratio of 1.4. At the lower space velocity, a prediction of 5000 hours is obtained and the catalyst life is now close to the 1500 psig case. This space velocity effect with pressure compares favorably with the Esso Tokyo paper, Figure 7, [4]. Data showed that catalyst life was the same when operating at 1500 and 800 psig provided space velocity compensation was employed. The relative catalyst activity in the Esso data was also about 1.4.

CONCLUSIONS

A pore-plugging model for residuum hydroprocessing in axial-flow trickle-bed reactors has been proposed in order to quantitatively describe catalyst deactivation. The pore-plugging is due to the deposition of reaction products, metal sulfides and coke,during the (desired) desulfurisation reaction. The desulfurisation and demetallation reactions were considered in parallel in order to make predictions for catalyst life. A simplified approach was taken in describing catalyst pore size destributions and approximating the equations for diffusion and reaction in a catalyst pore.

Predictions for catalyst life were made when process conditions and catalyst parameters were changed. As a check on the initial assumptions and the simplified approach, comparison with commercial data was made and showed good order-of-magnitude agreement.

A more rigorous approach should now be considered as more data becomes available. Design of new and improved catalysts and reactor systems should be the result.

NOMENCLATURE

A_M, A_G	absolute frequency of pore sizes
C	concentration of reactant, metal containing molecules, inside the catalyst pores, mol. cm^{-3}.
C_o	concentration of reactant at the pore mouth.mol. cm^{-3}.
D	diffusivity of metal containing molecules in the oil, cm^2 $sec.^{-1}$.
F_t	flux of metal containing molecules into the pellet at time t, mols. hr^{-1} gm^{-1}.
k	first order intrinsic reaction rate constant,cm $sec.^{-1}$.
k_2	second order reaction rate constant, cm^3 $hr^{-1}mol^{-1}$.
K_1	catalyst parameter, equation (3), cm^2 gm^{-1}.
K_2	pore penetration parameter, equation (16), cm.
L	pore length, equation (2), cm.
$L_M(r)$	total length of pores of radius r per gram of catalyst in Maxwellian distribution, cm gm^{-1}.
n	number of reactants in the feed.
N	total number of pores per gram of catalyst, equation (3), gm^{-1}.
N_E	number of pores per gram of catalyst in which pore plugging occurs, equation (4), gm^{-1}.
Pl_{MS}	metal sulfide pore plugging rate, cm^3 hr^{-1} gm^{-1}.
Pl_c	coke pore plugging rate, cm^3 hr^{-1} gm^{-1}.
Pl_T	total pore plugging rate.
Q	coke on catalyst, % by weight.
r	pore radius, cm.
r_o	most probable pore radius in Maxwellian pore size distribution, cm.
R_{HDS}	desulfurisation rate, mol. hr^{-1} gm^{-1}.
R_{HDM}	demetallation rate, mol. hr^{-1} gm^{-1}.
R_{MS}	metal sulfides deposition rate hr^{-1}.
R_c	coke deposition rate, hr^{-1}.
S	pellet surface area, cm^2.
S_g	catalyst surface area, cm^2 gm^{-1}.
v	pellet volume, cm^3.
V_g	catalyst pore volume, cm^3 gm^{-1}.
w_f	fresh catalyst weight, gm.
w_c	coke weight, gm.
w_{MS}	metal sulfides weight, gm.
	reactant penetration length into the pore,
(LHSV)	liquid hourly space velocity, hr^{-1}.
D_{eff}	effective diffusivity of catalyst pellet,equation(34), $cm^2.sec^{-1}$.
E_{INT}	intrinsic activation energy kcals.gm mol^{-1}.
E_{OBS}	observed activation energy kcals.gm mol^{-1}.
R	radius of catalyst pellet, cm.
Z	catalyst deactivation rate ratio.

NOMENCLATURE

Greek letters.

δ	thickness of deposit in catalyst pores, cm.
Δ	element of time for reaction, hr.
Δl	length of volume element in plug flow reactor, cm.
Θ	total catalyst porosity.
Θ_{c_I}	catalyst porosity lost to coke during rapid initial deactivation.
Θ_{c_E}	catalyst porosity lost to coke after initial coke formation.
Θ_{MS}	catalyst porosity lost to metal sulfides after initial coke formation.
η	"time averaged" effectiveness factor.
ρ_c	coke density, gm. cc^{-1}.
ρ_B	catalyst bulk density, gm, cc^{-1}.
ρ_F	density of feed stream, gm cc^{-1}.
ρ_{MS}	metal sulfides density, gm. cc^{-1}.
ρ_P	catalyst particle density gm cc^{-1}
ρ_S	catalyst skeletal density gm cc^{-1}

Subscripts.

A,B	catalyst with different porosity distributions.
m	any pore in the catalyst of radius r.
t	any time on-stream (> 50 hours).
o	time initial for pore plugging (= 50 hours).
i	any reactant in the feed.

REFERENCES

[1] Duprey, R.L., C.E.P. 68, February, (1972), 70-76.
[2] "Energy: a look ahead", Humble Oil and Refining Co., July (1971).
[3] McKinney, J.D., Stipanovich, J., Hydrocarbon Processing, May (1971), 97-102.
[4] "Fuel Oil Desulfutisation Symposium", Japan Petroleum Inst., Tokio, Japan, March 10-11, (1970).
[5] Newson, E.J., Div.Pet.Chem. Preprints, 160th. Natl. ACS Meeting, Chicago, Ill., USA, Sept.(1970) A141-152.
[6] Satterfield, C.N., "Mass Transfer in Heterogeneous Catalysis", M.I.T.Press, Cambridge, Mass., (1970), Chapter 3.
[7] Heimenz, W. Discussion, Paper 20, Sixth World Petroleum Congress, Frankfurt, June (1963), Section 3, p 307.
[8] Beuther, H., Schmid, B., Paper 20, ibid, 297-307.
[9] Wheeler, A., "Advances in Catalysis", Vol III, (1951), 250-326, Academic Press, N.Y.
[10] Debaun, R.M., et al, J.Chem. and Eng. Data, 7, No.1, (1962), 94-97.
[11] Audibert, F., Duhaut , P., 35th Midyear Mtg.,API Div. of Refining. Houston, Texas, Preprint No. 50-70, May 15, (1970).
[12] Radford, H.D., Rigg, R.G. Div.Pet.Chem.ACS Preprints, 160th Meeting, Chicago, Ill., Sept. (1970),A 131-140.
[13] Egi, K., Matsumoto, K.Chemical Economy and Engineering Review, November (1970), 7-14.
[14] Weisz, P.B., Parter, C.D., "Advances in Catalysis", Vol VI, (1954), Academic Press, N.Y.
[15] Cecil, R.R., et al., 61st Annual AIChE, Los Angeles, Calif., December (1968), Paper 12a.
[16] Voorhies jr.,A, IEC 37, No. 4, (1945),318-322.
[17] US 3, 577, 353, May(1971).
[18] NL 7110729 (1972).
[19] Schuman, S.C., Shalit, H.Catalysis Reviews 4(2), (1970) 245-318.

Figure 4: Catalyst particle diameter v. effective diffusivity.

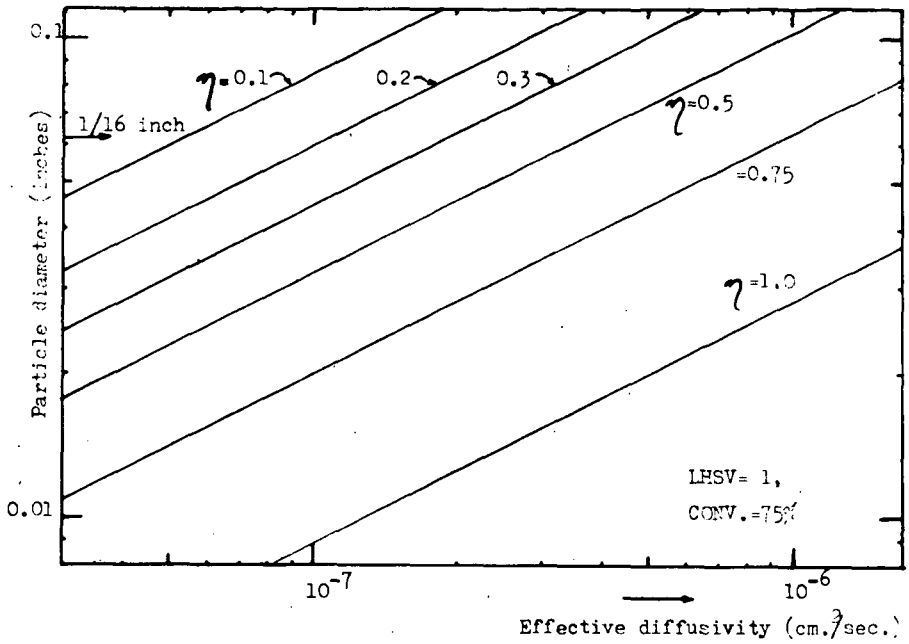


Figure 5: Catalyst pore size distributions.

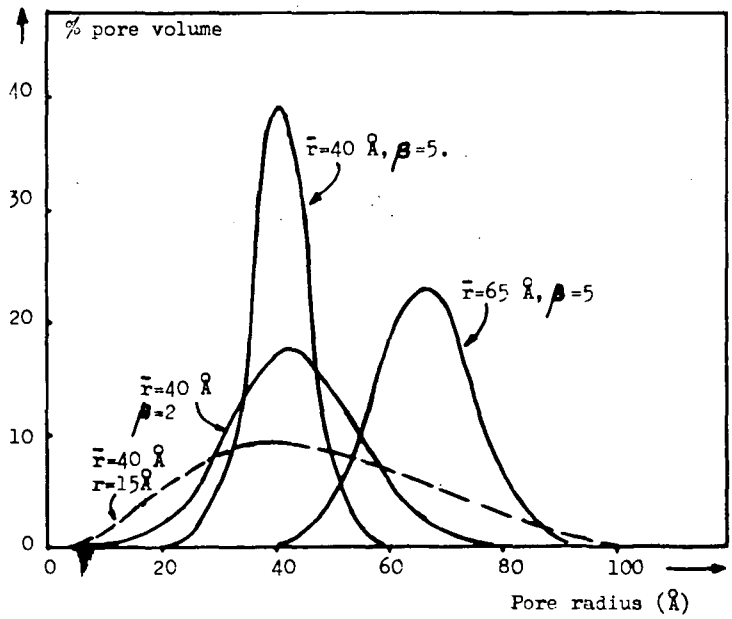


Figure 6: Effect of process conditions on catalyst life

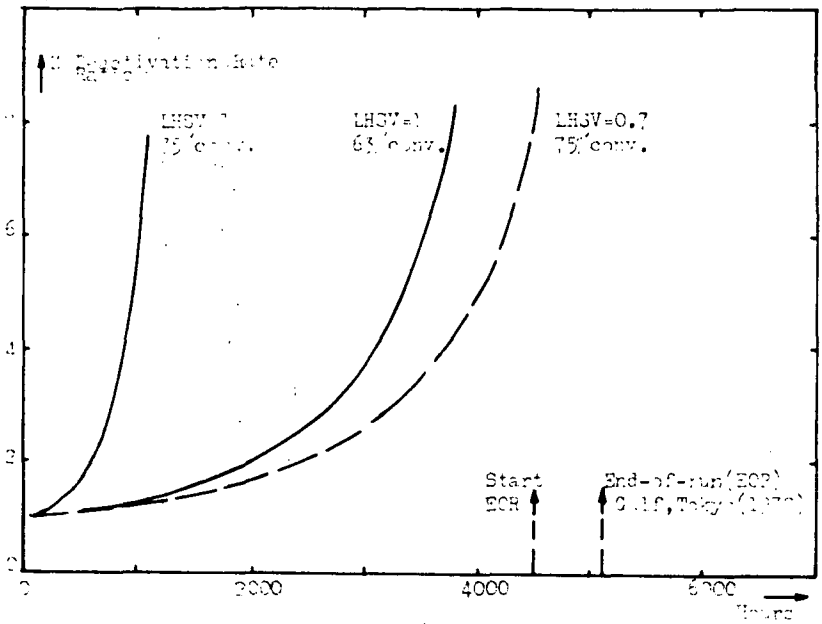


Figure 7 : Effect of pore size distributions, $\bar{r}$-shift.

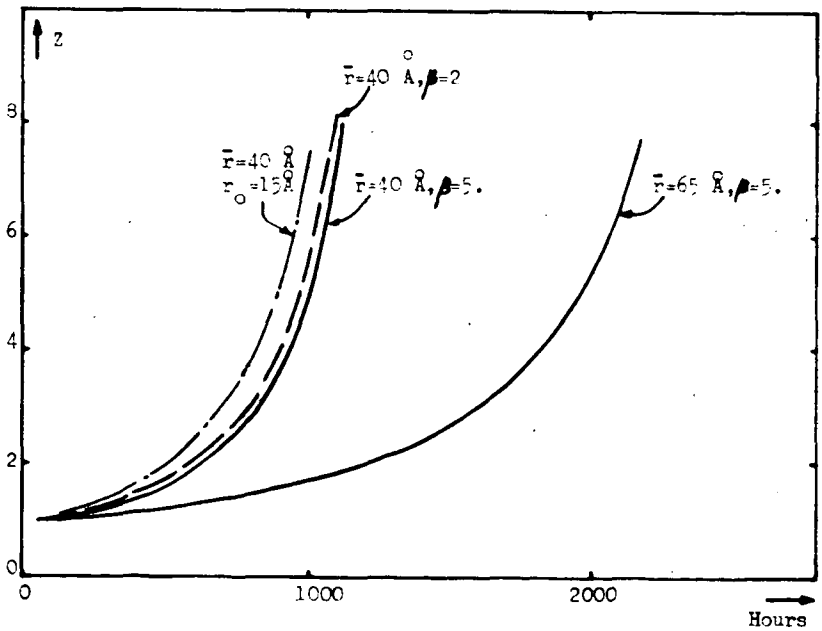


Figure 8: Effect of macropores, particle size on catalyst life.

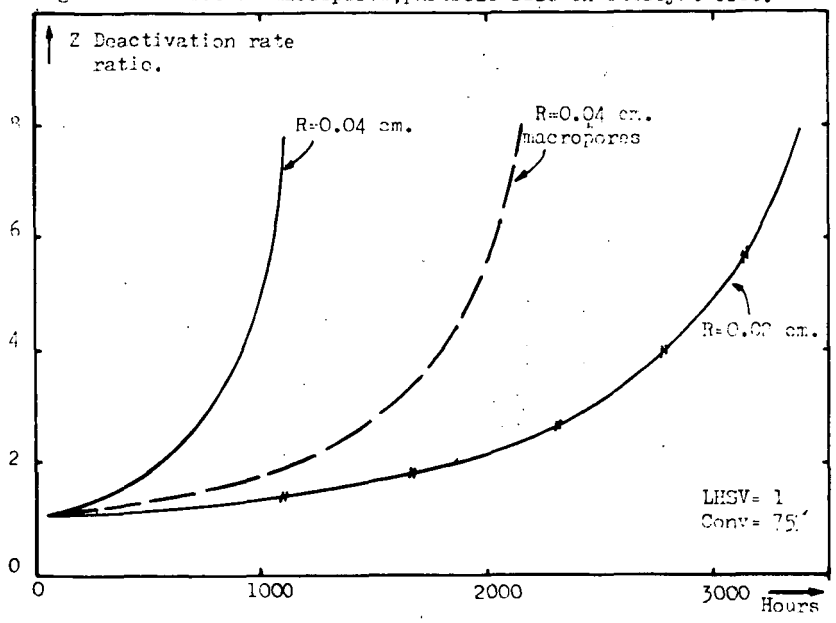
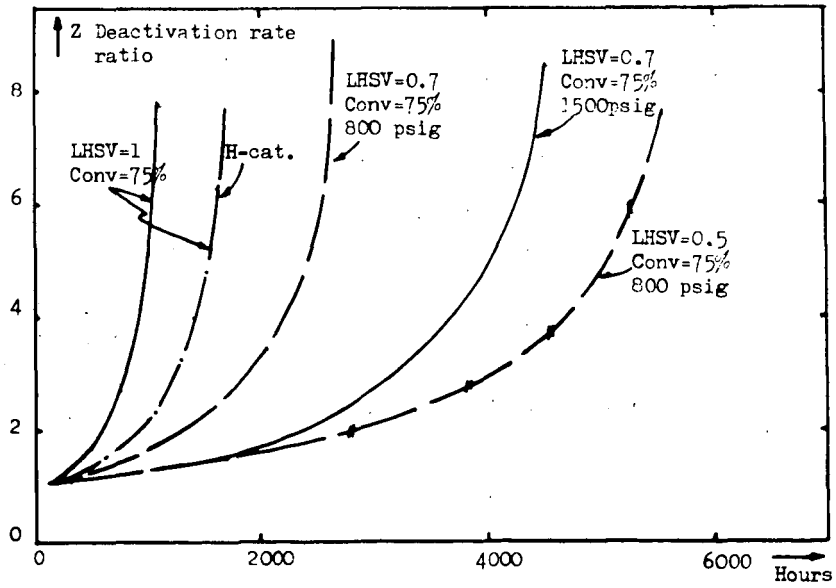


Figure 9: Effects of coke, total pressure on catalyst life.



H-OIL DESULFURIZATION OF HEAVY FUELS

Axel R. Johnson, Vice President - Sales
Ron H. Wolk, Director of Pilot Plants
Ray F. Hippeli, Process Engineer
G. Nongbri, Research Engineer

Hydrocarbon Research, Inc.
New York, New York

INTRODUCTION

In many areas of the world residual fuel oil has become the principal source of industrial, commercial and utility fuel. In these services it has historically been the marginal energy source with locally produced coal or natural gas being the fuel of choice on economic grounds. At present, however, air pollution control regulations relating to fuel sulfur content have limited the use of many sources of coal, and in many important areas low cost natural gas is becoming critically short in supply. Because of these factors, fuel oil consumption is growing rapidly - and in many instances at a rate substantially above the normal growth in energy demand. This growth in demand - coupled with increasingly stringent sulfur content specifications, is leading in the direction of a shortage in residual fuels - particularly those of lower sulfur contents.

These factors have already led to a substantial investment in fuel oil desulfurization facilities in several parts of the world - notably in Japan, the Middle East and the Caribbean area. With some few exceptions these facilities have been based on indirect desulfurization - i.e. vacuum distillation, desulfurization of the vacuum gas oil and reblending. This technique has a real limitation in a market for fuels below the 1% sulfur level since none of the heavy high sulfur vacuum residue is processed. To some extent this can be mitigated by preferentially blending this material to bunkers and by the use of naturally occurring low sulfur residues as blending stocks.

In many supply and consumption areas we are now nearing - or have passed - the limits of these approaches, and the industry is giving serious consideration to the installation of facilities which will process the entire residue to achieve the desired end product. It is the purpose of this paper to consider some of the problems associated with processing residual oils and to present some major new developments in the H-Oil process which relate to the solution of these problems. Because of these new developments it is now possible to design a processing facility which can economically produce fuel oils of 0.3% sulfur content, interchangeably from a broad range of feedstocks encompassing most of the commercially important residues. One of the most significant aspects of these new developments involves the ability to economically desulfurize the high metals content residues from Venezuela.

FACTORS AFFECTING A FUELS PROCESSING FACILITY

In this paper we will concentrate on the problems associated with a market-related fuels process facility - specifically one which would serve the East Coast of the United States. Planning such a facility involves the several fundamental questions considered below.

Source of Supply

The traditional source of fuel oil supply for the U.S. East Coast has been Venezuelan imports. Under the impact of the newer sulfur content specifications, an increasing portion of this fuel is being obtained from African crudes, and it is possible that the Middle East may also become an important factor in this market. For these reasons, as well as from a national security standpoint - particularly as we become more dependent on fuel oil for basic energy - the refiner will be faced with the problem of providing the capability to handle a broad range of feedstocks.

Market Requirements

The requirements for low sulfur fuel oil have become increasingly stringent, and the market requirements for this product is subject to the vagaries of local and national regulations. Consequently, market requirements cannot be forecast with a high degree of accuracy. For this reason the facility must be flexible in terms of the quality of product produced.

Adaptability

At a future date the market for low sulfur fuel oil may become less attractive due to several factors. Among these are: increasing use of nuclear energy, the installation of stack gas desulfurization processes or increased availability of low sulfur fuels. Should this occur it would be desirable to make alternate use of any facility installed today to desulfurize fuel oil. At such a time the market could revert to the traditional U.S. pattern in which high sulfur residual oil is a low value material, and there would be a consequent economic incentive to convert it into lighter products.

Considering these factors an optimum fuels processing facility should possess the following basic characteristics:-

1. The ability to process fuel oil at low unit cost
2. Be able to handle a broad range of residual fuels as feedstock
3. Have the capability of meeting changing fuel oil specification requirement
4. Have an economical alternate use in the event of a decreased demand for low sulfur fuel oils.

In a later section of this paper we describe a facility which meets these requirements. First, however, we would like to consider some of the technical problems associated with residual oil processing - and how the solutions to these problems are approached in the H-Oil process.

TECHNICAL ASPECTS OF RESIDUE DESULFURIZATION

Reaction Mechanism

Various investigators have shown that a first order kinetic model adequately describes the desulfurization of the individual sulfur compounds contained in petroleum fractions. In the case of residual oils, however, we are not dealing with individual compounds or with a few similar species, but rather with a complex mixture of compounds having widely differing reaction rates. Since the compounds which are easier to react will tend to disappear first, while those having a lower reaction rate constant will desulfurize last, desulfurization of these materials, viewed on an overall basis, does not follow a first order kinetic model. Beuther and Schmid[1] found that desulfurization of residues can be represented adequately by use of a second order model. These authors recognized that the individual reactions were probably first order, but that a second order model would best represent the overall data. By using a psuedo second order approach, the fact of increasing difficulty of desulfurization is reflected in the concentration term of the rate equation, enabling one to use a fixed reaction rate constant.

Our work in this area has confirmed the observations of Beuther and Schmid and in Figure 1 we show, for the desulfurization of Kuwait atmospheric residue, a comparison of the fit of the data to first and second order models. In developing this plot, average first and second order K-values were calculated from data obtained under various operating conditions over fresh catalyst. The curves shown were then prepared and compared with the data. It is apparent that the second order relationship more accurately represents the situation. In use of these relationships, however, it should be borne in mind, that this is an empiricism and data extrapolations must be treated with caution.

A practical consequence of the psuedo second order model is, that as market requirements dictate a lower sulfur content product, the reaction rate in the final stages of a process will be quite low. With a second order model the reaction rate in the final incremental portion of a reactor system will be only one tenth at the 0.3% sulfur level what it would be at the 1% sulfur level.

Catalyst Aging

In hydroprocessing of residual oils, catalysts lose activity at a much higher rate than is the case in gas oil processing. This is due to the presence of organometallic compounds, asphaltenes and the general higher molecular weight of the material being processed. Further, since there is a considerable range in the metals contents of the various stocks available for processing, residues from different crudes will deactivate catalysts at different rates. Figure 2 illustrates this point by comparing the aging characteristics of Kuwait and Venezuelan atmospheric residues. Psuedo second order reaction rate constant is plotted versus catalyst age for these two stocks processed under the same conditions. While both stocks exhibit a rate of activity decline considerably above that which would be experienced in processing of gas oils, the effect of the higher metals content in the Venezuelan oil is rapidly apparent from the higher rate of activity decline.

Effect of H_2S on Reaction Rate

As the desulfurization reaction proceeds, H_2S is produced. This material, while mainly in the vapor phase, is in equilibrium with a concentration of dissolved H_2S in the liquid. Under certain conditions the mass action effect of this material can have a strong effect on the overall rate of the desulfurization reaction. Figure 3 shows the effect, for one set of circumstances, of H_2S partial pressure on the psuedo second order reaction rate constant. Again, it should be emphasized that the constant shown is not a true reaction rate constant - which would be independent of such parameters - but is rather an overall representation of several simultaneously occurring forward and reverse desulfurization reactions.

When operations are directed to achieving very low levels of sulfur in the product, this effect-coupled with the other difficulties of such an operation - can have important design consequences.

THE H-OIL APPROACH TO THE PRODUCTION OF LOW SULFUR FUEL OILS

Several previous papers by HRI and Cities Service Research and Development Company 2,3,4,5 have reviewed the H-Oil process with respect to its principal characteristics and commercial performance. The major difference between H-Oil and the other processes for production of low sulfur fuels is a novel reactor system in which the oil and hydrogen are passed upflow through the reactor at a velocity sufficient to maintain the catalyst in a suspended or ebullated state. This reactor system offers several advantages:-

1. It is isothermal,
2. It is not susceptible to pressure drop build up due to suspended materials contained in the feed,
3. Catalyst can be added and withdrawn during operation to maintain a constant level of catalyst activity.

Reactor Staging

For practical purposes, the H-Oil reactor can be considered as a completely back mixed system. In such a reactor, the character of the reacting mixture is essentially identical to the material leaving the reactor. From the point of view of the desulfurization reaction then, as a consequence of the second order rate equation,

$$r = kc^2$$

the reaction rate will be proportional to the square of the concentration of the effluent. As the process is required to produce a lower sulfur content product then, the reaction rate will decrease rapidly. As noted earlier the rate at 0.3% sulfur will be only one tenth that at 1% sulfur. In theory then a single reactor to produce a 0.3% sulfur product would be well over ten times as large as one producing a 1% sulfur product - all other factors being equal.

In the H-Oil process this problem is solved by staging the reactor system by using two or more reactors in series. In this way the reaction is carried out at several decreasing sulfur contents. This provides for higher reaction rates in those reactors in which the bulk of the desulfurization is occurring.

Figure 4 illustrates this effect for the processing of Kuwait atmospheric bottoms at various sulfur contents. Relationships are shown for the desulfurization efficiency of one, two and three stages in series versus a theoretical plug flow reactor.

Catalyst Counterflow

A further area of design optimization relates to the catalyst aging effects discussed earlier. If we use three H-Oil stages in series in order to achieve a very high degree of desulfurization, then there is a distinct advantage in charging all of the makeup catalyst to the third reactor stage. This material would then be withdrawn, charged to the second stage and in like fashion the second stage catalyst would be then charged to the first reactor. We thereby achieve a counter-current flow of oil and catalyst, in which the freshest catalyst is exposed to the cleanest oil in the reactor which requires a high degree of catalyst activity in view of the low sulfur concentration present. At the same time, the faster reactions take place in a reactor in which the catalyst has reached its final equilibrium level prior to being discarded. The line for the back staging of catalyst in a three stage system, shown in Figure 4, indicates that by this approach virtual equivalence is attained between the H-Oil system and a theoretical plus flow reactor.

Split H_2 Recycle

A process flow scheme using the backflow catalyst/three stage system is shown in Figure 5. This is basically the reactor scheme which would be utilized within an H-Oil unit designed to achieve very low sulfur contents. A further aspect of this system, shown in Figure 5, is the use of a split recycle system. In this way H_2S free hydrogen would be sent to the third reactor thereby maintaining an extremely low H_2S partial pressure at this critical point in the reactor system.

Residue Demetallization

One of the most difficult problems associated with design of a facility to process a broad range of feedstocks has been the problem of handling those residues having a high concentration of organo-metallic compounds. Figure 2, shown earlier, illustrates the rate at which H-Oil catalyst deactivates while processing a medium Venezuelan residual oil. Operation with this feed to produce a low sulfur fuel would require a very high rate of catalyst addition.

A joint HRI/CSRD research program has been underway for more than three years at the HRI laboratories to develop a demetallization procedure which would reduce the nickel and vanadium contents of fuel oils in order to produce an oil for further processing by H-Oil at low catalyst addition rates. These research efforts have resulted in the development of solid adsorbent materials which are low in cost, and effectively remove the bulk of the organo-metallic compounds present in such oils. These solids are used in an H-Oil reactor with the conventional ebullated bed principle, which is then followed by one or more H-Oil stages using conventional catalysts.

Figure 6 shows the effect of using this newly developed procedure in the processing of Venezuelan oil. The upper curve in Figure 6 shows the desulfurization of a medium Venezuelan residual oil as a function of catalyst age. The lower curve represents the performance of the same oil, over the same catalyst, after it has been processed through the newly developed demetallization procedure. The advantage of such operation are obvious, and this procedure makes practical the processing of these oils at low rates of catalyst usage. This procedure removes the limits previously placed on residue processing by metals content and all of the presently produced crudes can be considered for the production of low sulfur fuels.

New Catalyst Developments

In addition to the processing approaches discussed above, HRI and CSRD, together with several catalyst suppliers have engaged in continuing development activities relating to the development of improved H-Oil catalysts. These studies have covered catalyst composition, pore size distribution, catalyst size, etc. Figure 7 illustrates one of the more promising newer catalysts compared with the H-Oil catalyst which has been used in most commercial operations to date.

CHARACTERISTICS OF A MULTI-PURPOSE DESULFURIZATION PLANT

We have noted earlier that a refiner or fuel processor must live in an uncertain environment. He is subject to the vagaries of the supply of crude, the requirements of the market, and the perpetual question of the future markets for residual fuel. We have developed a processing approach - using the H-Oil process which provides the degree of flexibility necessary to cope with this uncertain environment. A schematic flow diagram of such a multi-purpose plant is shown in Figure 8. The basic features of this plant, which has been designed for the prodution of 0.3% sulfur fuel oil from various atmospheric residua, are its flexibility with respect to feedstock, product specifications and future alternate uses of the plant.

The data developed in this illustration have been based on the use of conventional H-Oil catalyst. If one of the newer catalysts, referred to earlier, were used, the same results would be achieved at somewhat lower investment and at substantially reduced rates of catalyst usage.

Base Operation

The feedstock flexibility of the plant is illustrated by the data in Table 1. Using the identical plant, we show the ability of this facility to process Venezuelan, Kuwait and West Texas atmospheric residues as well as West Texas vacuum residue to produce 0.3% sulfur fuel oil product. The capacity of the plant varies with each of these stocks because of the varying sulfur contents and difficulty of processing of the various raw materials. The refiner with such a unit should be able to change his source of supply amongst most of the commercially important crude sources, thereby optimizing his operation with respect to raw material supply.

When changing crude type certain operational changes would be required. For example, the optimum catalyst will vary with different crudes, and in the case of high metals stocks such as Venezuelan, the first reactor would be used for the demetallization procedure. These changes, however, would not require extensive shut down and apart from the change of catalyst type, the rest of the processing facility is completely adequate for all of the services.

Flexibility with Respect to Product Specifications

Again, considering the same processing facility, if it were desired for market reasons to produce a product of higher sulfur content or a variety of grades of products this could be readily accomplished. In such a case plant throughput would increase since hydrogen consumption per barrel of feed would be less.

Should it be necessary at some future date to produce fuel oils having sulfur contents lower than 0.3%, in the same facility, this can be achieved either by reducing flow rate through the plant or by separating some of the desulfurized vacuum residue for sales as bunkers, thereby decreasing the sulfur content of the lighter product.

Future Applications

If, in the course of time, nuclear power becomes more prevelant, or if stack gas desulfurization processes are brought to a point of economic application, the market for low sulfur fuel oil may contract and the price decrease. Under either of these circumstances we would revert to the classic U.S. position in which high sulfur vacuum residue is a marginal product and a candidate for conversion to lighter materials.

The type of unit described here can, if desired with this future use in mind, be used to convert vacuum residues to lighter materials or to prepare feedstock for low sulfur coke production. These applications of the process have been discussed in several previous papers. A good commercial example of this flexibility is shown in Table 2. These data, taken from a previous Cities Service publication, show operations of the Lake Charles H-Oil unit when processing for conversion and for desulfurization.

Fuel Oil Processing Costs

Figure 8 is a block flow diagram of the plant under consideration. Included are a hydrogen plant and a sulfur plant, as well as the H-Oil processing facility. The hydrogen plant is supplied with its fuel and raw material from the light products produced within the H-Oil system and therefore the entire complex requires no hydrocarbon raw material other than the fuel oil feed. This is therefore a completely self-contained facility - not dependent on the availability of natural gas or other hydrogen raw material.

Investment and operating requirements for the complex are presented in Table 3, and in Table 4 these factors have been converted into a daily processing cost exclusive of H-Oil catalyst. This latter item is specific to the feed in question.

Unit processing costs are summarized for the various feedstocks in Table 5 which then shows the relationship between feed type and processing costs as well as the effect of product sulfur content on processing cost.

FUELS REFINERY

The processing scheme just discussed uses atmospheric and vacuum residues as its raw material. Recently, consideration has been given to a fuels refinery concept in which whole crude oil is processed to yield only utility fuels. The processing sequence discussed in this paper would fit quite well into such a processing sequence. A block flow diagram of fuels refinery is shown in Figure 9.

Such a complex would produce low sulfur content fuel oil, turbine fuel, and naphtha. The naphtha product could be a raw material for the production of either SNG or petrochemicals.

In summary, new developments in the H-Oil process have made it possible and practical to design a fuel processing plant which would have the degree of flexibility necessary to handle raw crudes from various sources and to enable the processor to meet the varying requirements of the markets which may be imposed on him with changing product specifications and product requirement.

ACKNOWLEDGMENT

The writers wish to express their appreciation to the management of Hydrocarbon Research, Inc. and Cities Service Research and Development Company for permission to publish this work, and further we wish to recognize the contributions of many members of the staffs of both companies to the development presented herein. Specifically, the contributions of Messrs. M. C. Chervenak and L. M. Lehman of Hydrocarbon Research, Inc. and R. P. Van Driesen of Cities Service Research and Development Company are gratefully acknowledged.

BIBLIOGRAPHY

1) Beuther, H. and Schmid, B.K. Section III, Paper 20-PD7 World Petroleum Congress, Frankfurt, 1963

2) Griswold, C.R. and Van Driesen, R.P. Paper 53-66 API Division of Refining, May 11, 1966

3) Van Driesen, R.P. and Rapp, L.M. Paper I.P. No. 32 World Petroleum Congress, Mexico City, 1967

4) Johnson, A.R., Papso, J.E., Hippeli, R.F. and Nongbri, G. Paper 48-70 API Division of Refining, May 15, 1970

5) Johnson, A.R., Papso, J.E., Hippeli, R.F. and Wolk, R. Paper AM-71-17 NPRA Annual Meeting, March 21-23, 1971

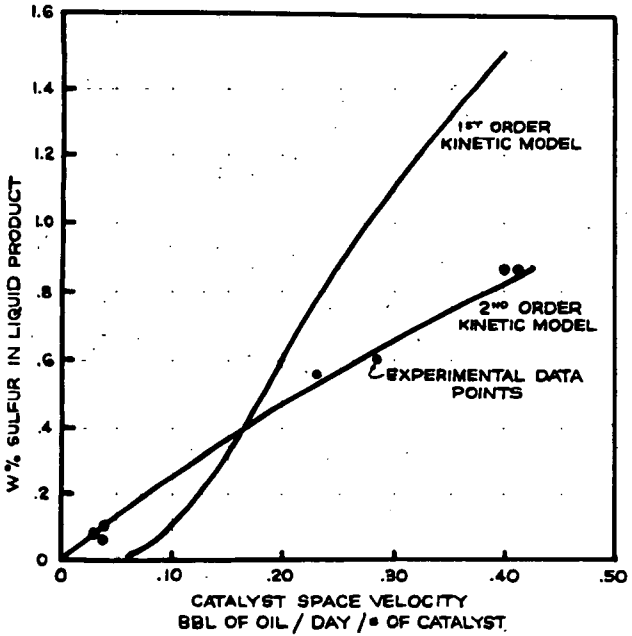


FIGURE 1

COMPARISON OF KINETIC MODELS WITH EXPERIMENTAL DATA

KUWAIT ATMOSPHERIC RESIDUE

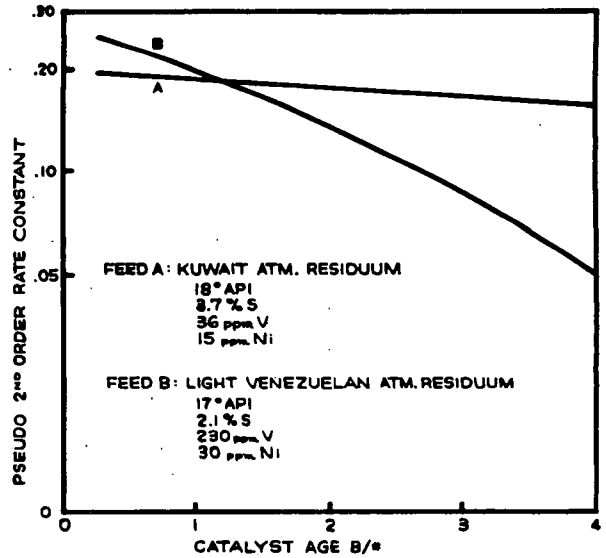


FIGURE 2

VARIATION OF RATE CONSTANT WITH CATALYST AGE

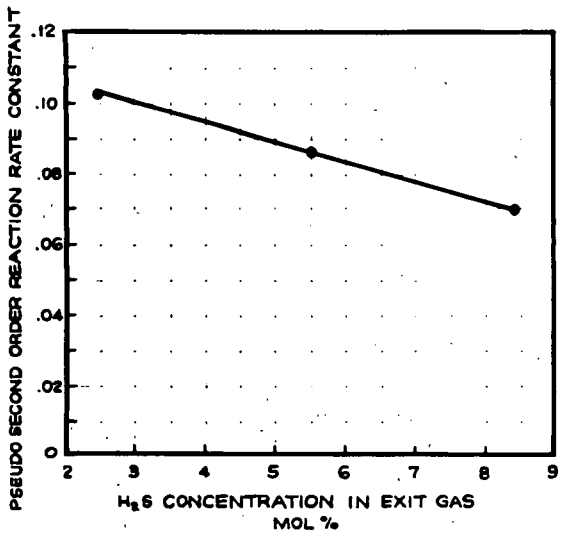


FIGURE 3

EFFECT OF H_2S ON REACTION RATE CONSTANT

KUWAIT FEED

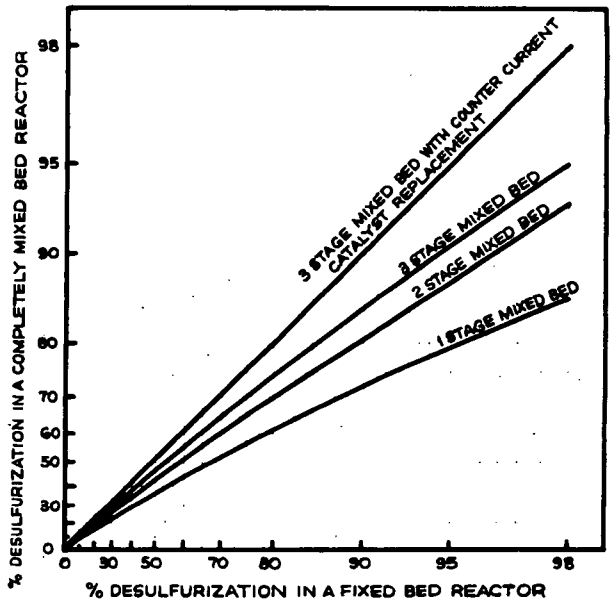


FIGURE 4

EFFECT OF STAGING ON REACTION EFFICIENCY OF A COMPLETELY MIXED BED VERSUS FIXED BED REACTORS

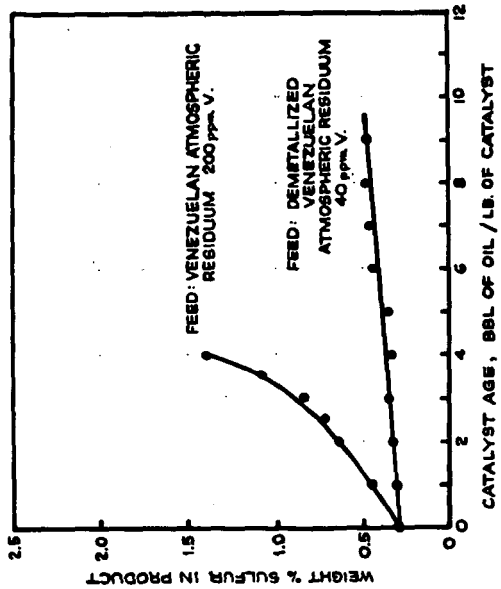


FIGURE 6
COMPARISON OF CATALYST DEACTIVATION WHEN DESULFURIZING VIRGIN AND DEMETALLIZED VENEZUELAN ATMOSPHERIC RESIDUA

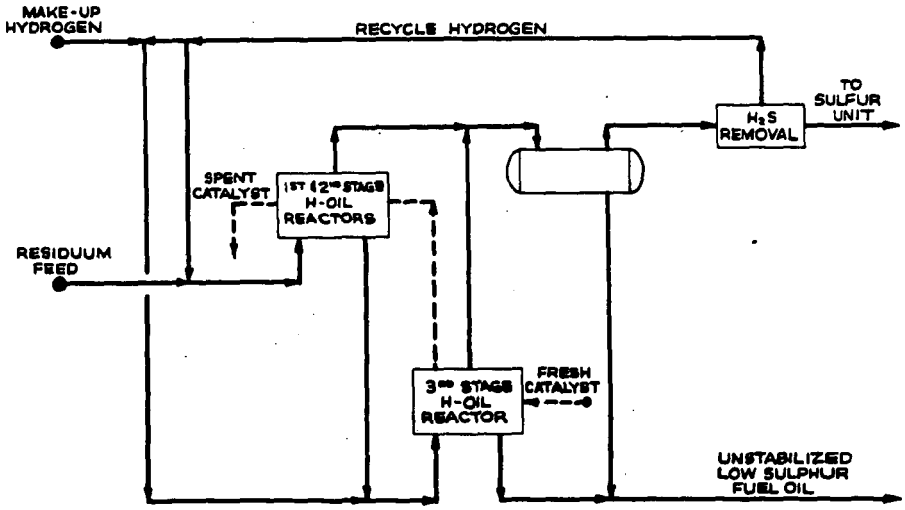


FIGURE 5
THREE STAGE H-OIL SYSTEM WITH CATALYST BACKFLOW

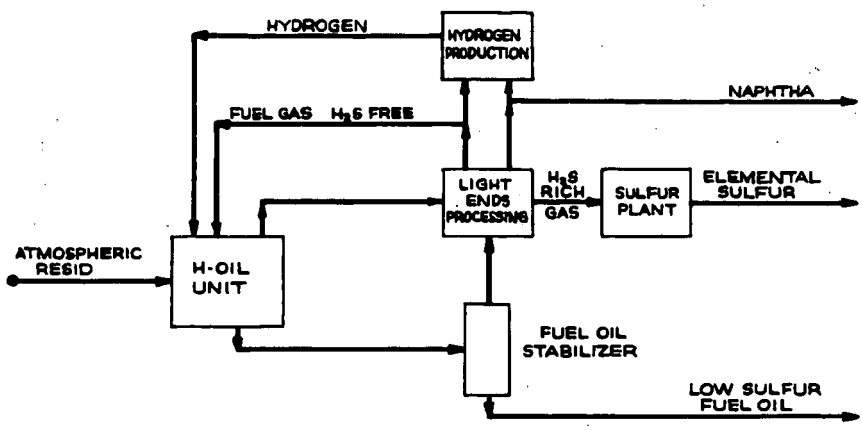


FIGURE 8

BLOCK FLOW DIAGRAM
MULTI-PURPOSE DESULFURIZATION PLANT

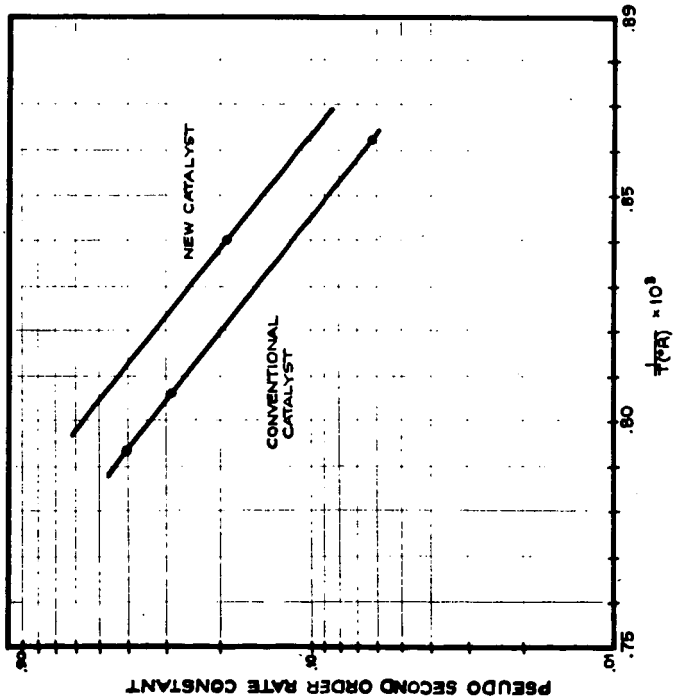


FIGURE 7
COMPARISON OF NEW AND CONVENTIONAL H-OIL CATALYSTS
KUWAIT FEED

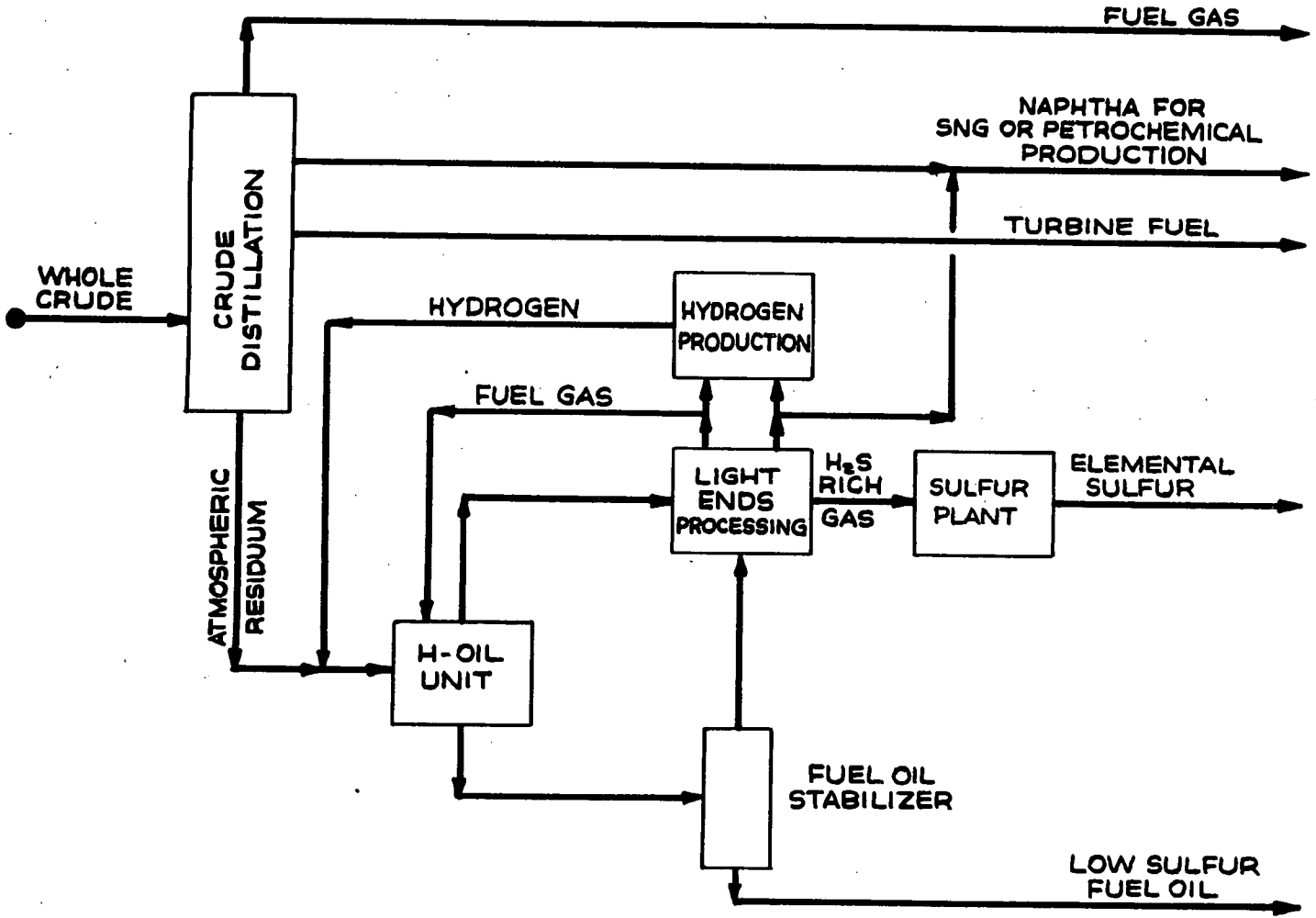


FIGURE 9
FUELS REFINERY

TABLE 1

H-OIL PLANT PERFORMANCE

MANUFACTURE OF 0.3% S FUEL OIL FROM VARIOUS FEEDS

Feedstock	Kuwait Atm. Resid.	Medium Venezuelan Atm. Resid.	West Texas Atm. Resid.	West Texas Vac. Resid.
Gravity, °API	17.0	17.2	17.7	10.5
Feed Sulfur, Wt.%	3.8	2.2	2.2	3.2
Vol.% 975°F.+	40.0	45.0	41	80.0
Plant Throughput, BPSD	30,000	30,000	42,100	18,250
Total H_2 Consumption, MM SCFD	21.9	21.9	21.9	21.9
H-Oil Unit Yields				
H_2S (Wt.%)	3.7	2.3	2.1	3.4
C_1-C_3 (Wt.%)	1.6	2.3	0.8	2.8
C_4-350°F. (Vol.%)	7.8	9.6	3.9	11.5
350°F.+ Fuel Oil (Vol.%)	95.0	94.0	98.7	94.9
Fuel Oil Sulfur, Wt.%	0.3	0.3	0.3	0.3
Catalyst Replacement Cost, $/B	0.15	0.16	0.04	0.18

TABLE 2

COMMERCIAL H-OIL OPERATIONS
Lake Charles, Louisiana

VARIOUS WEST TEXAS FRACTIONS

Feedstock	Sour Atm. Resid.	Vac. Resid.
°API	17.1	10.9
% S	2.80	1.95
% 975°F.+	47.0	82.0
Operation	Desulfurization	Conversion
Goal Achieved	100 Vol.% yield of stabilized 300°F.+ fuel oil of 0.28% S	49% conversion of 975°F.+ total product at 0.62% S

TABLE 3

FUELS PROCESSING COMPLEX

INVESTMENT AND OPERATING REQUIREMENTS

BASIS: Operations Described in Table 1

Investments

H-Oil Unit	$ 13,400,000
Light Ends & Gas Processing	1,300,000
Hydrogen & Sulfur Plants	7,100,000
Offsites	5,500,000
Total Investment	$ 27,300,000

Operating Requirements

Fuel, MM BTU/Hr.	(1)
Power, KW	12,700
Steam, Lb/Hr.(2)	65,000
Cooling Water, GPM	4,750
Boiler Feed Water, GPM	135
Catalyst & Chemicals (other than H-Oil), $/D	225
Labor, Men/Shift	6

(1) Supplied from H-Oil Gases and Light Ends

(2) Net External Steam Requirement

TABLE 4

FUELS PROCESSING COMPLEX

DAILY PROCESSING COSTS
(Basis: 330 Days)

	$/SD
Investment Related Costs @ 20% of Total Capital	16,600
Labor Related Items	1,440
Utilities(1)	3,550
Catalyst & Chemicals (Ex H-Oil)	225
Total Processing Cost	21,815

(1) Utility Unit Costs:

Power	0.8¢/kwh
Steam	70¢/1000 lbs.
Cooling Water	0.3¢/1000 gal.
BFW	3.0¢/1000 gal.

Hydrogen Plant Feed and Fuel for the complex supplied from H-Oil gases, light ends and 150 BPSD of product fuel oil.

TABLE 5

FEEDSTOCK PROCESSING COST

Feedstock	Charge (BPSD)	Fuel Oil* Product (BPSD)	Operating Cost (Ex H-Oil Cat) ¢/B feed	H-Oil Catalyst Replacement Cost ¢/B feed	Total Processing Cost ¢/B feed
Kuwait Atm Resid.	30,000	28,350	73	15	88
Lt. Venezuelan Atm. Resid.	30,000	28,050	73	16	89
West Texas Atm. Resid.	42,100	41,400	52	4	56
West Texas Vac. Resid.	18,250	17,165	$ 1.20	18	$ 1.38

*after plant fuel consumption

LOW-SULFUR FUEL BY PRESSURIZED ENTRAINMENT CARBONIZATION OF COAL

By Robert J. Belt and Michael M. Roder

U. S. Department of the Interior, Bureau of Mines
Morgantown Energy Research Center
P. O. Box 880, Morgantown, W. Va. 26505

INTRODUCTION

Rapid entrainment carbonization of powdered coal under pressure in a partial hydrogen atmosphere was investigated as a means of producing low-sulfur char for use as a powerplant fuel. Specific objectives of the research were to determine if an acceptable product could be made and to establish the relationship between yields and chemical properties of the char, with special emphasis on type and amount of sulfur compounds in the product. The experiments were conducted with a 4-inch-diameter by 18-inch-high carbonizer according to a composite factorial design (2, 3).[1] Results of the experiments are expressed by empirical mathematical models and are illustrated by the application of response surface analysis.

Previous work with a 4-inch-diameter by 12-inch-high entrainment-type carbonizer showed that chars containing considerably less sulfur than the parent coals could be produced by rapid carbonization (1), and that the most important variables were temperature, pressure, and type of entraining gas. In the experiments with the 18-inch-high carbonizer, all other variables–coal rate, size range and type, residence time, entraining gas rate, and run length–were held constant to determine the effect of the three main factors on char yield and volatile matter concentration and the content of organic, pyritic, and sulfate sulfur in the char.

EQUIPMENT AND PROCEDURE

Carbonization runs were made with the equipment shown in figure 1. The carbonizer was designed for temperatures to 2,000° F, pressures to 500 psi, and coal rates to 500 grams per hour. Coal from a closed pressure-equalized hopper was injected by a vibratory screw feeder into a gas stream that carried the particles at high velocity into the carbonizer. Another stream of gas entered the top of the carbonizer via a preheater that heated the gas to the carbonization temperature.

The carbonizer was 4 inches in diameter by 18 inches long and was made of type 310 alloy steel, schedule 40 pipe. Three pairs of 6-inch-long, semi-circular electrical heating elements enclosed the carbonizing tube. The preheater was a 4-inch-diameter by 2-foot-long coil of ¼-inch stainless steel tubing surrounded by two pairs of 12-inch-long semi-circular electrical heating elements.

All solid and liquid products were recovered from the gas stream. Coarse particles of char were recovered in the lock hopper at the bottom of the carbonizer; char fines and carbon fines were extracted by a hot-dust knockout chamber. Tar and pitch were removed by two knockout chambers in series, and water and light oil were separated by means of a water condenser followed by dry-ice and silica-gel traps. Clean gas was passed through a pressure letdown system, metered, and vented. Yields of dust, tar, light oil, and gas were not determined.

The carbonizer was preheated to the desired (constant) temperature, the system was pressurized to the desired level, and gas flows were set to the predetermined rates and compositions. Coal was then injected to begin the run. The carbonizer was designed to rapidly heat the coal particles as they passed through the 18-inch-long hot zone. Pyrolization and devolatilization were effected in less than 1 second. Two hundred grams per hour of 70-percent-through-200-mesh Pittsburgh-bed high-volatile A bituminous coal was processed in 2-hour runs. Entraining gas was admitted at a rate of 20 actual cubic feet per hour. During the run, char was periodically removed from the bottom lock hopper and gas samples were removed for analysis.

---

[1] Underlined numbers in parentheses refer to references at the end of this paper.

EXPERIMENTAL PLAN

Experiments in the carbonization of coal to produce low-sulfur char were carried out and evaluated by means of a 3-step procedure. Carbonization runs were first conducted to obtain data at various combinations of the three major independent variables. These data were then used to develop an empirical mathematical model that described the carbonization system. Finally, response surface analysis was used to interpret the empirical model and predict the relationship between process variables and char yield and quality.

The carbonization runs were carried out according to a composite factorial design covering temperature, pressure, and entraining gas composition—each at five levels. Carbonization temperature was varied from 1,500° to 1,900° F in 100-degree increments and is represented by X_1. Operating pressure, X_2, was varied from 0 to 400 psig in 100-psig increments. Entraining gas composition (hydrogen in nitrogen), X_3, was varied from 0 percent H_2 to 100 percent H_2 at 25 percent intervals. Table 1 shows the levels of the operating conditions.

As illustrated by figure 2, a 3-dimensional coordinate system was assumed with temperature, pressure, and entraining gas composition as the axes. Points at the eight corners of the cube represent the 2-level part of the factorial design; the remaining points represent the composite portion of the design. Each numbered point represents one experimental run and the center represents five additional runs, making a total of 19 runs. Computation of the variance of the system was based on the five runs shown at the center. Actual experimental conditions are shown in the table that accompanies the sketch.

RESULTS

The following results are based on the analyses of data by means of response surface analysis. The 3-dimensional empirical models were developed at the 95-percent confidence level. In other words, 95 percent of the time the results obtained from the empirical model will match the actual data obtained.

As stated, char yield and char quality were of primary interest, the latter being dependent on the concentration of total sulfur, organic sulfur, pyritic sulfur, sulfate sulfur, and volatile matter, and on the heating value and ratio of sulfur content to the heating value. Concentrations of constituents in the char are given as a weight percentage. Table 2 gives the actual experimental data for runs at various combinations of operating conditions.

Char Yield

Figure 3 shows predicted char yield plotted as a function of temperature, pressure, and entraining gas composition. Char yield values of 800, 880, and 960 pounds per ton of coal are shown. Within the limits of the experiments, yields ranged from 646 pounds per ton of coal to 1,222 pounds per ton (table 3). Temperature had a considerable effect on char yield, as was also found in the prior work (1): yields decreased with an increase in temperature. Although pressure variation alone had little effect on char yield, the combined effect of temperature and pressure was important. For example, yields were lower when temperature and pressure were both high or both low. However, when the temperature was the lowest and the pressure was the highest, yields were higher, as was also true when the temperature was the highest and the pressure was the lowest.

Char Quality

Total, Organic, Pyritic, and Sulfate Sulfur

Sulfur does not occur as an element in coal or char; it is present in chemical combination in the form of organic compounds, iron sulfides, and sulfates (4). Total sulfur is the sum of the weight percentage concentrations of all three. As shown in table 3, total sulfur left in the char ranged from 0.7 to 2.5 percent, often a substantial decrease from the amount in the parent coal (2.55 percent). Figure 4 shows total sulfur surfaces for values ranging from 1.0 to 2.5 percent. Crowding of the curved surfaces in the upper left hand corner of the cube clearly shows the decrease in amount of sulfur in the char with increase in the temperature, pressure, and percent hydrogen in the entraining gas. Within the experimental limits, the models indicate that a char can be produced containing a minimum amount of sulfur (0.7 percent) at a temperature of 1,900° F,

pressure of 400 psig, and 91 percent hydrogen in the entraining gas. Production of 0.7 percent sulfur char amounts to more than a 70-percent reduction in sulfur from the original coal.

Organic sulfur accounts for about three-fourths of the total sulfur in the char. A 3-dimensional plot of the values of organic sulfur as a function of temperature, pressure, and entraining gas composition is shown in figure 5. By comparing this figure with the one for total sulfur (figure 4), a similar relationship between the two plots can readily be observed. For instance, as in the case of total sulfur, an increase in temperature, pressure, and percent hydrogen in the entraining gas decreased the amount of organic sulfur in the char. Theoretically, as indicated in table 3, carbonization at 1,900° F, 400 psig, and 100 percent hydrogen in the entraining gas would produce a char containing virtually no organic sulfur.

Approximately one-fourth of the total sulfur in the char is in the form of pyritic sulfur. As shown by figure 6, the amount of pyritic sulfur reached a minimum value of about 0.25 percent at 1,650° F, 230 psig, and 50 percent hydrogen in the entraining gas. Increasing or decreasing values of the variables tends to increase the amount of pyritic sulfur. Pressure and temperature had a greater effect on pyritic sulfur than did percent hydrogen in the entraining gas.

Sulfate sulfur remaining in the chars ranged from 0.01 to 0.06 percent, as indicated in table 2. Since the parent coal contained only 0.06 percent, a change in one or all three variables had no effect on the amount of sulfate sulfur.

Char Sulfur Content Per Unit Heating Value

From a process standpoint, probably the best way to express the amount of sulfur concentration of a fuel is in pounds of sulfur per million Btu heating value of the fuel (char). Ordinarily, this ratio would be a function of the amount of total sulfur in the char and the heating value of the char. However, since the heating value of the char changes very little within the experimental limits (discussed later in this paper), values for the amount of sulfur per heating value are essentially the same as those obtained for percent total sulfur. Figure 7 shows that an increase in temperature, pressure, and percent hydrogen in the entraining gas decreases the amount of sulfur per million Btu. Within the experimental limits, the model indicates that a char containing a minimum of 0.49 pound of sulfur per million Btu could be produced at 1,900° F, 400 psig, and 91 percent hydrogen in the entraining gas.

Volatile Matter and Heating Value

As expected from the results of this experiment and prior work (1), char containing a maximum of volatile matter was produced at relatively low temperatures, and char containing the minimum was produced at higher temperatures. Pressure and type of entraining gas had little effect on the amount of volatile matter remaining in the char. Table 3 indicates that (within the experimental limits) char produced at 1,900° F, 320 psig, and 25 percent hydrogen in the entraining gas would contain the minimum volatile matter–3.8 percent. Char produced at conditions that give the minimum total sulfur content (0.7 percent) would contain 7.38 percent volatile matter. Figure 8 is a graphic portrayal of predicted char volatile matter curves as a function of temperature, pressure, and entraining gas compositions.

As shown in table 2, char heating values ranged between 12,350 and 13,380 Btu/lb. In the 3-dimensional plot (not shown), the portion of the curves that fell within the experimental limits were nearly flat. Because of the narrow range in the data and the flatness of the curves, it can be concluded that neither temperature, pressure, nor percent hydrogen in the entraining gas affected the char heating value.

SUMMARY AND CONCLUSIONS

A low-sulfur char was successfully produced by pressurized carbonization of coal using hydrogen in nitrogen as a hot entraining gas. According to empirical models, a char containing 0.7 percent sulfur, or 0.49 pound sulfur per million Btu, could be produced at 1,900° F, 400 psig, and 91 percent hydrogen in nitrogen. Theoretical characteristics and properties of char produced under these conditions are compared with those of the parent coal in table 4.

Major conclusions drawn from this work are:

(1) Total sulfur and organic sulfur content of the char and sulfur content per unit of heating value decreased with increase in temperature, pressure, and hydrogen concentration in the entraining gas.

(2) Pyritic sulfur content depended only on the carbonization temperature and pressure.

(3) Sulfate sulfur was unaffected by temperature, pressure, or entraining gas composition.

(4) Carbonization temperature, as would be expected, was of prime importance in regard to the concentration of volatile matter in the resulting char; relatively low temperatures produced a char with a high-volatile matter content, and vice versa.

(5) Char yield decreased with increase in temperature; pressure and entraining gas composition had no effect. Char heating value was not significantly influenced by any of the three variables.

An empirical approach that included a mathematical model was found to be beneficial in predicting the sulfur content of chars produced from coal over a specified range of operation conditions. The technique was useful for predicting the conditions required for a specified product. For instance, the model for total sulfur indicates that a char containing less than 0.7 percent sulfur could probably be produced at temperatures and pressures higher than those investigated in this experiment.

REFERENCES

1. Belt, R. J., J. S. Wilson, and J. J. S. Sebastian. Continuous Rapid Carbonization of Powdered Coal by Entrainment and Response Surface Analysis of Data. Fuel, v. 50, No. 4, October 1971, pp. 381–393.

2. Davies, O. L. Design and Analysis of Industrial Experiments. Editor, Hafner Pub. Co., New York, 1967, 2d ed.

3. Himmelblau, D. M. Process Analysis by Statistical Methods. John Wiley & Sons, Inc., New York, 1968.

4. Walker, F. E., and F. E. Hartner. Forms of Sulfur in U. S. Coals. BuMines Inf. Circ. 8301, 1966, 51 pp.

TABLE 1. – Design of the experiment

Factor	Coded design coordinate					Symbol
	-2	-1	0	1	2	
Temperature, °F	1,500	1,600	1,700	1,800	1,900	X_1
Pressure, psig	0	100	200	300	400	X_2
Hydrogen in nitrogen, percent	0	25	50	75	100	X_3

NOTE: Table 2 follows Table 3.

TABLE 3. – Predicted minimum and maximum values for char yield and properties and corresponding process conditions

Char yield and properties	Minimum				Maximum			
	Temp., °F	Pres., psig	[1] EGC, pct H_2	Value	Value	Temp °F	Pres., psig	[1] EGC, pct H_2
Yield, lb/ton	1,900	400	55	646	1,222	1,500	400 0	0
Total sulfur, pct	1,900	400	91	.70	2.8	1,500	0	100
Organic sulfur, pct	1,900	400	100	.00	1.9	1,600	0	100
Pyritic sulfur, pct	1,650	230	50	.24	1.0	1,900	0	100
Sulfate sulfur, pct	1,900	300	25	.01	.06	1,500	400	0
Sulfur content per heating value, lb/MM Btu	1,900	400	91	.49	2.1	1,600	0	100
Volatile matter, pct	1,900	320	25	3.80	16	1,500	0	100
Heating value, Btu/lb	1,770	0	10	12,300	14,800	1,900	400	0

[1] Entraining gas composition, hydrogen in nitrogen.

TABLE 2. – Data representing char yield and quality as a function of variable operating conditions [1/]

Run	X_1: Temperature, °F	X_2: Pressure, psig	X_3: Hydrogen, percent	Sulfur content [2/]				Sulfur per heating value, lb/MM	Volatile matter, pct of char	Heating value, Btu/lb	Char yield, lb/ton coal
				Total	Organic	Pyritic	Sulfate				
1	1,600	100	25	2.00	1.72	.23	.05	1.561	9.9	12,810	1,010
2	1,600	100	75	1.98	1.67	.27	.04	1.549	9.9	12,790	922
3	1,600	300	25	1.79	1.47	.27	.05	1.398	8.3	12,800	1,062
4	1,600	300	75	1.72	1.44	.24	.04	1.339	9.4	12,850	1,012
5	1,800	100	25	1.79	1.29	.48	.02	1.450	5.7	12,350	916
6	1,800	100	75	1.88	1.33	.51	.04	1.482	8.0	12,690	934
7	1,800	300	25	1.56	1.01	.54	.01	1.166	4.8	13,380	908
8	1,800	300	75	1.16	.66	.49	.01	.926	5.5	12,530	854
15	1,900	200	50	1.29	.80	.46	.03	.997	5.7	12,940	752
14	1,500	200	50	1.83	1.22	.56	.05	1.434	10.6	12,770	858
17	1,700	400	50	1.43	1.00	.38	.05	1.092	7.3	13,100	914
16	1,700	0	50	2.28	1.60	.64	.04	1.811	10.4	12,590	890
19	1,700	200	100	1.69	1.23	.41	.05	1.290	10.8	13,100	936
18	1,700	200	0	2.16	1.73	.39	.04	1.701	7.7	12,700	1,036
9	1,700	200	50	1.53	1.20	.31	.02	1.209	7.1	12,660	856
10	1,700	200	50	1.64	1.19	.43	.02	1.288	8.3	12,730	920
11	1,700	200	50	1.58	1.13	.40	.05	1.254	7.8	12,600	866
12	1,700	200	50	1.62	1.29	.27	.06	1.310	7.2	12,370	884
13	1,700	200	50	1.58	1.40	.16	.02	1.243	7.2	12,710	886

1/ Coal carbonized was Pittsburgh-bed high-volatile A bituminous with the following analysis: sulfur, 2.55 percent, volatile matter, 34.0 percent, and heating value, 14,090 Btu per pound.

2/ Concentration in char, weight-percent.

TABLE 4. – Comparison of Pittsburgh-bed high-volatile A bituminous coal and char produced at 1,900° F, 400 psig, and 91 pct H_2, 9 pct N_2 entraining gas

	Coal	[1] Char
Char yield, wt pct		34.0
Sulfur, wt pct		
Total	2.55	.70
Organic	1.49	.00
Pyritic	.93	.77
Sulfate	.13	.038
Sulfur-Btu ratio, lb/MM Btu	1.81	.49
Analysis, wt pct		
Volatile matter	33.98	7.38
Ash	7.28	15.68
Hydrogen	5.23	2.19
Total carbon	76.4	80.3
Fixed carbon	53.51	76.41
Water	.8	.8
Calorific value, Btu/lb	14,300	13,300

[1] All values are theoretical. Sum of the organic, pyritic, and sulfate sulfur percentages will not necessarily equal the value for total sulfur.

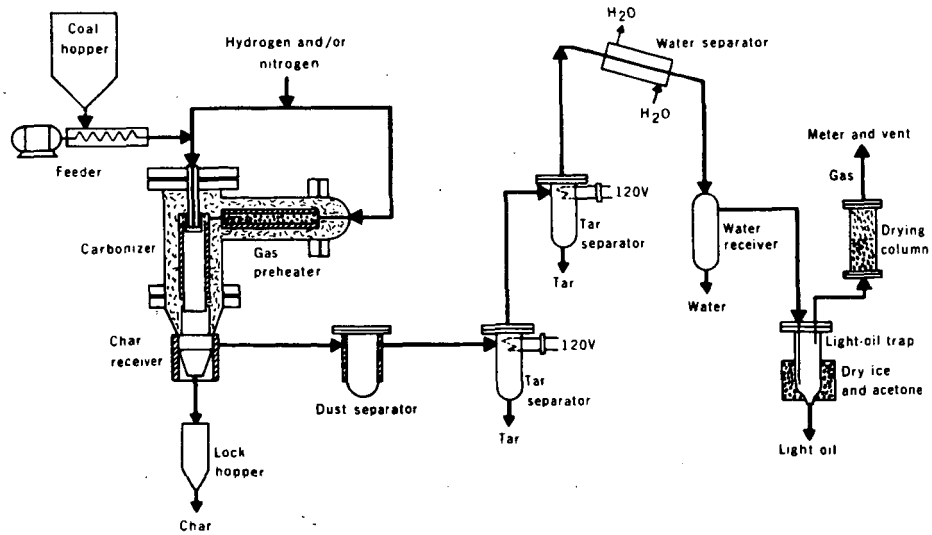
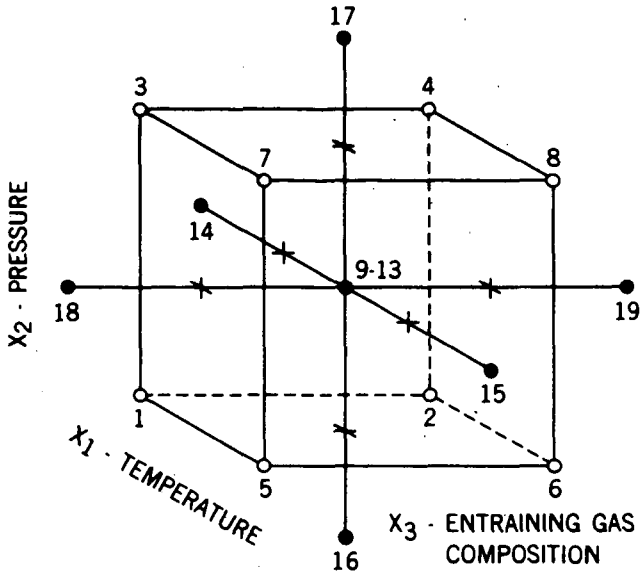


FIGURE 1. – Flow Diagram of Pressurized Coal Carbonization System



Location of Experimental Points

Experiment	Operating Variables		
	Temperature, °F	Pressure, psig	Entraining gas composition [1]
1	1,600	100	25
2	1,600	100	75
3	1,600	300	25
4	1,600	300	75
5	1,800	100	25
6	1,800	100	75
7	1,800	300	25
8	1,800	300	75
9-13	1,700	200	50
14	1,500	200	50
15	1,900	200	50
16	1,700	0	50
17	1,700	400	50
18	1,700	200	0
19	1,700	200	100

[1] Volume-percent H_2 in N_2

FIGURE 2. – Three-Factor Composite Design

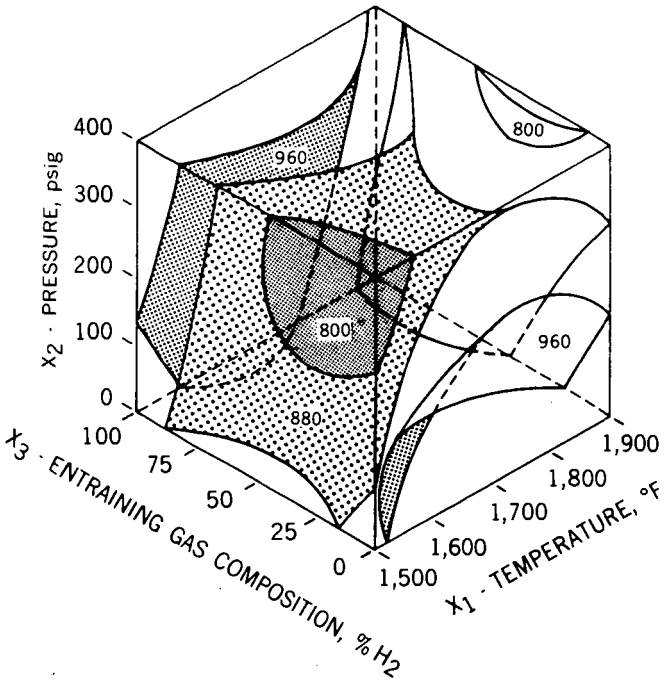


FIGURE 3. – Char Yield, lb/ton Coal

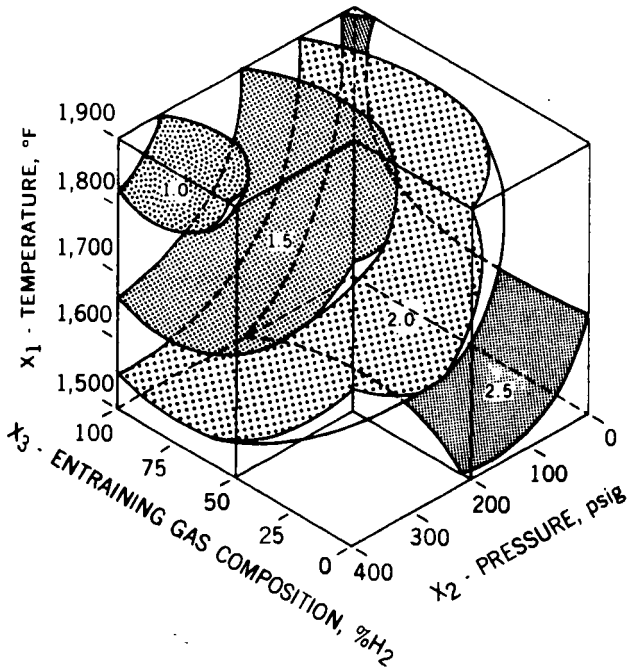


FIGURE 4. – Total Sulfur in Char, pct

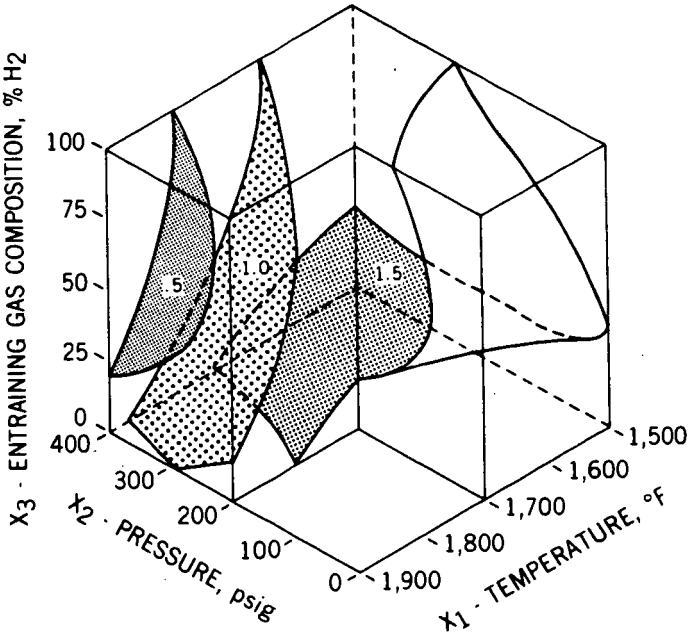


FIGURE 5. – Organic Sulfur in Char, pct

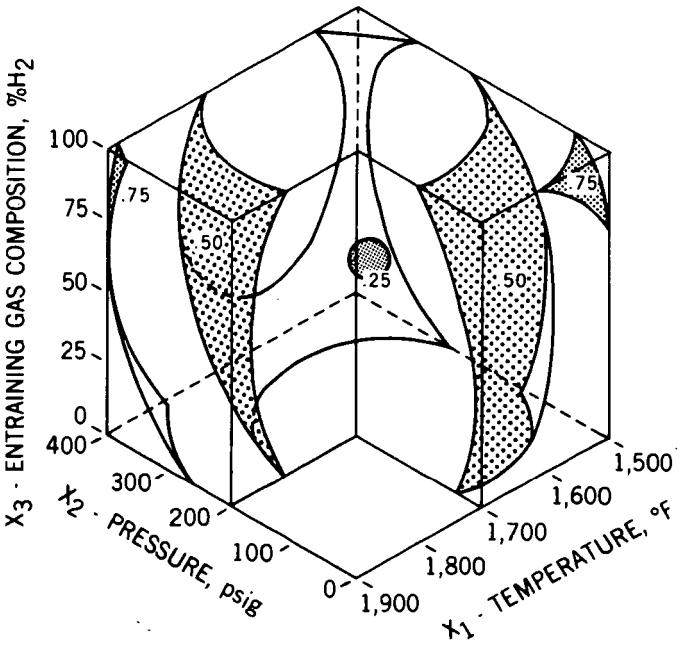


FIGURE 6. – Pyritic Sulfur in Char, pct

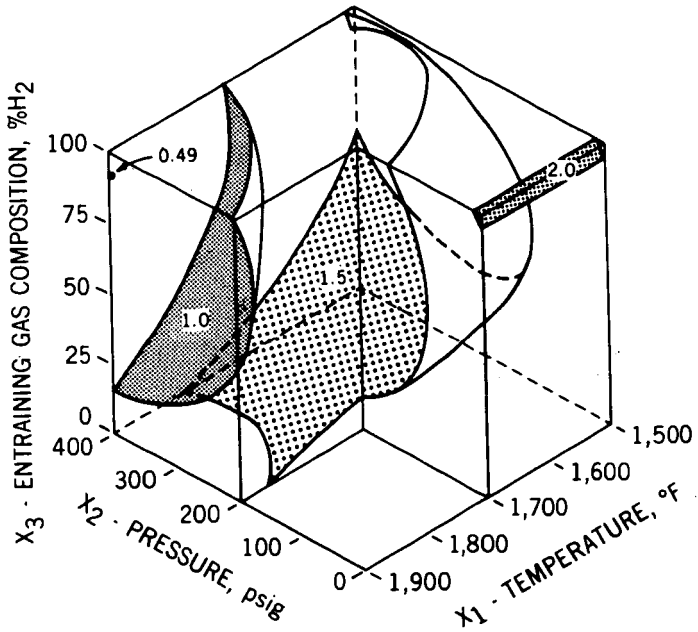


FIGURE 7. – Sulfur in Char per Unit Heating Value, lb S/10^6 Btu

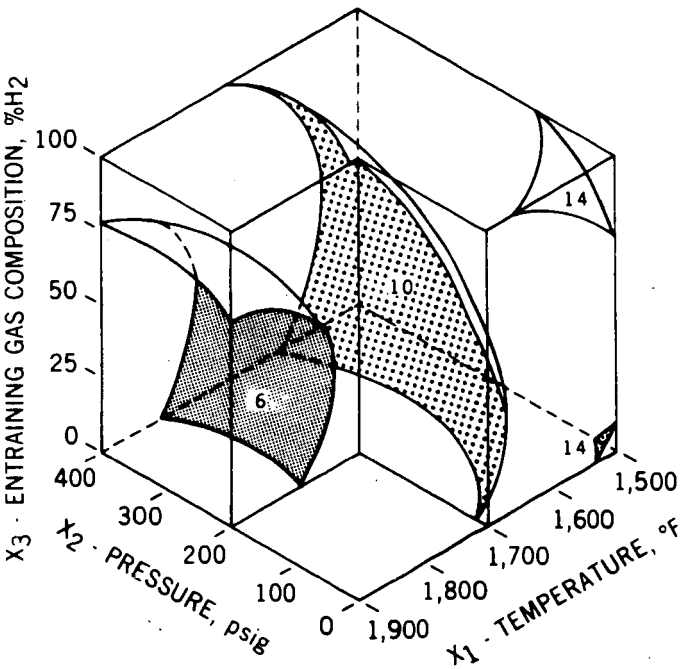


FIGURE 8. – Volatile Matter in Char, pct

WET SCRUBBING OF SULFUR OXIDES FROM FLUE GASES. James Jonakin and A. L. Plumley, C-E Combustion Division, Combustion Engineering Inc., Windsor, Connecticut.

Much research and development work has been directed toward reducing sulfur oxides emissions from steam generating units. The three methods of minimizing SOx emissions are using a low sulfur fuel, removing the sulfur from the fuel before combustion, and removing SOx from flue gases. Wet scrubbing of flue gases, which removes both SOx and particulates, has received the most attention because of low cost and simplicity. Combustion Engineering is offering two wet scrubbing systems: furnace injection and tail end.

This paper will describe these systems including discussions of laboratory and field studies and operating experience. The systems sold to date will be listed.

The chemical reactions that occur during operation of the system will be summarized. Also, the various by-product utilization schemes that are being investigated for recycling of the sludge from the wet scrubbing system will be outlined.

LIMESTONE WET SCRUBBING OF SULFUR DIOXIDE FROM POWER GENERATION FLUE GAS FOR HIGH AND LOW SULFUR FUELS. Robert J. Gleason, Research-Cottrell, P.O. Box 750, Bound Brook, New Jersey 08805; Frank Heacock, Arizona Public Service Company, P.O. Box 21666, Phoenix, Arizona 85036.

Limestone wet scrubbing has become the first process approach for sulfur dioxide emission control on coal-fired power generation boilers. Systems under development have been concerned primarily with operational reliability while SO_2 absorption efficiency has been given secondary treatment. Pilot plant studies on high and low sulfur fuels using packed tower absorbers have shown the inlet SO_2 concentration and slurry composition as significant factors in the removal efficiency and operational reliability. Mass transfer coefficients have been developed for a wetted film packing. Variable height packed absorbers can provide high absorption efficiency for both high and low sulfur fuels. Hence, compliance with state and federal regulations can be achieved even in the extreme low sulfur coal conditions.

SO_2 ABATEMENT WITH THE TAIL-END LIMESTONE SCRUBBING PROCESS. John M. Craig, Ph. D., Southern Services, Inc. P.O. Box 2625, Birmingham Alabama, 35202; M. Dean High and Burke Bell, Engineering Science, Inc. 600 Watergate, 600 New Hampshire Avenue, N.W. Washington D.C. 20037

A 1500 CFM mobile pilot plant was operated in an open-loop configuration to evaluate the Zurn Industries, Inc. scrubber in the tail-end limestone wet scrubbing process for SO_2 abatement. The pilot plant was installed on both oil-fired and coal-fired power plants. Various operating parameters associated with SO_2 abatement were studied in the pilot plant in a series of statistical designs. Operating parameters investigated included: pressure drop, gas flow rate, stoichiometry, slurry concentration, particle size and reactant type. The reactant types included: coral marl, Fredonia Valley limestone, dolomite aragonite, lime and precipitated calcium carbonate. Results from the statistical design indicate that pressure drop, stoichiometry, and gas flow rate had significant influence upon SO_2 removal efficiency, Coral marl and Fredonia Valley limestone removed 65-75 percent of the SO_2 depending upon the level of the various operating parameters. The other calcium-based reactants provided SO_2 removal efficiencies between 45-90 percent depending upon reactant and level of operating parameters. The Zurn Industries, Inc. scrubber had no operating set-backs due to scale formation in the scrubber system and it appears to offer an alternative for reducing the SO_2 emissions in a variety of industries.

PROCESS EXPERIENCE OF THE RC/BAHCO SO_2 REMOVAL SYSTEM. Dr. Richard S. Atkins, Research-Cottrell, P.O. Box 750, Bound Brook, New Jersey 08805

This paper examines the operating experiences of several Bahco SO_2 removal systems. SO_2 removal technology developed by AB Bahco Ventilation Enkoping, Sweden, is being successfully applied in thirteen commercial installations. Each of these units has exhibited on-stream reliability and high SO_2 adsorption efficiency. The oldest unit has almost three years of operating experience. Bahco design flexibility permits the use of Na and K bases, slurries of Ca and Mg bases and less expensive materials such as dolomite, burned lime, limestone, sodium carbonate and ammonia as potential scrubbing reagents. The process is amenable to by-product recovery such as sodium sulfate, sodium sulfite, gypsum, and ammonium sulfate which reduces the threat of discharging secondary pollutants. The paper also explores the possibilities of reverse fuel switching. That is the burning of high sulfur fuels in conjunction with using a RC/Bahco SO_2 scrubber and obtaining a more economic less pollutant situation than switching to low sulfur fuels. Research-Cottrell has the rights for applying the Bahco SO_2 removal technology in the U.S. and Canada.

CHEMICO PROCESS EXPERIENCE IN SCRUBBING SO_2 FROM STACK GASES.

Robert Quig, PE, and I. Shah, Chemical Construction Corporation, 320 Park Avenue, New York 10022

The operating experience at two 150 MW power plants using the Chemico stack gas scrubbing system with chemical additives will be discussed. One is a two-stage calcium oxide additive sulfur oxide scrubbing and disposal system for the Mitsui Aluminum Companies, Ohmuto Station, Japan. The other is a magnesium oxide sulfur oxide scrubbing and remote recovery system for the Boston Edison Company.

In addition, the sulfur oxide removal observed by the utilization of alkaline fly ash solutions as recycled slurry in two major Chemico scrubbing projects in operation on western coal-fired boilers will be presented.

THE CHEMISTRY OF THE MOLTEN CARBONATE PROCESS FOR SO_2 REMOVAL FROM STACK GASES*

S. J. Yosim, L. F. Grantham and D. E. McKenzie

Atomics International
A Division of North American Rockwell Corporation

G. C. Stegmann
Consolidated Edison Co. of New York, Inc.

INTRODUCTION

The Atomics International Molten Carbonate Process for removal of sulfur oxides from power plant stack gases has been under development since 1966. A 10 Mw pilot plant is now under construction. This paper describes the process chemistry. Brief descriptions of the pilot plant and of process economics are also given.

PROCESS DESCRIPTION

In the Molten Carbonate Process, a molten eutectic mixture of lithium, sodium, and potassium carbonates is used to scrub the power plant gas stream. The sulfur oxides in the gas stream react with the carbonates to form sulfites and sulfates, which remain dissolved in excess unreacted carbonate melt. The molten carbonate-sulfite-sulfate mixture is then treated to convert the sulfite and sulfate back to carbonate and to recover the sulfur as elemental sulfur. The regenerated carbonate is then recirculated to the scrubber to repeat the process cycle.

The regeneration of carbonate is done in two steps: 1) the reduction of the sulfite and sulfate to sulfide, and 2) the conversion of the sulfide to carbonate plus hydrogen sulfide. The reduction step is accomplished by reaction with a form of carbon, such as petroleum coke. The conversion of the sulfide to carbonate is accomplished by reacting the melt with steam and carbon dioxide, liberating hydrogen sulfide. The hydrogen sulfide is then converted to elemental sulfur in a Claus plant.

The process flow diagram is shown in Figure 1. The process steps are as follows:

1) The gas to be treated is removed from the boiler at about 450°C and, if the boiler is burning coal, the gas passes through a high temperature, high efficiency electrostatic precipitator where essentially all the fly ash is removed. The gas then passes through the scrubber, where the sulfur oxides are removed by contacting the gas stream with a spray of molten carbonate at 450°C. This gas-liquid contact removes 95% or more of the sulfur oxides and most of the remaining ash from the gas stream. The cleaned gases are then returned to the boiler for further heat recovery, and eventually pass out the stack.

2) The molten salt stream containing carbonate (M_2CO_3, where M = the mixture of Na, K, and Li), sulfite (M_2SO_3), sulfate (M_2SO_4) and ash from the scrubber is pumped to a purification system and filtered to remove the ash. The ash filter cake is subsequently treated to recover the contained lithium carbonate.

*A portion of the work upon which this paper is based was performed under Contract No. CPA 70-78 with the U.S. Environmental Protection Agency

3) The filtered melt is fed into the reducer, and reacted with carbon. The melt temperature is raised from 450°C to ~850°C by heat from the combustion of part of the carbon with air, and the sulfite and sulfate in the melt are completely reduced to sulfide (M_2S).

4) The melt stream from the reducer is passed into a quench tank where its temperature is lowered from 850°C to 450°C by mixing with cooler melt and by passing through a heat exchanger. The effluent from the quench tank is filtered to remove unreacted coke and coke ash and then passed on to the regenerator.

5) In the regenerator, the reduced melt is reacted with carbon dioxide (produced in the reduction step) and steam in a multi-stage, countercurrent sieve-tray column. The sulfide in the melt is completely regenerated to carbonate (M_2CO_3), and the sulfur is released as hydrogen sulfide (H_2S). The hydrogen sulfide is passed to the Claus plant, where it is converted to elemental sulfur.

6) The regenerated melt is recirculated to the scrubber, with the small filter melt losses being made up by addition of fresh carbonate.

CHEMISTRY OF THE PROCESS

The alkali carbonate eutectic melt[1] used in the process is a mixture of 32 wt % lithium carbonate, 33 wt % sodium carbonate, and 35 wt % potassium carbonate. The physical properties of the eutectic are given in Table 1.

TABLE 1

PHYSICAL PROPERTIES OF THE ALKALI CARBONATE EUTECTIC

Property	Magnitude	Reference
Melting Point	397°C	2
Molecular Weight	100 gm/mole	2
Heat of Fusion	6.6 kcal/gm-mole @ 397°C	2
Density	2.12 gm/cc @ 450°C	3
Viscosity	9.82 cp @ 450°C	4
Heat Capacity	40.39 cal/gm-mole @ 450°C	2
Surface Tension	236.9 dynes/cm @ 450°C	3

The melt has several chemical and physical properties which offer advantages for scrubbing sulfur dioxide from flue gas. It is a liquid which is easy to handle, pump and transport, and has a negligible vapor pressure so that it is not lost by evaporation and does not require high-pressure equipment. It is a strong base; therefore it reacts rapidly with acidic sulfur oxides, so that scrubbing contact time can be short. Since the entire liquid is a strong base, it has a high capacity for sulfur oxides and the amount of melt which must be regenerated continuously is relatively small. The great affinity of the melt for sulfur oxides leads to the removal of large percentages of the sulfur oxides from even very dilute gas streams. The use of this melt in the scrubber at 450°C does not cool off the gas stream or saturate it with water vapor. Finally, the carbonate will react with other acidic gaseous pollutants such as NO_2 and HCl; therefore the potential exists for control of other pollutants such as NO_x by the same process.

The chemistry of each step of the process has been studied in detail and is summarized below.

1. The Scrubbing Step

The reactions taking place in the scrubber are

SO_2 absorption: $SO_2(g) + M_2CO_3(\ell) \rightarrow M_2SO_3(\ell) + CO_2(g)$ (1)

SO_3 absorption: $SO_3(g) + M_2CO_3(\ell) \rightarrow M_2SO_4(\ell) + CO_2(g)$ (2)

M_2SO_3 oxidation: $M_2SO_3(\ell) + 1/2\ O_2(g) \rightarrow M_2SO_4(\ell)$ (3)

Absorption of SO_2 and SO_3 (Eq 1 and 2) is very rapid. For example in the laboratory when pure SO_2 is bubbled through 2 in. of melt, no odor of SO_2 can be detected in the exit gas (CO_2). The presence of O_2, CO_2, N_2, H_2O and fly ash does not affect the SO_2 removal. Melt which was regenerated 3 times in a series of cyclic tests was equally effective in removing SO_2. These results are not surprising in view of acid-base considerations in which the acidic SO_2 is neutralized by the basic alkali carbonate melt.

In an actual plant good contact must be made between the large volumes of flue gas and the relatively small melt stream. However, power plant integration requirements make it important to impose as small a pressure drop as possible on the gas stream. Because of this, a spray contactor has been selected as the molten salt scrubber concept. The spray contactor utilizes spray nozzles to break the melt up into small droplets for good gas-liquid contact, and a very efficient mist eliminator to prevent the gas stream from carrying melt mist out of the scrubber.

For example, in bench scale tests where hot synthetic flue gas was forced past a single melt spray nozzle at 25 ft/sec, sulfur oxide removal efficiencies of 97-100% were obtained and little (if any) melt in the exit gas could be found. The oxidation of M_2SO_3 (Eq 3) does not appear to be very rapid at the scrubber temperature. For example, when synthetic flue gas containing 1 vol % O_2 and 0.1 vol % SO_2 was bubbled through molten carbonate eutectic at 450°C, only 18, 31, and 44 wt % of the sulfite, formed from the absorbed sulfur dioxide, was oxidized to sulfate in 4, 7, and 14 hours, respectively. When the synthetic flue gas contained 5 vol % O_2 and 0.3 vol % SO_2, 42, 49, and 55 wt % of the absorbed sulfur oxide was oxidized to sulfate at similar times. Neither water nor fly ash had any appreciable effect on the oxidation rate.

2. The Reduction Step

The principal reactions occurring in the reduction step are disporportionation (Eq 4) and reduction (Eq 5 and 6).

Disproportionation: $4M_2SO_3(\ell) \rightarrow 3M_2SO_4(\ell) + M_2S(\ell)$ (4)

Reduction: $2M_2SO_3(\ell) + 3C(s) \rightarrow 3CO_2(g) + 2M_2S(\ell)$ (5)

Reduction: $M_2SO_4(\ell) + 2C(s) \rightarrow 2CO_2(g) + M_2S(\ell)$ (6)

The disproportionation rate of sulfite to form sulfide and sulfate (Eq 4) has been measured. Rate measurements indicate that disproportionation is a first order reaction which is not important at scrubber temperature (450°C) but is rapid at reduction temperatures (850°C). Therefore, in the process the major sulfur compound undergoing reduction is sulfate.

The sulfate (Eq 6) and sulfite (Eq 5) can be reduced by numerous substances. Fluidized coke is particularly good for this application since it is relatively inexpensive and has a low ash content. The reaction rate increased by about 2-3 for

each 50°C temperature rise; reduction times of 170, 30, 15, and 4 min were observed at 700, 800, 875, and 950°C, respectively. Therefore, the reduction reaction is carried out at temperatures of about 850°C or above.

In order to raise the temperature from 450°C to about 850°C and to supply the endothermal heat of reduction (~40 kcal/mole) considerable heat must be supplied. Because of materials limitations at this high temperature, the most feasible way to supply the heat of reaction is to generate the heat internally, by the combustion of carbon with air. This eliminates the need for heat transfer surfaces operating at high temperatures in a corrosive environment.

3. The Regeneration Reaction

Two important reactions occur in the regenerator: adsorption of carbon dioxide (Eq 7) and regeneration of carbonate (Eq 8).

Adsorption of CO_2: $$M_2S(\ell) + CO_2(g) \rightarrow M_2CO_2S(\ell) \quad (7)$$

Regeneration: $$M_2S(\ell) + CO_2(g) + H_2O(g) \rightarrow M_2CO_3(\ell) + H_2S(g) \quad (8)$$

Carbon dioxide is readily absorbed by molten melts containing sulfide. The amount of carbon dioxide absorbed increases as the temperature decreases and as the carbon dioxide partial pressure increases. Although the thiocarbonate intermediates (M_2CO_2S, M_2COS_2 and M_2CS_3) have not been identified in the melts, the chemistry involved indicates that the formation of these substances is the most likely explanation for carbon dioxide absorption. These intermediates are quite stable at temperatures of about 450°C and even appear to exist to some extent at temperatures as high as 950°C. Depending on the carbon dioxide partial pressure, about 0.5 to 1.5 moles of CO_2 are absorbed per mole of sulfide at 450°C. These absorption reactions are exothermic (15-20 kcal/mole) and are reversible.

Both carbon dioxide and steam must be reacted with the melt before regeneration occurs (Eq 8), although a substantial amount of carbon dioxide must be absorbed (Eq 7) before any evolution of hydrogen sulfide begins. However, since the intermediate has not been identified, the overall regeneration reaction is given in Eq 8. This reaction is rapid and complete, particularly at temperatures of about 450°C. Since the regeneration reaction is exothermic, the melt must be cooled during regeneration in order to maintain optimum regeneration temperatures (450-500°C). The concentrated hydrogen sulfide stream evolved from the regenerator is fed to a Claus plant for conversion to sulfur.

4. Lithium Recovery

The melt used in this process is relatively inexpensive except for the lithium carbonate, therefore it is desirable to recover the lithium from the process filter cakes. An aqueous process has been developed for this purpose. The filter cakes are slurried with water and filtered to extract the very soluble sodium and potassium carbonates; lithium carbonate remains with the ash since it is relatively insoluble under these conditions. The ash-lithium carbonate cake is slurried in water and the lithium is solubilized by conversion to the bicarbonate. The ash is removed by filtration and the soluble bicarbonate in the filtrate is precipitated as the carbonate. The lithium carbonate is separated by filtration and returned to the process stream; the saturated lithium carbonate filtrate is recycled to conserve lithium. Laboratory tests have demonstrated that over 90% of the lithium can be recovered by this technique.

5. Materials and Components

A test program to select materials of construction which resist corrosion by the process melts has been underway for over 5 years. At first, all of the common metals, alloys, and ceramics were given screening tests. Successful candidates were then subjected to long-term tests, including one-year tests in rotating capsules. As a result, it was found that 300 series stainless steel was the best of the conventional alloys for service below 550°C, and that high density alumina was very corrosion-resistant even at 950°C.

After the preliminary selection of 300 series stainless steel, this alloy was subjected to further tests to study the effect of stress in the presence of chloride, oxygen, and water vapor, the effect of sensitization, and the rate at which the alloy constituents are leached out and transported under the influence of a temperature gradient. A molten salt loop has been in operation for several months as a part of these tests. The results indicated Type 304 and 347 stainless steel as the best of the conventional alloys for service below 550°C. High density alumina was very corrosion-resistant even at 950°C, therefore alumina bricks will be used to line the pilot plant reducer vessel.

The success of the type 300 series stainless steel in molten carbonates is due to the protective $LiCrO_2$ film which forms a compact, tenacious and self-healing layer. This film forms in about 500 hours and decreases the corrosion rate to a few mils per year. It has been shown that this film is essentially chromium oxide, with the vacant interstices filled with lithium. Lithium is the only stable ionic species present in the melt which is capable of filling the vacant interstice without expanding the oxide lattice.[5] Thus a stable diffusion barrier is formed which limits further corrosion.

ECONOMICAL EVALUATION OF THE PROCESS

An economic analysis of the process has been done to estimate the capital and operating costs of a large commercial plant. The economic analysis was made for a plant treating the gas stream from an 800 Mw generating station, operating at a 70% plant factor and burning coal containing 3% sulfur. A penalty charge for the high-temperature electrostatic precipitator was assessed. The cost of the Claus sulfur plant was also included. The total capital requirement is about $15 million, or $18.70 per kilowatt of generating capacity. This cost appears to be quite competitive with that for any other stack gas treatment process which recovers the sulfur in useful form.

The estimated annual operating cost for the 800 Mw plant assuming capital charges of 14% per year is 0.87 mills/kwh, without any credit being taken for the by-product sulfur produced. A return of $20/long ton for the sulfur is equivalent to a credit of 0.18 mills/kwh, reducing the operating costs to about 0.7 mills/kwh. This compares quite well with present estimates of 0.7 to 1.4 mills/kwh for low-sulfur or desulfurized fuels.

A thorough engineering and economic evaluation of the Molten Carbonate Process has recently been completed by Singmaster and Breyer, under contract to EPA.[6] For the same plant situation, their cost estimates were $16.81/kw for the capital investment (not including the Claus plant) and 0.95 mills/kwh for operating costs without by-product credit. The differences between the two estimates are probably well within the accuracy of the calculations.

PILOT PLANT PROGRAM

The pilot plant, funded by Consolidated Edison, Northeast Utilities, and North American Rockwell, will process a side stream of stack gases from a 335 Mw boiler at the Consolidated Edison Arthur Kill Station on Staten Island. It is planned to vary the SO_2 concentration at the inlet to the scrubber in order to map process performance over a wide range of conditions. The side stream will correspond to approximately 10 Mw equivalent of gas.

The gases, at 125°C, will be heated to about 450°C by an in-line burner firing the same fuel as the boiler. The flue gases produced by the boiler when burning the fuel oil presently specified will contain ~200 ppm sulfur oxides. This concentration is low when compared to the 2000 ppm typical of gases produced by boilers burning coal containing 3% sulfur. In order to provide the flexibility needed to operate over a range of sulfur oxide concentrations, the pilot plant will be designed to recycle some sulfur dioxide from its Claus plant.

Construction of the pilot plant is underway. Plant start-up is scheduled in January, 1973. A one-year test program is contemplated. During this period of time all system and component performance tests and optimization studies can be completed.

REFERENCES

1. G. J. Janz, "Molten Salt Handbook," Academic Press, New York (1967)
2. G. J. Janz, E. Neuenschwander, and F. J. Kelly, Trans. Faraday Soc., 59, 841 (1963)
3. A. T. Ward and G. J. Janz, Electrochim. Acta, 10, 849 (1965)
4. G. J. Janz, "Thermogravimetric and Corrosion Studies, and Phase Equilibria for Lithium, Sodium, and Potassium Carbonates," NP7015 (1958)
5. L. F. Grantham, P. H. Shaw and R. D. Oldenkamp, "Corrosion of Metals in Molten Mixtures of Alkali Metal Carbonates Containing Sulfur Compound," in "High Temperature Metallic Corrosion of Sulfur and Its Compounds," Z. A. Foroulis, Ed., The Electrochemical Society, Inc., New York
6. S. Finkler, D. R. Whitlock and W. Drobot, "An Evaluation of the Atomics International Molten Carbonate Process," EPA Contract CPA-70-76, Singmaster and Breyer, 235 East 42nd St., New York, N.Y. 10017

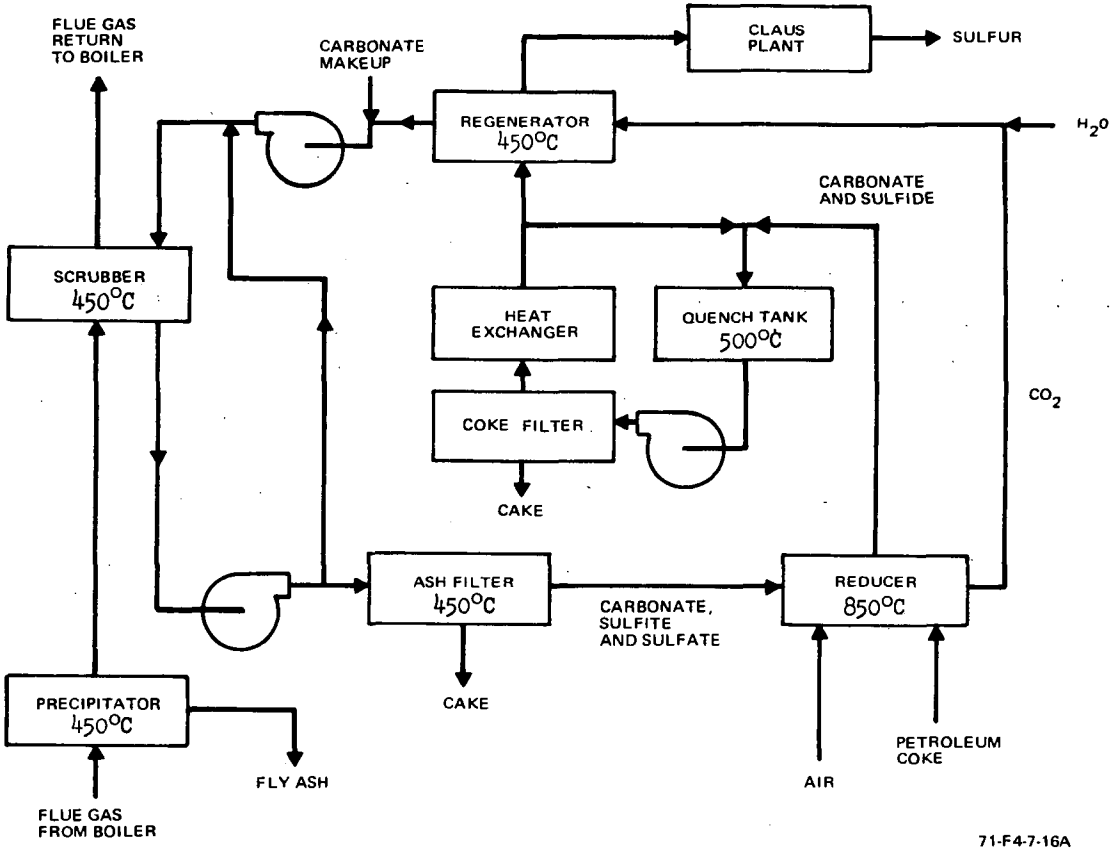


Figure 1. Molten Carbonate Process Flow Diagram

RECOVERY OF SO_2 FROM STACK GASES AS ELEMENTAL SULFUR BY A DRY FLUIDIZED ACTIVATED CARBON PROCESS. J. E. Davis, F. J. Ball, G. N. Brown, A. J. Repik, S. L. Torrence, Westvaco Corporation, Box 5207, N. Charleston, S. C. 29406.

A dry fluidized activated carbon process is being developed at the continuous pilot stage for recovery of SO_2 from waste or flue gases as elemental sulfur. The SO_2 is removed from the gases as sulfuric acid on carbon by sorption, catalytic oxygenation and hydrolysis. This is accomplished in a fluidized bed sorber cooled by water sprays at 150 to 300°F. An important development is the direct conversion of sorbed sulfuric acid to elemental sulfur by reaction with internally produced hydrogen sulfide. The product sulfur is recovered as molten sulfur by vaporization at 1000°F and condensation. The residual sulfur on the carbon is then reacted with hydrogen at 1000°F to produce the required hydrogen sulfide and complete the carbon regeneration. All regeneration steps employ fluid bed reactors. Adsorption of SO_2 at up to 25,000 cfh has been demonstrated on power boiler flue gases and simulated Claus tail gas. Feasibilities of the regeneration steps at comparable carbon rates have been shown and continuous integration of the pilot equipment is currently being achieved. Economic projections based on a 1000 MW conceptual design compare favorably with published figures on alternate measures to control SO_2 emissions. The current use of fluidized carbon beds to continuously desolvate air streams of up to 500,000 cfm with minute carbon attrition should expedite scale-up.

AMMONIA INJECTION: A ROUTE TO CLEAN STACKS

By C. C. Shale

U. S. Department of the Interior, Bureau of Mines
Morgantown Energy Research Center
P. O. Box 880, Morgantown, W. Va. 26505

INTRODUCTION

Reduction in SO_2 emissions from coal-burning powerplant stacks is essential to minimize atmospheric pollution from this source. Projections of energy demand show that by 1980 coal will account for about 25 million tons of total sulfur oxides output, mostly SO_2, unless effective control methods are developed.

A vapor phase ammonia injection process for SO_2 removal is being developed at the Morgantown (W. Va.) Energy Research Center. In laboratory research with simulated stack gas containing 4,200 ppm SO_2 (equivalent to 6.0 percent sulfur in coal), essentially complete removal of SO_2 from the gas phase was effected by ammonia injection (2).[1] Preliminary work has since been carried on with a small pilot-scale installation in which the sulfur products from the vapor phase reaction are removed in a water scrubber. This paper presents additional data from the laboratory work and the pilot-scale installation.

DESCRIPTION OF PROCESS

In the vapor phase ammonia injection process water (or steam) and gaseous ammonia are injected to the stack gas while the gas is at some temperature (> 160° F) above that at which ammonium sulfite, the principal product, decomposes (140° to 158° F) (4). After the water is vaporized and the reactants thoroughly mix, the gas is cooled below 140° F and the finely divided salt particles separate from the gas as a smoke or fume (d_p = 0.01 to 1.0 micron). The entrained solids, salt particles and fly ash, are then recovered concurrently.

The process offers high versatility in the removal of the entrained solids. They can be removed in either a dry or wet state, and if removed by a wet method, several alternatives are available for regenerating ammonia for reuse. Furthermore, since each salt particle could contain over a million SO_2 molecules, removal of SO_2 as a solid could provide more effective gas cleaning at reduced capital and operating costs. For example, the usual method for cleaning stack gas in modern powerplants is depicted in figure 1(A); after partial recovery of heat, ash is removed in an electrostatic precipitator prior to release of the gas to the atmosphere. Proposed modifications to this mode of cleaning in conjunction with ammonia injection also are shown for dry removal of the salt particles along with the ash in a precipitator as indicated in figure 1(B), or by dry removal of ash followed by wet removal of the salts and residual ash as indicated in figure 1(C). Results of qualitative tests in a precipitator indicate the salts are collectible in the dry state, as suggested, but no attempts have been made to secure quantitative data. If collected dry, the salt-ash mixture could be utilized as a soil conditioner or low-grade fertilizer and regeneration of ammonia would not be necessary.

If a wet method for collection is selected, ammonia can be regenerated from the salt solution by reaction with a readily available metal oxide, such as lime or zinc oxide, with formation of a stable sulfur product for disposal. These metal oxides, however, as well as their reaction products, are insoluble and could cause deposition on heat transfer surfaces and/or clogging in the regenerating equipment. Therefore, as indicated in figure 2, to insure continuity and reliability of the process, a soluble metal oxide was utilized (in the form of sodium hydroxide solution) to regenerate the ammonia in the experimental work described. This procedure also allows more effective utilization of the metal oxide; the soluble oxide (NaOH) can be regenerated in batch equipment outside the continuous portion of the process by reaction with either the aforestated insoluble reactants, lime or zinc oxide. Better control is afforded in a batch reactor with more efficient use of reactants.

LABORATORY DATA

Published data (2) from the laboratory work on the vapor phase reaction as well as unpublished data on kinetics of the reaction are presented for purposes of clarity.

[1] Underlined numbers in parentheses refer to references at the end of this paper.

Figure 3 shows the effect of adding various quantities of ammonia to an SO_2-laden gas stream in the presence of an excess of water vapor in the laboratory-scale equipment. Essentially complete removal of SO_2 from the gas phase is effected when ammonia additions are actually slightly less than the calculated stoichiometric quantity for sulfite formation. For example, at a gas flow rate of 10 scfh the calculated rate of ammonia addition for 3.6 percent solution is 1.86 milliliters per minute for removing all SO_2 from a gas containing 4,200 ppm, but no SO_2 was detected at the rate of 1.74 milliliters per minute. It is obvious that some bisulfite salt is formed in the reaction of SO_2 with ammonia and water vapor. The kinetics of the reactions are indicated to be adequate for commercial utilization by the curves given in figure 4, wherein residence time in the reactor was less than 0.4 second at a gas flow rate of 70 scfh, the highest tested.

PILOT-SCALE EQUIPMENT

The entire pilot-scale installation consists of a coal combustor, cyclone separator, two heat exchangers, scrubber, regenerator, and exhaust fan. The scrubber and regenerator are equipped with heat transfer coils and all equipment in contact with the scrubber liquid is made of stainless steel. Gas-sampling ports are installed upstream and downstream of the scrubber. Process data are provided by three recording instruments: a liquid conductivity meter, a pH analyzer, and a flame photometric SO_2 analyzer. This type of analyzer detects sulfur regardless of the compound in which the sulfur occurs.

Combustion gas is generated by burning coal at rates up to 10 lb/hr. A portion of the gas is cooled to about 400° F, is passed through the cyclone to remove most of the fly ash, and is further cooled (to about 160° F) before entering the scrubber vessel above the liquid level as shown previously in the flowsheet of figure 2. A liquid spray in the lower portion of the vessel cools the gas to about 130° F prior to actual scrubbing. After scrubbing, the clean gas, saturated with water vapor, flows through a mist eliminator to a stack at about 115° F. Sulfur dioxide content of the gas is monitored at the cyclone outlet (before reactant injection) and at the scrubber outlet.

Most of the scrubber liquor is cooled (105° F) and recycled in the raw state. Part of the cooled liquor is filtered to remove accumulated ash particles and flows through the pH meter, conductivity meter, and then to the cooling spray. Another portion (without cooling) is filtered and flows to the regenerator at a controlled rate. As shown, sodium hydroxide solution also flows to the regenerator at a controlled rate. The mixture of solutions is heated to about 220° F and chemical reaction releases the ammonia and steam; these products return to the system under the force created by their vapor pressures.

Prior to use of sodium hydroxide, lime and zinc oxide slurries were tested successfully for regenerating ammonia, but these insoluble metal oxides could not be effectively maintained as a suspension. Both reactant and product settled in the regenerator to ruin heat transfer and/or clog the liquid drain. Therefore, as stated earlier, sodium hydroxide was utilized to promote continuity and reliability to the system.

PILOT-SCALE OPERATIONS

Total liquid in the scrubber system in the pilot equipment is maintained at about 16 liters. The raw solution in the scrubber is recycled to the distribution plate at rates from 0.2 to 0.7 gal per minute. The filtered portion that flows through the monitoring instruments and the cooling spray is maintained constant at a rate of 0.2 gal per minute. Flow of solution to the regenerator is controlled from zero to 4.2 liters per hour, depending on the rate at which ammonia is needed for the vapor phase reaction.

At the start of an operation, water or ammonium sulfite solution can be used as the scrubbing liquid. If water is used, primary ammonia and steam must be injected to the gas and the scrubbing operation must continue for several hours prior to regeneration of any ammonia. This builds up a salt solution. If a sulfite solution is used (3.0 percent), ammonia regeneration can begin immediately.

Preliminary tests with the pilot-scale unit confirmed laboratory results and showed that essentially complete removal of SO_2 from the gas phase could be achieved in the larger equipment by injecting ammonia and steam. Many other tests were conducted to isolate the effects of some operating variables, including minimal development of the water scrubber. Results of these tests, however, are not described; the data are outside the scope of this paper.

Final selection of scrubbing medium allowed provision for a liquid reservoir on a distribution plate as described by Kempner, et al (1), and indicated in figure 2. Single or multiple layers of 50-mesh screen were used to obtain liquid-solid contact and to cause wetting and removal of the solids. Results of selected tests of a few hours duration are given in table 1, wherein, unless otherwise noted, 1.0 scfh ammonia and 2.0 lb per hour steam were injected into a flow of 500 scfh combustion gas. Under these conditions mass flow rate was about 350 lb/hr-ft^2. Calculated salt content of the gas was 0.13 gram per cubic foot based on SO_2 concentration of 900 ppm, as determined by wet chemical analysis (analyzer not installed). Ash content was determined by sampling the gas at the specified isokinetic rate. Because of combustor limitations, higher mass flow rates could not be tested on a continuous basis.

As shown, the scrubber removes well over 90 percent of the salt and residual ash particles using a single screen atop the liquid reservoir. This degree of removal is attainable at a pressure loss under 2 inches of water and demonstrates that the solids are removed with very short contact time in the cleaning equipment.

After installation of the sulfur analyzer, continuous monitoring was provided. Results of a continuous operation using this scrubber concept in the pilot-scale unit covering 105 consecutive hours (4.4 days) are summarized in table 2. During this period the scrubber was off line only one hour to clean a clogged line. At the start of the operation the scrubber contained a 2.9 percent solution of ammonium sulfite which had been prepared and used previously for almost 8 hours. During extended tests, pressure loss through the scrubber ranged from 2.0 to 2.2 inches of water. The liquid-gas ratio was about 5.0 lb/lb. Throughout the test all ammonia was regenerated from the scrubber liquor using sodium hydroxide solution except for a single 3-hour span during which 1.0 scfh of ammonia was added to test the effect of higher pH in the scrubbing liquid. Operation during the final 20 hours is not representative. This period was devoted to obtaining specific essential data for other purposes.

A calculated ammonia balance (using conductivity and pH measurements) over the first 83 hours of operation showed 4.23 g-moles ammonia loss due to all causes, which is representative of a maximum stack loss of 3.53 cubic feet of ammonia. Since a total of 41,500 ft^3 of gas was processed, ammonia loss was about 85 ppm. On a once-through basis this represents about a 4 percent loss, using an average SO_2 inlet of 1,050 ppm with 90 percent removal. Other potential losses can occur as solid salts out the stack, unregenerated salt solution, and leakage. Sulfur dioxide concentration in the effluent gas remained consistent, always ranging below about 220 ppm (usually below 100 ppm) and demonstrating a removal efficiency above 77 percent. This removal effectiveness was accomplished at a pH that never exceeded 5.4 and usually was in the range 3.5 to 4.5.

Further analysis of the data in table 2 reveals apparent irregularities in performance of the process. For example, at an elapsed time of 61 hours scrubber solution was being regenerated at a rate of 2.1 liters per hour to supply ammonia for the vapor phase reaction. Removal efficiency was only 77 percent. Six hours later while SO_2 content of the inlet gas was higher (1,000 vs 910 ppm) scrubber solution flow rate to the regenerator was zero, but the SO_2 content of the purified gas was only 10 ppm; removal efficiency was 99 percent. Other similar examples can be isolated. These conflicting data indicate some of the complexities of the process:

1. If all SO_2 is not converted to the solid state, part or all of the remainder is absorbed during the scrubbing operation. The degree to which this action occurs appears to be directly proportional to the pH of the scrubbing solution and the rate at which scrubber solution is recycled to the distribution plate.

2. At any given flow rate of scrubber solution to the regenerator, the volume of ammonia regenerated appears to vary directly with solution pH, salt concentration, and regenerator temperature (up to about 220° F).

3. Excess sodium hydroxide solution (metal oxide) must be available at all times in the regenerator for reaction with the scrubber salt solution.

PROCESS CHEMISTRY

Initial chemical reactions in the vapor state are postulated as,

$$2NH_3 + SO_2 + H_2O \rightleftharpoons (NH_4)_2SO_3, \text{ and} \quad (1)$$

$$NH_3 + SO_2 + H_2O \rightleftharpoons NH_4HSO_3. \quad (2)$$

After the scrubbing operation, the solution of salts is exposed to sodium hydroxide solution; chemical reaction releases ammonia and steam for recycle,

$$(NH_4)_2SO_3 + 2NaOH \rightleftharpoons Na_2SO_3 + 2NH_3 + 2H_2O, \text{ and} \quad (3)$$

$$NH_4HSO_3 + NaOH \rightleftharpoons NaHSO_3 + NH_3 + H_2O. \quad (4)$$

During the scrubbing operation some of the sulfites are oxidized to sulfates; the oxidation products appear to be continuously removed from the scrubbing liquor by similar reactions in the regenerator,

$$(NH_4)_2SO_4 + 2NaOH \rightleftharpoons Na_2SO_4 + 2NH_3 + 2H_2O, \text{ and} \quad (5)$$

$$NH_4HSO_4 + NaOH \rightleftharpoons NaHSO_4 + NH_3 + H_2O. \quad (6)$$

Moreover, it is evident that sulfur trioxide also is removed from the gas as shown by the analyses listed in table 2 (0 ppm SO_2, 72–89 hours). Ammonia can be regenerated from the sulfates as shown in reactions (5) and (6). Other reactions that may occur could remove selected components from the combustion gas, such as NO_2 or CO_2, but the high reactivity of the sodium ion should induce reaction with the ammonium salt produced, and thereby minimize this potential loss of ammonia.

As previously indicated, other chemical means are available for regenerating ammonia, such as reaction with lime or zinc oxide slurries, both of which have been tested successfully in the pilot installation. These reactions are demonstrated by the equation,

$$CaO + (NH_4)_2SO_3 \rightleftharpoons CaSO_3 + 2NH_3 + H_2O. \quad (7)$$

In this reaction, however, both the reactant and the sulfur product are insoluble and could interrupt process continuity by deposition and clogging if installed in the continuous portion of a recycle system. Furthermore, the sodium salt solution from the regenerator can be isolated for batch reaction with a cheap insoluble metal oxide, such as lime slurry,

$$Na_2SO_3 + Ca(OH)_2 \rightleftharpoons CaSO_3 + 2NaOH, \text{ or} \quad (8)$$

$$Na_2SO_4 + Ca(OH)_2 \rightleftharpoons CaSO_4 + 2NaOH. \quad (9)$$

After concentration, the sodium hydroxide can be recycled. In addition, all disposable salts can be oxidized to the most stable state, e.g., calcium sulfate.

Another means for disposal of a sulfur product could involve reaction of hydrogen sulfide with either the ammonium or sodium sulfite solution to produce elementary sulfur. Additional processing is required, but the weight of disposable product could be reduced by a factor of about four. Moreover, under select conditions sale of sulfur could offset at least part of the processing costs.

DISCUSSION

The vapor phase reaction between water, ammonia, and sulfur dioxide is essentially instantaneous in the presence of an excess of water vapor. The reaction occurs when the mixture is cooled below the decomposition temperature of the product compound(s). In the presence of adequate ammonia virtually complete removal of SO_2 is available providing that the reactants are thoroughly mixed prior to the cooling operation.

The apparent cause for such effective removal of the finely-divided salt particles (dp = 0.01 to 1.0 micron) and the residual ash particles is the process of nucleation that occurs when excess water in the gas condenses on the solids during the cooling operation. This process allows the soluble particles to be dissolved in the scrubbing liquid and the insoluble ones to be enlarged for easier capture. Theoretically, the ash particles could serve as

condensation nuclei for the salt particles; the ash particles then could be wetted by dissolution of the adhering salts and could cause effective size growth in the insoluble solids with concurrent ease of removal.

Scrubber liquid can be recycled to obtain a salt solution of any desired concentration prior to regeneration of ammonia from the solution. The upper limit on solution concentration presumably will be controlled by the vapor pressures of the components, ammonia and sulfur dioxide. At high pH, ammonia vapor predominates; at low pH, sulfur dioxide is the dominant vapor. Therefore, optimum recycle of the scrubber liquid will be controlled at low pH and dilute solution concentration concurrent with and relative to equipment (capital) and operating costs. A solution having low pH (e.g., < 6.0) requires stainless steel or protected carbon steel to prevent corrosion.

The process of nucleation apparently is dominant in removal of the entrained solid salts, whereby most of the residual ash also is removed by the scrubbing liquid with low contact time. Whatever the reason, the process is effective at low pressure loss.

Batch processing of the sodium salt solution from the regenerator allows more effective utilization of lime. However, disposal of product salts remains a problem.

Furthermore, after ammonia injection, effective removal of sulfur dioxide as a solid can be accomplished with water or a dilute salt solution. As exemplified by work conducted at Tennessee Valley Authority (TVA) (3) for removal of SO_2 by scrubbing with ammoniacal solution, the scrubber solution must have high pH (~ 6.4) and must be relatively concentrated to provide the required driving force for effective absorption. Under these conditions at least one additional stage of scrubbing is required (with increased pressure loss) to prevent gross loss of ammonia.

CONCLUSIONS

Ammonia injection followed by gas cooling is demonstrated as an effective means for removing SO_2 from the gas phase in combustion gas mixtures. Product sulfur-bearing salts, which are entrained in the gas, can be removed in a single stage water scrubber, and ammonia is effectively regenerated from the scrubber liquid through reaction with sodium hydroxide solution. Ammonia losses are minimal and presumably can be reduced even further through use of a second stage of scrubbing. All reactants and products in the continuous cycle of the process are water soluble, so no equipment clogging occurs; process continuity and reliability are not interrupted.

REFERENCES

1. Kempner, S. K., E. N. Seiler, and D. H. Bowman. Performance of Commercially Available Equipment in Scrubbing Hydrogen Chloride Gas. J. APCA, v. 20, No. 3, March 1970, pp. 139–143.

2. Shale, C. C., D. G. Simpson, and P. S. Lewis. Removal of Sulfur and Nitrogen Oxides from Stack Gases by Ammonia. Chem. Eng. Prog. Symp. Ser., v. 67, No. 115, 1971, pp. 52–58.

3. Tennessee Valley Authority. Sulfur Oxide Removal from Power Plant Stack Gas; Ammonia Scrubbing. Conceptual Design and Cost Study Series, Study No. 3. Prepared for Nat. Air Pollution Control Assn., PB 196804, September 1970, pp. 58–61.

4. Weast, R. C., S. M. Selby, and C. D. Hodgman. Handbook of Chemistry and Physics, 45th ed., The Chemical Rubber Co., Cleveland, O., 1964, p. B-152.

TABLE 1. – Scrubber operating data

Test no.	Scrub. medium, screen	Liquid recycle rate, gpm	Pressure loss in H_2O	[1]Resid. NH_3, $gm/ft^3 \times 10^{-3}$	[2]Resid. ash $gr/ft^3 \times 10^{-3}$	Removal eff., percent	
						Salt	Ash
1	[3]None	0.4	1.5	15.5	23	88.1	92.8
2	1	.4	2.5	6.8	13	94.8	95.9
3	1	.4	2.5	6.4	20	95.1	93.7
4	[4]1	.2	1.8	6.6	0.6	94.9	99.8
5	[4]1	.4	2.9	5.8	0.3	95.5	99.9
6	2	.2	3.5	4.8	11	96.3	96.6
7	3	.2	4.0	5.5	11	95.8	96.6
8	[4]3	.4	4.6	5.6	12	95.7	96.2
9	[5]3	.2	3.8	5.5	15	95.8	95.3
10	3	.4	5.5	5.4	9	95.8	97.2

[1] Calculated salt produced, 0.13 gram per ft^3.
[2] Ash concentration inlet gas, 0.32 grain per ft^3.
[3] Distribution plate only, 0.1- in holes.
[4] Steam rate 3.0 pph.
[5] Steam rate 4.0 pph.

TABLE 2. – Representative data on continuous SO_2 removal by NH_3 injection

Cumulative time, hrs	pH scrubber solution	Solution conductivity, mhos x 10^4	SO_2, ppm		Solution regeneration rate, cc/hr	Removal efficiency, pct
			Inlet	Outlet		
3.0	5.20	5.40	1,000	150	2,400	85
9.5	4.85	5.40	1,000	45	2,000	95
15.0	4.30	5.18	1,000	120	1,056	88
20.0	4.45	5.01	1,225	130	1,440	89
24.0	4.30	5.10	1,250	90	1,056	93
29.0	4.18	5.30	1,250	220	1,056	82
35.0	5.02	5.50	1,650	220	1,056	87
43.0	4.30	4.89	885	25	600	97
47.0	3.80	4.80	1,030	39	240	96
51.0	3.03	4.83	930	51	240	94
55.0	4.23	4.11	910	[1]20	2,100	97
61.0	4.39	3.69	910	210	2,100	77
67.0	5.42	3.49	1,000	10	0	99
72.0	4.02	4.45	930	0	0	100
76.0	3.16	4.74	1,090	0	1,056	100
83.0	4.54	3.90	1,200	0	2,100	100
89.0	4.29	3.50	1,100	0	2,100	100
93.0	4.02	2.90	1,030	220	2,400	79
97.0	2.90	3.05	780	760	2,700	3
101.5	3.98	1.93	780	[2]505	> 4,200	35
102.0	3.78	1.80	1,030	505	> 4,200	50
104.0	4.72	1.55	1,400	590	> 4,200	58
105.0	3.95	1.50	1,900	910	> 4,200	52

[1] Analysis by wet chemical method, 30 ppm.
[2] Analysis by wet chemical method, 510 ppm.

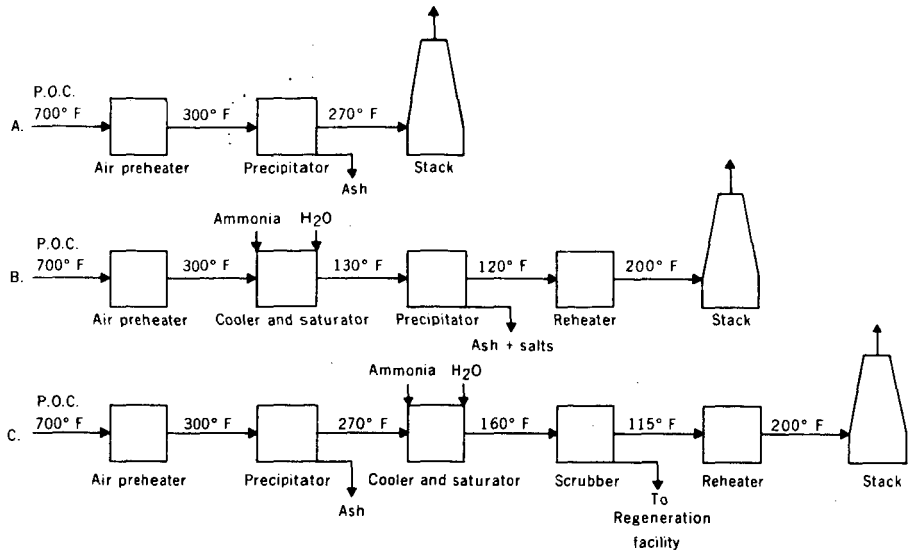


FIGURE 1. – Proposed Modifications for Stack Gas Cleaning Methods

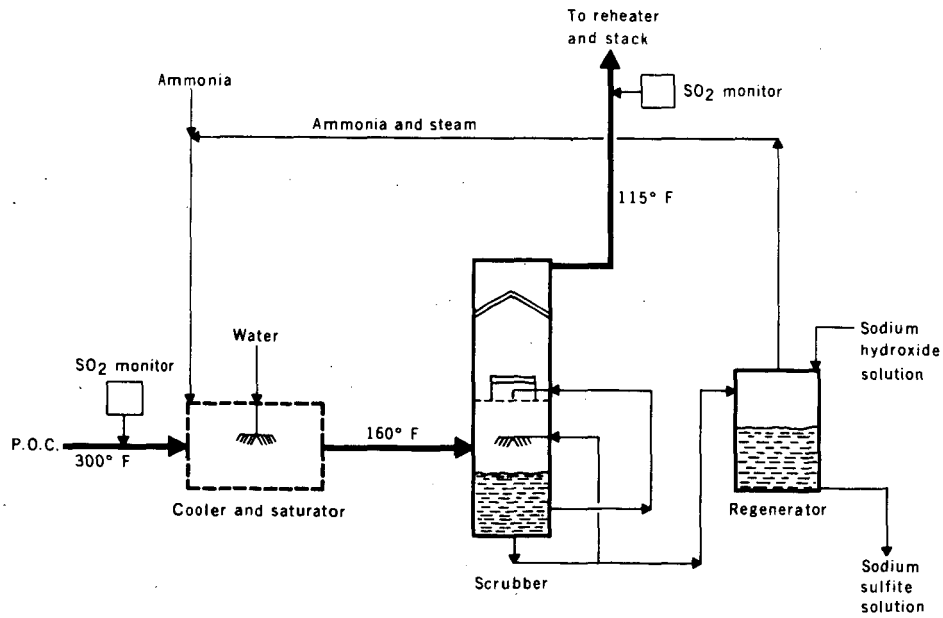


FIGURE 2. – Flow Diagram for Pilot-Scale SO_2 Removal System

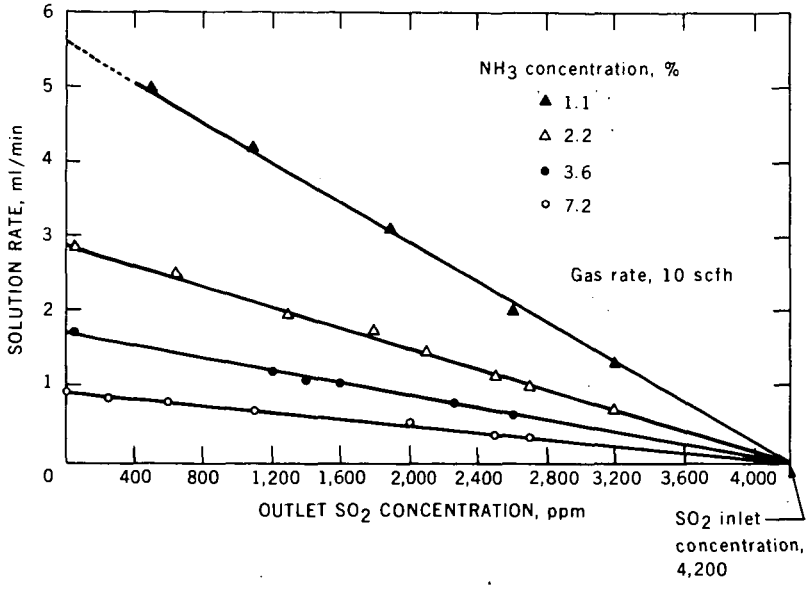


FIGURE 3. – Effect of Ammonia for Removing SO_2 From Gas Phase

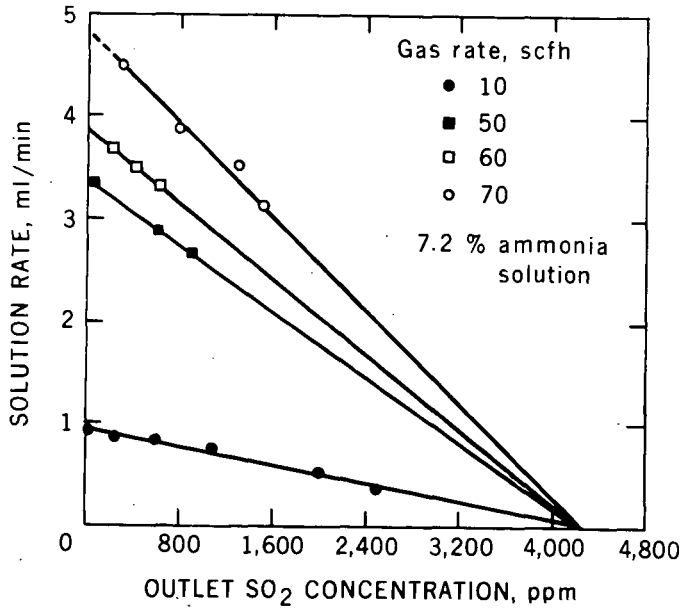


FIGURE 4. – Effect of Gas Flow Rate on Removal of SO_2 Using Ammonia

AQUEOUS SCRUBBING OF NO_x FROM STACK GASES. G. A. Chappell, Esso Research and Engineering Company, Linden, New Jersey, 07036.

A bench-scale batch scrubbing unit has been used to screen various solutions for NO_x absorption from synthetic flue gas. The blended gas stream contained 12% CO_2, 3% O_2, 700 ppm NO_x, 8% steam, variable SO_2, and N_2. The mixture, flowing at 3200 cc/min, bubbled through one liter of scrubbing solution maintained at 125°F. The effluent gas was analyzed spectrophotometrically for NO, NO_2 and SO_2. We investigated the effect of NO_2 addition on the sorption of NO by using a flue gas containing 350 ppm each of the two oxides. Of the many solutions and slurries studied, sulfites and amines were the most effective at NO_x absorption. Concentrated ammonium hydroxide (65°F) removed 74% of the NO and 80% of the NO_2 whereas a saturated sodium sulfite solution (125°F) absorbed 16% of the NO and 100% of the NO_2. A slurry of $CaSO_3$ absorbed 35% of the NO and 66% of the NO_2. The sulfite systems are quite unreactive toward NO in the absence of NO_2; however, the presence of NO has little effect upon the absorption of NO_2. These and other results will be presented and discussed in more detail.

THE CHEMISTRY OF POLLUTION CONTROL THROUGH COMBUSTION MODIFICATIONS, D. W. Pershing and E. E. Berkau, Environmental Protection Agency, Office of Air Programs, Research Triangle Park, North Carolina 27711.

The major pollutant emissions from fossil-fuel burning boilers and furnaces are sulfur oxides (SO_x), nitrogen oxides (NO_x), and particulates. Of these, NO_x and particulates are strong functions of the combustion system and are, therefore, amenable to control through combustion modification. Techniques such as flue gas recirculation, stagged combustion, and off stoichiometric firing have been extremely effective in reducing NO_x emissions from many gas fired boilers and to a lessor extent from oil and coal-fired units. Recent studies have also shown that burner design and air introduction scheme can have pronounced effects on NO_x formation. In an effort to better understand the controlling phenomena kinetic and aerodynamic modelling programs were initiated. Their results indicate that for natural gas systems it is possible to utilize existing chemical rate data and predict qualitatively the results observed in the field. Unfortunately, similar successes were not achieved with oil and coal-fired systems. Thus, this paper is an attempt to review and explain the existing control techniques, to show the theoretical basis upon which they are founded and to point out those areas where more experimental work is needed, especially in the areas of chemical kinetics and reaction mechanism.