APPLICABILITY OF THE MEYERS PROCESS FOR DESULFURIZATION OF U.S. COAL (A SURVEY OF 35 COALS)

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I. INTRODUCTION

The Meyers Process (1,2) is a new chemical leaching process which will allow many coal-fired power plants and industrial sources to meet Federal and State sulfur oxide emission standards without the use of flue gas cleaning. This process utilizes a regenerable aqueous ferric sulfate leaching unit to chemically convert and remove the pyritic sulfur content of the coal as elemental sulfur and iron sulfate. Although only pyritic sulfur is removed (organic sulfur remains), the Meyers Process has wide applicability for converting U.S. coal reserves to a sulfur level consistent with present and proposed governmental sulfur oxide emission standards.

Thirty-five mines from the major coal basins were investigated in this study. Because of the relatively high pyritic sulfur and low organic sulfur contents, and high production (70 percent of current U.S. output) of Appalachian coals, the Meyers Process appears to have major impact in this area.

In the Meyers Process, aqueous ferric sulfate is used at 90-130°C to selectively oxidize the pyritic sulfur content of coal to yield iron sulfate and free elemental sulfur as shown in Equation 1. The iron sulfate dissolves in solution while the free sulfur is removed from the coal matrix either by vaporization or solvent extraction. The leaching (oxidizing) agent is then regenerated at a similar temperature using oxygen or air and recycled, while product iron sulfates are removed by liming and/or crystallization.

$$4.6\ Fe_2(SO_4)_3 + 4.8\ H_2O + FeS_2 \longrightarrow 10.2\ FeSO_4 + 4.8\ H_2SO_4 + 0.8S \qquad 1)$$

The detailed chemistry, leaching conditions, reaction kinetics, process engineering, and cost estimates have been published (3,7) and a reactor testing unit is being built.

This paper presents experimental results and discussion for: a) pyritic sulfur removal from coal, b) pyritic sulfur

partition by float-sink separation from the same coals, c) the effect of the Meyers Process on the trace element content of the treated coals and d) applicability of the Meyers Process for meeting air pollution control standards. This work was performed under contract to the Environmental Protection Agency (8,9).

II. SULFUR REDUCTION

A summary of the sulfur analyses of the run-of-mine coals utilized in this study is shown in Figure 1. The organic and pyritic sulfur contents are plotted along the x and y axis while the sum of these values for a given coal can be read from the diagonal lines. The average coal for this survey contained 2.02% pyritic sulfur and 3.05% total sulfur which corresponds to the U.S. Bureau of Mines average for 325 raw coals (10), indicating that the surveyed coals are reasonably representative of the sulfur distribution in U.S. coal.

The results to date for chemical removal of pyritic sulfur (100-150 micron top-size coal) and the optimal results for conventional coal washing (based on the 1.4 mm, 1.90 float fraction of a float-sink analysis) are shown in Table 1 and in graphical form in Figure 2. The table describes the results obtained on coals which contained sufficient pyritic sulfur for accurate sulfur removal determination (i.e., >0.25% w/w). Three of the mines sampled were below this limit and, therefore, do not appear in the table. Actual total sulfur values before and after chemical removal are shown in Columns 4 and 5. These may be compared with Column 6, which shows sulfur values which can be obtained with full process optimization. This latter value was calculated by adding the residual pyritic sulfur and sulfate contents of the coal to the initial organic sulfur value after correction for any concentration effects due to ash removal. In the survey program, complete removal of residual elemental sulfur and sulfate was not always obtained since conditions were standardized but not optimized for each individual coal. Thus, for example, although 96 percent pyrite conversion was obtained for the Bird No. 3 coal, the total sulfur was reduced to 0.80 percent, not the theoretical 0.45 percent due to these effects. These processing problems have now been resolved as part of other projects (3,9) and the values shown in Column 6 can be considered to represent the true potential of the process. Because of the widespread application of physical cleaning techniques for removal of non-combustible rock (which includes varying amounts of pyrite, along with some carbon) from coal, float-sink fractionation was performed in order to define the relative utility of washing and chemical desulfurization for each coal. The results are shown in Column 9 and also in Figure 2.

The sulfur reduction potential of the Meyers Process was found to be highly attractive and in particular it was found

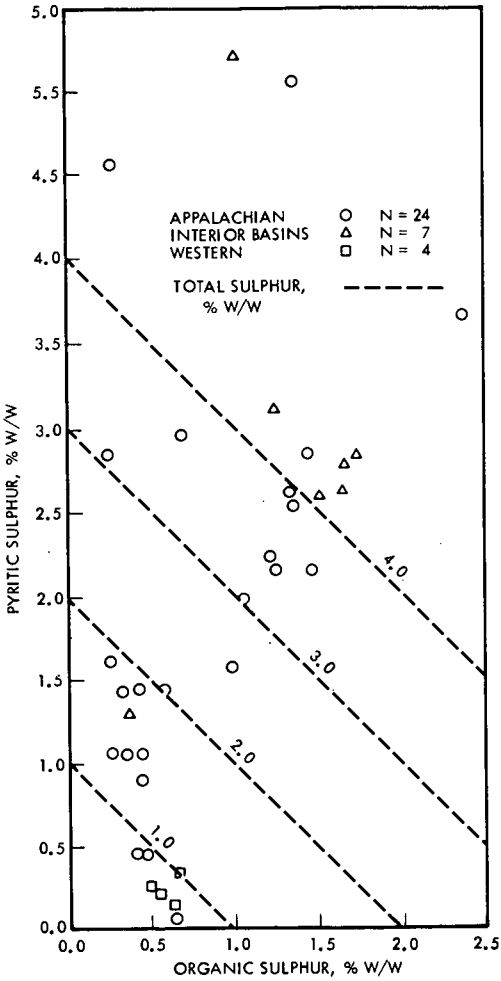

Figure 1. Sulfur Forms of Sampled U.S. Coals

Table 1. Summary of Pyritic Sulfur Removal Results (100-150 micron top-size coal)

Mine	Seam	State	% Total Sulfur w/w in Coal[a]			Meyers Process Pyrite Conversion % w/w	Meyers Process Total Sulfur Decrease % w/w	% Sulfur in Coal[b] After Float-Sink
			Initial	After Meyers Process: Current Results	After Meyers Process: Revised Processing[c]			
Navajo	Nos. 6,7,8	N. Mexico	0.8	0.6	0.5	90	25	--
Kopperston No.2	Campbell Creek	W. Virginia	0.9	0.6	0.5	92	33	0.8
Harris Nos. 1&2	Eagle & No.2 Gas	W. Virginia	1.0	0.8	0.6	94	23	0.9
Colstrip	Rosebud	Montana	1.0	0.6	0.7	83	30	--
Warwick	Sewickley	Pennsylvania	1.4	0.6	0.4	92	54	1.0
Marion	Upper Freeport	Pennsylvania	1.4	0.7	0.6	96	50	1.2
Mathies	Pittsburgh	Pennsylvania	1.5	0.9	0.5	95	36	1.7
Isabella	Pittsburgh	Pennsylvania	1.6	0.7	0.5	96	54	1.5
Orient No. 6	Herrin No. 6	Illinois	1.7	0.9	0.8	96	44	1.4
Lucas	Middle Kittanning	Pennsylvania	1.8	0.6	0.5	94	64	0.7
Jane	Lower Freeport	Pennsylvania	1.8	0.7	0.6	91	63	0.8
Martinka	Lower Kitttaning	W. Virginia	2.0	0.6	0.8	92	70	0.8
North River	Corona	Alabama	2.1	0.9	0.8	91	55	2.2
Humphrey No. 7	Pittsburgh	W. Virginia	2.6	1.5	1.2	91	42	1.9
No. 1	Mason	E. Kentucky	3.1	1.6	1.4	90	48	2.3
Bird No. 3	Lower Kittanning	Pennsylvania	3.1	0.8	0.4	96	75	1.5
Williams	Pittsburgh	W. Virginia	3.5	1.7	1.4	96	50	2.3
Shoemaker	Pittsburgh	W. Virginia	3.5	1.7	1.5	96	51	3.6
Meigs	Clarion 4A	Ohio	3.7	1.9	1.7	93	48	2.8
Fox	Lower Kittanning	Pennsylvania	3.8	1.6	1.2	89	57	2.0
Dean	Dean	Tennessee	4.1	2.1	1.6	94	49	3.0
Powhattan No. 4	Pittsburgh N. 8	Ohio	4.1	1.9	1.9	85	53	3.3
Eagle No. 2	Illinois No. 5	Illinois	4.3	2.0	1.9	94	54	2.9
Star	No. 9	W. Kentucky	4.3	2.5	1.8	91	43	3.0
Robinson Run	Pittsburgh	W. Virginia	4.4	2.2	1.6	97	50	3.0
Homestead	No. 11	W. Kentucky	4.5	1.7	1.6	93	47	3.2
Camp Nos. 1&2	No. 9 (W. Ky.)	W. Kentucky	4.5	2.0	2.1	89	55	2.9
Ken	No. 9	W. Kentucky	4.8	2.8	2.2	91	42	3.5
Delmont	Upper Freeport	Pennsylvania	4.9	0.8	0.5	96[d]	80	2.1
Muskingham	Meigs Creek	Ohio	6.1	3.2	2.7	94	47	4.4
Weldon No. 11	Des Moines No. 1	Iowa	6.4	2.2	1.7	92	65	3.9
Egypt Valley No. 21	Pittsburgh No. 8	Ohio	6.6	2.7	2.1	89	59	4.6

[a] Dry, moisture-free basis

[b] 1.90 float material, 14 mesh x 0, is defined here as the limit of conventional coal cleaning

[c] Calculated using latest process improvement

[d] Run at 200m x 0

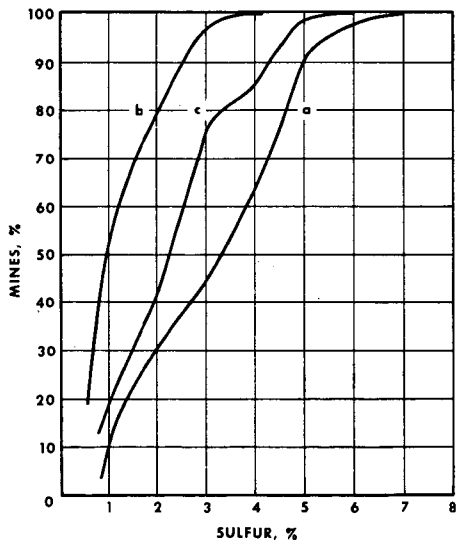

Figure 2. Sulfur Content of Survey Run-of-Mine Coals(Curve a), the Same Coals Physically Cleaned(Curve c) and Chemically Desulfurized(Curve b)

that: a) the Meyers Process, at its current state of development, removed 83 to 99 percent of the pyritic sulfur content of the 32 coals studied, resulting in total sulfur content reductions of 25 to 80 percent, b) twelve (38 percent) of the coals were reduced in sulfur content to the 0.6 to 0.8 percent sulfur levels generally consistent with the New Source Performance Standards and many state standards, c) in all cases, the Meyers Process removed significant to very large increments of sulfur over that separable by physical cleaning, and d) in two cases, the North River and Mathies mines, coal cleaning actually resulted in a sulfur content increase in the float product.

III. RATE OF PYRITIC SULFUR REMOVAL

The removal of pyritic sulfur was measured as a function of time at 100°C for 18 Appalachian and 3 Eastern Interior region coals. The results are displayed in Table 2, which shows the range of rates that were observed. It was assumed that the empirical kinetic rate expression (3) which was developed previously for this process is applicable to all coals in the survey. The kinetic equation can be simplified by holding the reagent concentration relatively constant, as was the case in this study, to yield Equation 2.

$$-d[Wp]/(dt) = k^{o}Wp^{2} = \text{rate of pyrite removal} \qquad 2)$$

where

Wp = weight percent pyrite in the coal, and

k^{o} = function of temperature, reagent concentration, coal type, and particle size.

By integrating Equation 2, the fraction of pyrite removed as a function of time is shown in Equation 3.

$$F/(1 - F) = k^{o}Wp^{o}t_{F} \qquad 3)$$

where

F = fraction of pyrite removed,

Wp^{o} = initial pyrite concentration, and

t_{F} = time to removal at fraction F.

The initial weight percent of pyritic sulfur Sp^{o} may be substituted for Wp^{o} and Equation 3 rearranged to Equation 4.

Table 2. Relative Rate Constants for Pyritic Sulfur Removal

Coal Mine	Seam	Top Size, Microns	Sp^o	$t_{80\%}$, hrs	Relative Rate Constants $\frac{1}{Sp^o t_{80\%}}$	Relative[a] Rate
Kopperston No. 2	Campbell Creek	149	0.47	2.0	1.1	16
Harris Nos. 1&2	Eagle & No.2 Gas	149	0.49	2.3	0.89	13
Marion	Upper Freeport	149	0.90	3.0	0.37	5.3
Lucas	Middle Kittanning	100	1.42	3.25	0.22	3.1
Shoemaker	Pittsburgh	149	2.19	2.9	0.16	2.3
Williams	Pittsburgh	100	2.23	3.0	0.15	2.1
Ken	No. 9	149	2.85	2.5	0.14	2.0
North River	Corona	149	1.42	5.0	0.14	2.0
Star	No. 9	100	2.66	3.0	0.13	1.9
Mathies	Pittsburgh	100	1.05	9.0	0.11	1.6
Powhattan No. 4	Pittsburgh No. 8	75	2.75	4.0	0.091	1.3
Homestead	No. 11	149	3.11	3.5	0.092	1.3
Fox	Lower Kittanning	75	3.09	4.5	0.072	1.0
Isabella	Pittsburgh	149	1.07	13.0	0.072	1.0
Martinka	Lower Kittanning	149	1.42	10.0	0.070	1.0
Meigs	Clarion 4A	149	2.19	8.5	0.054	0.77
Bird No. 3	Lower Kittanning	100	2.87	8.0	0.044	0.62
Dean	Dean	100	2.62	10.2	0.037	0.53
Muskingum	Meigs Creek No. 9	149	3.65	8.0	0.034	0.49

[a] $1/Sp^o t_{80\%}$ relative to value for Martinka Mine.

$$1/(Sp^{o}t_{F}) \propto k = \text{actual rate constant} \qquad 4)$$

Thus, assuming 80 percent removal as a point of comparison, the values of $1/Sp^{o}t_{80\%}$ shown in Column 6 of Table 2 are indicative of the reactivities of the pyrite contained in the coals that were studied. A large amount of experimentation and engineering has been performed using rate data obtained for Martinka (3) coal; therefore, the Martinka coal $Sp^{o}t_{80\%}$ has been set equal to 1 for a basis of comparison (as shown in Column 7).

It can be easily seen from Table 2 that there is a wide band of rate constants rather evenly spread over a factor of approximately 30. The Kopperston No. 2 and Harris Nos. 1 and 2 coals react more rapidly than the slowest coals (Dean and Muskingum) by a factor of about 30. Thus, it is apparent that real and significant rate differences do exist between pyrite in various coals. Characteristics of coal such as pore structure, size and shape distribution of pyrite, etc., may be the primary factors affecting the rate constant as reflected in the observed band of values found for the rates given in Table 2.

IV. TRACE ELEMENT REMOVALS

Because both chemical leaching and physical cleaning processes have the ability to remove potentially harmful trace elements from coal either by leaching or physical partitioning, 50 coal samples have been analyzed in duplicate or triplicate to determine the extent of the removal, if any, for 18 elements of interest to the Environmental Protection Agency. The samples included 20 as received, 20 chemically leached and 10 float-sink treated coal samples. The results are shown for 12 elements in Figure 3 in cumulative fashion. Six elements, B, Be, Hg, Sb, Se, and Sn yielded negative or inconclusive results due to low levels or analysis difficulties and thus are not plotted. Although the results varied greatly from coal to coal in respect to the elements extracted and the degree of extraction, some general conclusions can be reached.

- As, Cd, Mn, Ni, Pb, and Zn are removed to a significantly greater extent by the Meyers Process,
- F and Li are partitioned to a greater extent by physical separation procedures,
- Ag and Cu are removed with a slight preference for float-sink separation, and
- Cr and V are removed for both processes with equal success.

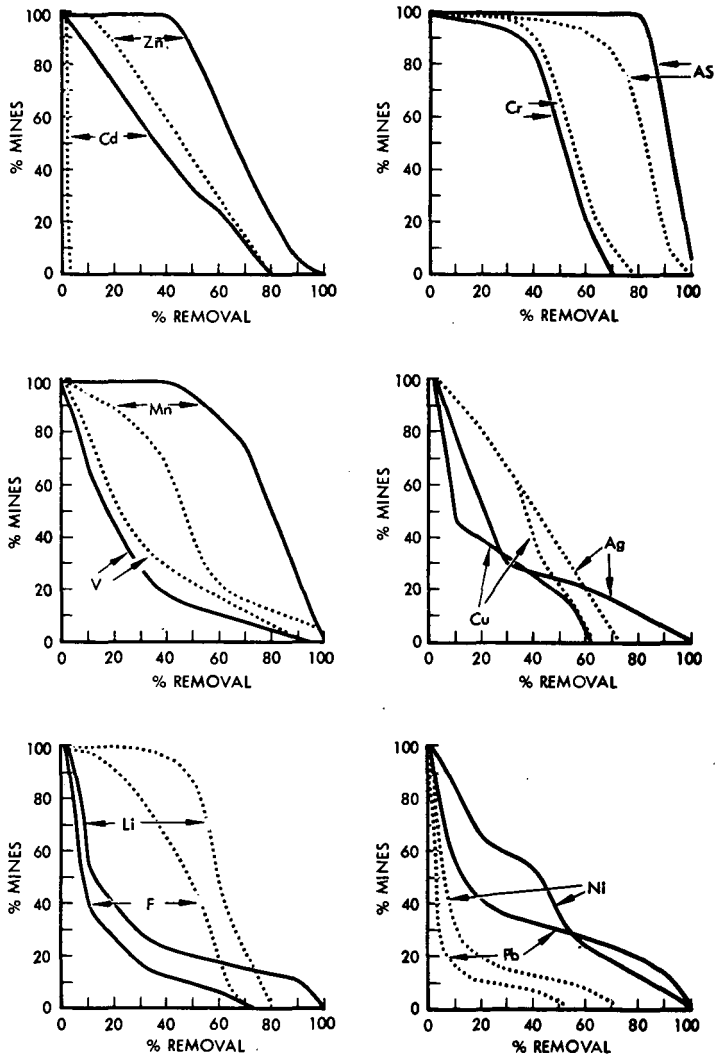

Figure 3. Trace Element Removal Data
(— Meyers Process, ···· Physical Cleaning)

The effective removal of As, Cd, Cr, Ni, Pb, and Zn from the coal by the Meyers Process is especially noteworthy as these compounds are concentrated (along with Se) in the fine particulates emitted from coal-fired power plants. This fine particulate matter has been demonstrated to pass through conventional fly-ash control devices.

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