FINAL REPORT TO DEPARTMENT OF ENERGY

"OPTIMIZATION OF BACTERIAL LEACHING OF PYRITE IN COAL"

Sept. 17, 1979

Re: Contract No. EF-77-G-01-2749
Project Director:
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INTRODUCTION:

This report presents an account of one year's research dealing with the solubilization of pyrite in coal by ferric ions, regenerated through bacterial action. The original plan of investigation set out a number of areas in which information was to be obtained relevant to the basic question: Can enhancement of the rate of bacterial oxidation of ferrous ions in a recirculated leaching system result in rapid removal of pyrite from coal? As work proceeded it became evident that, the rate of pyrite removal in the systems under investigation was rarely limited by the rate of reoxidation of iron, but rather by the rate of reaction of the dilute ferric solutions with the pyrite in coal. In some cases, the bacterial reoxidation of ferrous ions, in lixiviant solutions, resulted in the deposition of jarosite, which left the leached coal particles coated with an oxidized iron residue containing sulfur, thereby diminishing net sulfur removal as well as retarding pyrite oxidation. Accordingly, a portion of our effort was directed toward understanding the process of jarosite deposition and in seeking practical means by which this product could be removed from leached coal and either disposed of or utilized as a by-product of the leaching process.

Bacterial Reoxidation of Iron in Leaching Solutions;

Considering the bacterially catalyzed solubilization of pyrite to take place by the scheme shown in Figure 1, rate limitation of Fe^{2+} reoxidation should result in leach waters, initially rich in Fe^{3+}, becoming more reduced with time, if the rate of Fe^{3+} reduction by pyrite, exceeded the rate of reoxidation. Apparently, that situation rarely occurs in natural minewaters and is only a transient phenomenon of artificial leaching systems. Even if partially depleted of active iron oxidizing bacteria, natural minewater quickly regains the ability to maintain complete oxidation of recirculated iron in solution. Figures 2-7 compare the results of leaching six finely divided coals in minewater (which had been stored in a refrigerator for 8 weeks) with leaching in dilute, oxidized 9K solution (a synthetic medium for *Thiobacillus ferrooxidans*). In both cases, the Fe^{2+} concentration increased initially, when the rate of Fe^{2+} reoxidation was limiting. However, the rate of iron oxidation in minewater accelerated with time, so that oxidation exceeded reduction within 72 hours. This was due to the establishment of an active population of iron bacteria, resulting from proliferation of bacterial cells, present originally in the stored minewater. In contrast, very little reoxidation of iron occurred in the dilute 9K medium unless iron oxidizing bacteria were added. Inoculation of the dilute 9K-coal suspensions, with cells of *Thiobacillus ferrooxidans*, produced a steady state level of $[Fe^{3+}]$ comparable to that maintained in the dilute minewater by the activity of its endogenous bacterial population. Adding additional iron bacteria had little effect upon the steady state $[Fe^{3+}]$ of dilute minewater, actively oxidizing pyrite.

The process outlined in Figure 1 results in the increase of total iron in solution as leaching proceeds. Theoretically, for every two Fe^{3+} reduced a pyrite molecule is oxidized and one atom of iron is brought into solution. The six powdered coals used in our experiments, varied greatly in the ratio of ferric ions reduced to iron atoms solubilized, during the first 24 hours of leaching, in the absence of added iron bacteria (Table 1). The Maidsville (Sewickly Seam) coal, displayed particularly high ratios as consequence of meager release of iron despite significant reduction of Fe^{3+} (Fig. 4).

Departures from the 2:1 ratio, during the initial phase of leaching, may reflect the presence of iron compounds other than FeS_2 in the coal samples and of other substances which can be oxidized by Fe^{3+}. As leaching proceeded, in the uninoculated 9K solution, proliferation of iron bacteria, originating in the coal, caused some reoxidation of iron, thereby diminishing the apparent $\Delta Fe^{2+}/\Delta Fe$ solubilized, with time (Table 1). The ratio is altered further by factors which affect the solubility of oxidized iron derived from pyrite. Most important, in this regard, is the precipitation of bacterially oxidized iron as jarosite, $M^+Fe_3(SO_4)_2(OH)_6$, where M^+ is some univalent cation such as H_3O^+, NH_4^+, Na^+ or K^+. This sulfur containing ferric compound is a unique product of Fe^{2+} oxidation by Thiobacillus ferrooxidans under normal conditions of temperature and pressure. Although the mechanism of its formation is unclear, it reflects the sulfate requirement for oxidation of iron by Thiobacillus ferrooxidans.

Limitation of the rate of oxidation of pyritic inclusions in freshly prepared coal particles is due to the restricted ability of the leaching solution to penetrate the coal. This is deduced from experiments in which ferric solutions were used to leach sieved "foot-vein" coal particles of two different mesh sizes. The "foot-vein" coal was used because of its high pyrite content and the rapidity with which it reacts with ferric leaching solutions to produce ferrous ions. The "foot-vein" coal particles <88 μ in diameter reduced Fe^{3+} at a rate 40% faster than particles which were between 88 and 125 μ in size. (Fig. 8). Moreover, when "foot-vein" coal <88 μ in diameter was leached with minewaters diluted to different Fe^{3+} concentrations, the highest concentrations yielded the most rapid rates of Fe^{3+} reduction, initially; but rates of reduction, at the different Fe^{3+} concentrations, became nearly the same within a few hours (Fig. 9). The initial rates of oxidation may be interpreted to represent activities at the freely accessible surface sites where the higher concentrations of Fe^{3+} are accommodated by the availability of sufficient pyrite. When the surface pyrite is oxidized, rates of oxidation are limited by ability of the oxidant to penetrate the coal particles and not by the availability of Fe^{3+} at the surface.

Pyrite Solubilization

It was of interest to compare the leaching of high sulfur "foot-vein" coal to several commercial coals in terms of ferric iron reduction, as well as the solubilization of iron and sulfur in the presence or absence of added iron oxidizing bacteria (Figs. 2-7). The commerical coals included the following types: Middle Kittanning (Jand M), Sewickly Seam (Maidsville), Kentucky Fire-Clay (Greff), Upper Freeport (Sunbeam), and Pittsburgh Seam, (Champion). The coals used ranged from 8.5% total sulfur to 1.1% total sulfur and from 7.34% to 0.6% pyritic sulfur by weight. As might be expected, larger amounts of sulfur were removed per unit time from the coal particles containing the most pyrite (Table 2). Dilute minewater which had been stored for over two months prior to use, removed between 7 and 40% of the total sulfur from coal particles over a seven day period. This represented a decrease of 39 to 60% of the pyritic sulfur from high sulfur coals and 13 to 30% of pyritic sulfur from the low sulfur coals. The coal samples exhibited individual patterns of Fe^{3+} reduction relative to sulfur and iron removal, in dilute 9K solution (Table 1). Since the initial rate of Fe^{3+} reduction in this lixiviant was not confounded by bacterial iron oxidation, it could be used to estimate the amount of Fe^{3+} reduced (Fe^{2+} formed from Fe^{3+} reduction) for the total leaching period (170 hrs). Thus, $\frac{\Delta Fe^{2+} - \Delta Fe}{\Delta Fe} \times \Delta Fe_{170\ hrs} \approx \Delta Fe^{2+}_{calc.\ 170\ hrs}$. When divided by the loss in sulfur of the various coal samples, it provides the data shown under $\frac{\Delta Fe^{2+}(calc.\ 170\ hrs)}{\Delta S}$ in Table 1. Comparison of the various coal samples showed a wide range of values from 0.27 to 10.93 even though reduction of one Fe^{3+} is required, theoretically, for every sulfur atom released from pyrite. The variance between types is changed significantly if the actual Fe^{2+} concentration at the end of the 170 hrs is used as the basis for calculating the relationship of net Fe^{3+} reduction to S removal. Since the values of (Fe^{2+} - ΔFe) are diminished by bacterial reoxidation of Fe^{2+}, the trend toward uniformity of ratios, involving sulfur removal and Fe solubilized in the presence of active bacterial populations, suggests that bacterial action affects leachability in ways other than reoxidation of the Fe^{2+} formed from the lixiviant. This point is reinforced by consideration of the ratio of sulfur removal to iron solubilized in all the leached samples (Table 2). Here again the greatest variance of values occurred between coal types, while the ratios within types for different leaching conditions were relatively consistent or predictable. Table 3 indicates that the average variance of the mean for S removal/Fe solubilized for particular leaching treatments of the different coal samples, is over ten times as great as the average variance of the mean within individual coals undergoing different leaching treatments. A major contributor to variance between treatments of individual coal samples is the predictable effect of jarosite deposition on the analytical values. Since sulfur was measured as residual sulfur in the coal after leaching and iron was measured, in the leaching solution, deposition of jarosite would selectively decrease the values for iron; thereby increasing the ratio, particularly if the jarosite was not uniformly associated with the coal taken for sulfur analysis. Therefore, those leaching treatments, which produced active bacterial reoxidation of the ferric lixiviant, tended with one significant exception, toward highest sulfur removal/Fe solubilized ratios. The important exception is the high sulfur "foot-vein" coal in which the addition of T. ferrooxidans cells resulted in greater solubilization of iron in proportion to sulfur removed than in the absence of added bacteria. Conceivably, this could be due to the retention within coal particles of less soluble polysulfide or polythionate derivatives which were formed from pyritic sulfur by bacterial action as soluble Fe^{2+} escaped and was reoxidized in the leaching fluid.

Leaching Index

Given the variability with which different powdered coals are leached by dilute ferric solutions, it was important to develop a convenient means of expressing the effectiveness of the bacterial component in leaching processes carried out by different ferric lixiviants on different coals. Since the spectrophotometric analysis for soluble Fe^{2+} and Fe^{3+} is so easily performed[*] (and is suitable for continuous monitoring), the data obtained thereby offers a rapid means for evaluating the activity of the iron oxidizing bacteria in leaching coal suspensions. The increments of Fe^{2+} (as $\Delta Fe^{2+} - \Delta Fe$) per unit increment of total iron in solution (ΔFe) were compared in systems, without added iron oxidizing bacteria,

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[*] /See Steiner, M. and Lazaroff, N. 1974. Direct method for continuous determination of iron oxidation by autotrophic bacteria. Applied Microbiology 28, 872-880.

to the same systems containing an excess of active iron oxidizing bacteria. This provided an estimate of the effectiveness of iron oxidation and leaching in an uninoculated system (or natural minewater) compared to the same system with bacterial reoxidation of iron occurring at non-limiting rates. If the only iron solubilized were pyritic iron, and oxidation of Fe^{2+} did not occur, then $\Delta Fe^{2+} - \Delta Fe$ would express the amount of Fe^{3+} reduced by reaction with pyrite. The expression $\frac{\Delta Fe^{2+} - \Delta Fe}{\Delta Fe}$ would then represent the molar ratio of Fe^{3+} reduced (or the number of electrons transferred) per atom of iron or mole of pyrite solubilized. Under such conditions the ratio ideally equals to 2. It would be altered upward in circumstances where more than <u>2</u> Fe^{3+} were required to oxidize and solubilize molecules containing bound Fe^{2+}. It would be altered downward in circumstances where the Fe^{2+} produced is removed by oxidation. The latter situation occurs in lixiviants which have active iron oxidizing bacteria. Therefore if a natural minewater contained a bacterial population which oxidized Fe^{2+} optimally, the values for $\frac{\Delta Fe^{2+} - \Delta Fe}{\Delta Fe}$ would be similar, in the presence or absence of added iron bacteria and the value for

$$\left(\frac{\Delta Fe^{2+} - \Delta Fe}{\Delta Fe} \text{ uninoculated} - \frac{\Delta Fe^{2+} - \Delta Fe}{\Delta Fe} \text{ inoculated} \right)$$

would approach zero.

The total iron in solution is affected by the solubility of the oxidized iron species. Consequently ΔFe would be affected by bacterial activity which resulted in the release of pyritic Fe^{2+} and the incorporation of some of this iron into insoluble jarosite after bacterial oxidation. Table 4 indicates that the addition of iron bacteria to dilute minewater lixiviants after endogenous development of active bacterial iron oxidation, yielded absolute differences between the inoculated and uninoculated systems (leaching indices) ranging from 0.08 to 0.36. In contrast, the addition of bacteria to dilute 9K lixiviants possessing minimal bacterial iron oxidizing activity produced indices ranging from 1.33 to 42.3. Squaring the differences served to accentuate the comparisons by drawing attention to the convergence of values of $\frac{\Delta Fe^{2+} - \Delta Fe}{\Delta Fe}$ in leaching systems possessing optimal bacterial activity and the divergence in systems which do not.

Adherence of Jarositic Sulfur to Leached Coal Particles

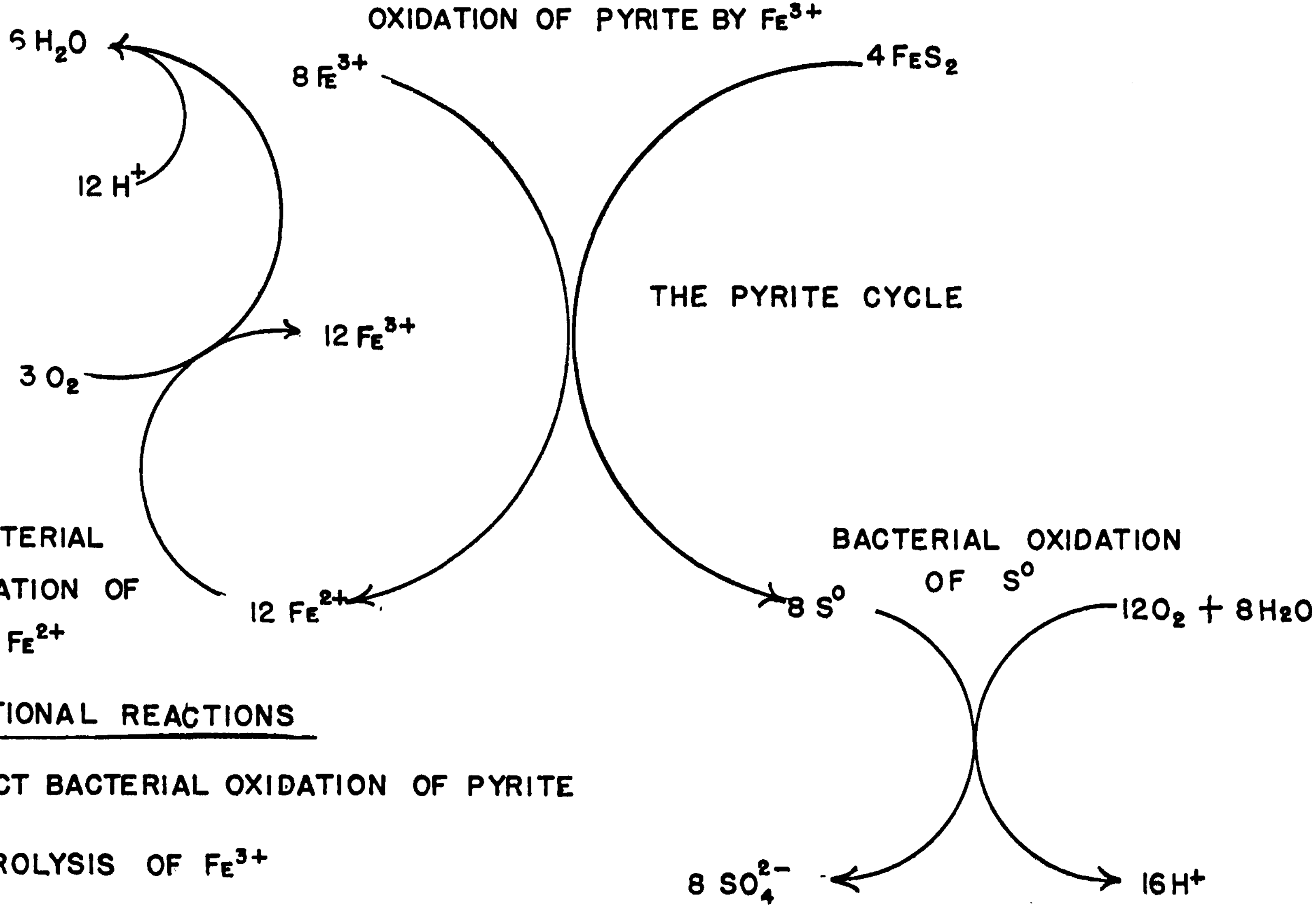
Our interim report described the development of a stirred airlift leaching apparatus which could be operated while the lixiviant was passed through the stirred suspended coal bed or over a settled powdered coal stratum (Fig. 10). Table 4 presents data for the operation of the stirred airlift leacher over a period of 15 days, in which time the total sulfur of the coal was reduced from 6.4 to 2.9%. During this period the coal particles became progressively denser, tending to aggregate and settle unless the rate of stirring was increased. When allowed to settle beneath the leaching solution, the total sulfur content of the coal increased to 6.71%. This is explained by the formation of jarositic sulfur which coats the particles of a high sulfur coal after leaching in the presence of iron oxidizing bacteria like Thiobacillus ferrooxidans. The bacterial oxidation of Fe^{2+} has a specific requirement for SO_4^{2-} and leads to the deposition of jarosite by a mechanism which is not completely understood. Unlike other species of ferric hydroxides, jarosite is insoluble at low pH in the presence of high concentrations of SO_4^{2-}. The precipitation which occurs on the coal increases the particle density and total sulfur content.

The association of jarosite with the leached coal particles was demonstrated by extracting coal with 6N HCl. The unleached "foot-vein-coal contained approximately 0.055 millimoles of HCl soluble iron per gram. After leaching with dilute minewater, particles of less than 1.5 mm diam. contained an increment of 1.9 millimoles of HCl soluble, H_2SO_4 insoluble iron per gram of coal (Table 7). If this is assumed to be jarositic iron it would contain two thirds as much sulfur as iron on a molar basis (approximately 1.28 millimoles or 41 mg of HCl soluble sulfur per gram). Using coal particles <1.5 mm in diameter, it was possible to upgrade the coal from 6.39% total sulfur initially to 2.6% after leaching and HCl washing. With coal particles, not exceeding 88 µ in diameter, a more rapid purification of "foot-vein" coal from 6.39% total sulfur to 2.1% has been obtained by similar treatment.

Treatment with dilute ammonium hydroxide is a more practical alternative than HCl washing, for removal of jarosite from leached coals. Ammonia is relatively cheap, can be easily removed from the coal and can be regenerated or used to form commercially desirable by-products from the coal leaching process. The reaction between aqueous ammonia and jarosite leads to deposition of $Fe(OH)_3$ while NH_4^+ and SO_4^{2-} are left in solution. If the ammonium sulfate containing solution, produced by jarosite removal is recirculated to the acid minewater leaching system, NH_4^+ will be incorporated into newly formed jarosite at the sites of bacterial activity. A choice exists for recovery of $(NH_4)_2SO_4$ or ammoniojarosite or NH_3 (after treatment with alkali).

Because of the importance of jarosite formation in the leaching process and the possibility of recovering ammoniojarosite as a useful by-product, chemical analyses and infra-red spectra were obtained of jarosites formed during bacterial oxidation of iron in the presence of different monovalent cations. The infra-red spectra, shown in Figs. 11-15, clearly distinguish hydronium and ammonium jarosite from each other and from sodium or potassium jarosite. Spectra of the last two substances are very similar, but their formation can be ascertained from flame photometric analyses of samples dissolved in dilute hydrochloric acid. Our studies have confirmed that jarosites are the characteristic products formed in large amounts during bacterial leaching of pyrite in coal. These substances are entirely different in chemical and spectrophotometric properties from the oxidized iron precipitates that are formed abiotically under comparable conditions.

LEACHING OF PYRITE BY BACTERIALLY OXIDIZED IRON



ADDITIONAL REACTIONS

- DIRECT BACTERIAL OXIDATION OF PYRITE
- HYDROLYSIS OF Fe^{3+}
- PRECIPITATION OF BACTERIALLY OXIDIZED IRON AS JAROSITE

Figure 1

Figure 2

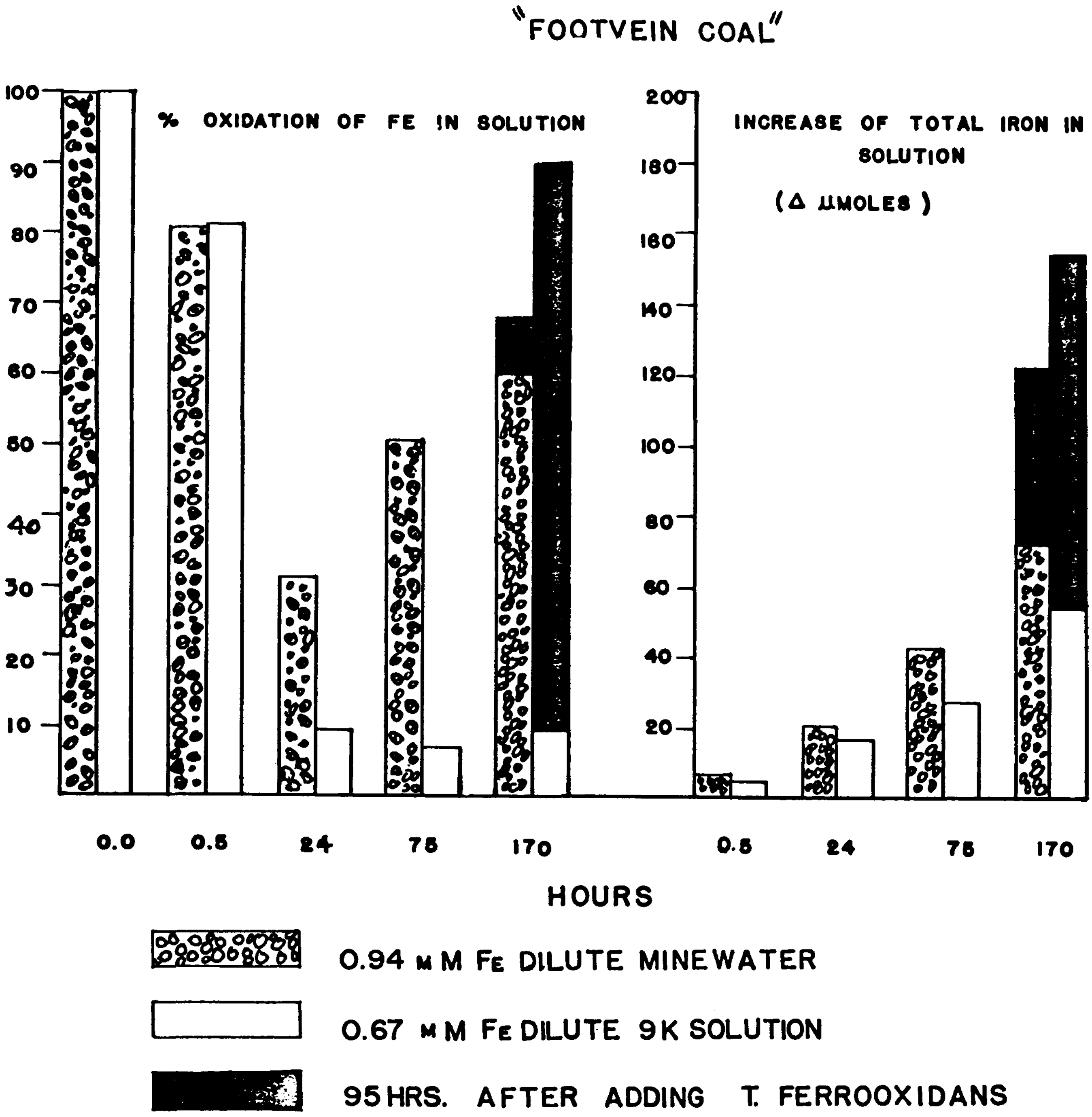

"FOOTVEIN COAL"
% OXIDATION OF FE IN SOLUTION
100
90
80
70
60
50
40
30
20
10
0.0
0.5
24
75
170
INCREASE OF TOTAL IRON IN SOLUTION
(Δ μMOLES)
200
180
160
140
120
100
80
60
40
20
0.5
24
75
170
HOURS
0.94 mM Fe DILUTE MINEWATER
0.67 mM Fe DILUTE 9K SOLUTION
95 HRS. AFTER ADDING T. FERROOXIDANS

Figure 3

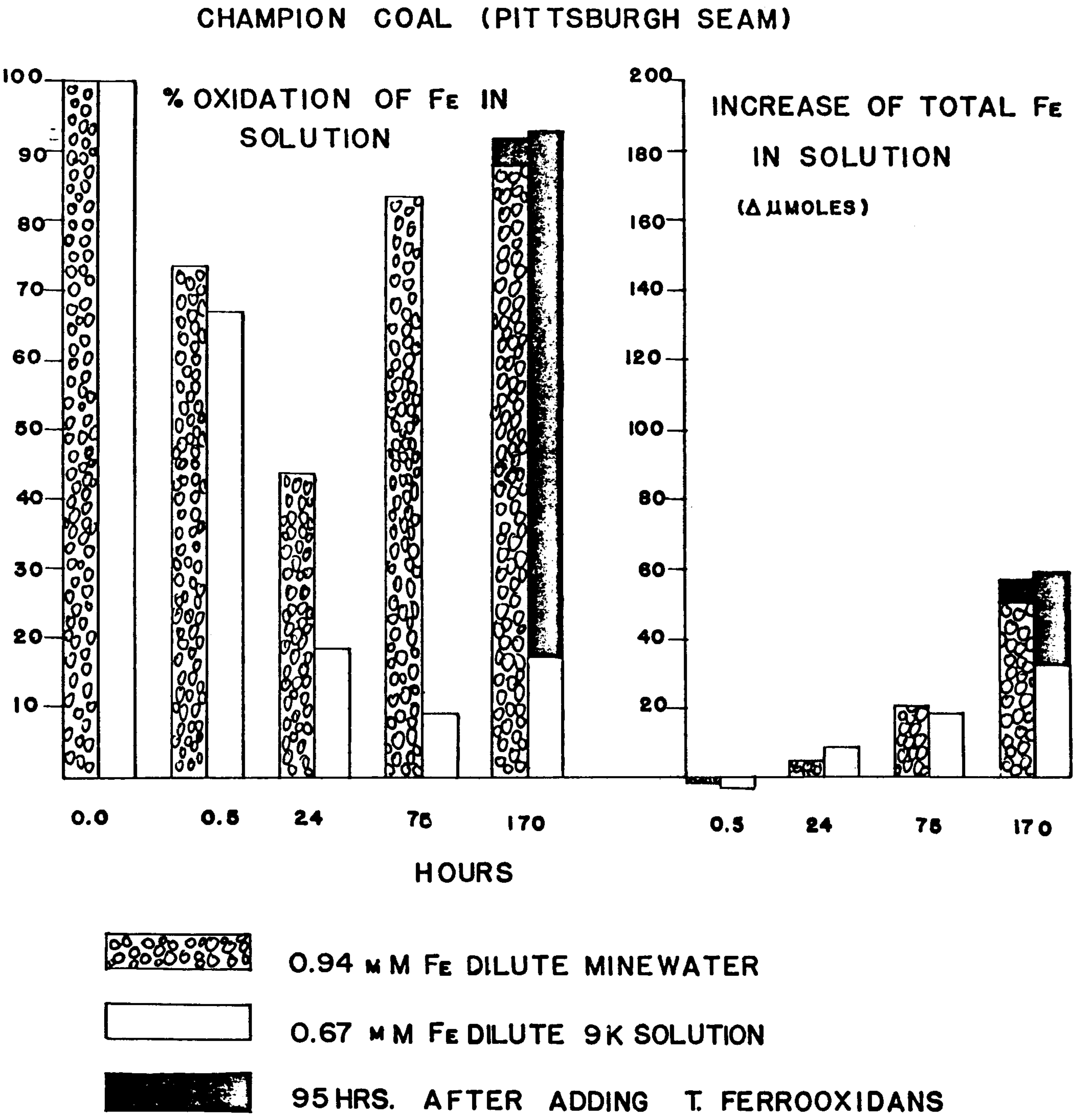

CHAMPION COAL (PITTSBURGH SEAM)
% OXIDATION OF FE IN SOLUTION
100
90
80
70
60
50
40
30
20
10
0.0
0.5
24
75
170
INCREASE OF TOTAL FE IN SOLUTION
(Δ µMOLES)
200
180
160
140
120
100
80
60
40
20
0.5
24
75
170
HOURS
0.94 mM FE DILUTE MINEWATER
0.67 mM FE DILUTE 9K SOLUTION
95 HRS. AFTER ADDING T. FERROOXIDANS

Figure 4

MAIDSVILLE COAL (SEWICKLY SEAM)

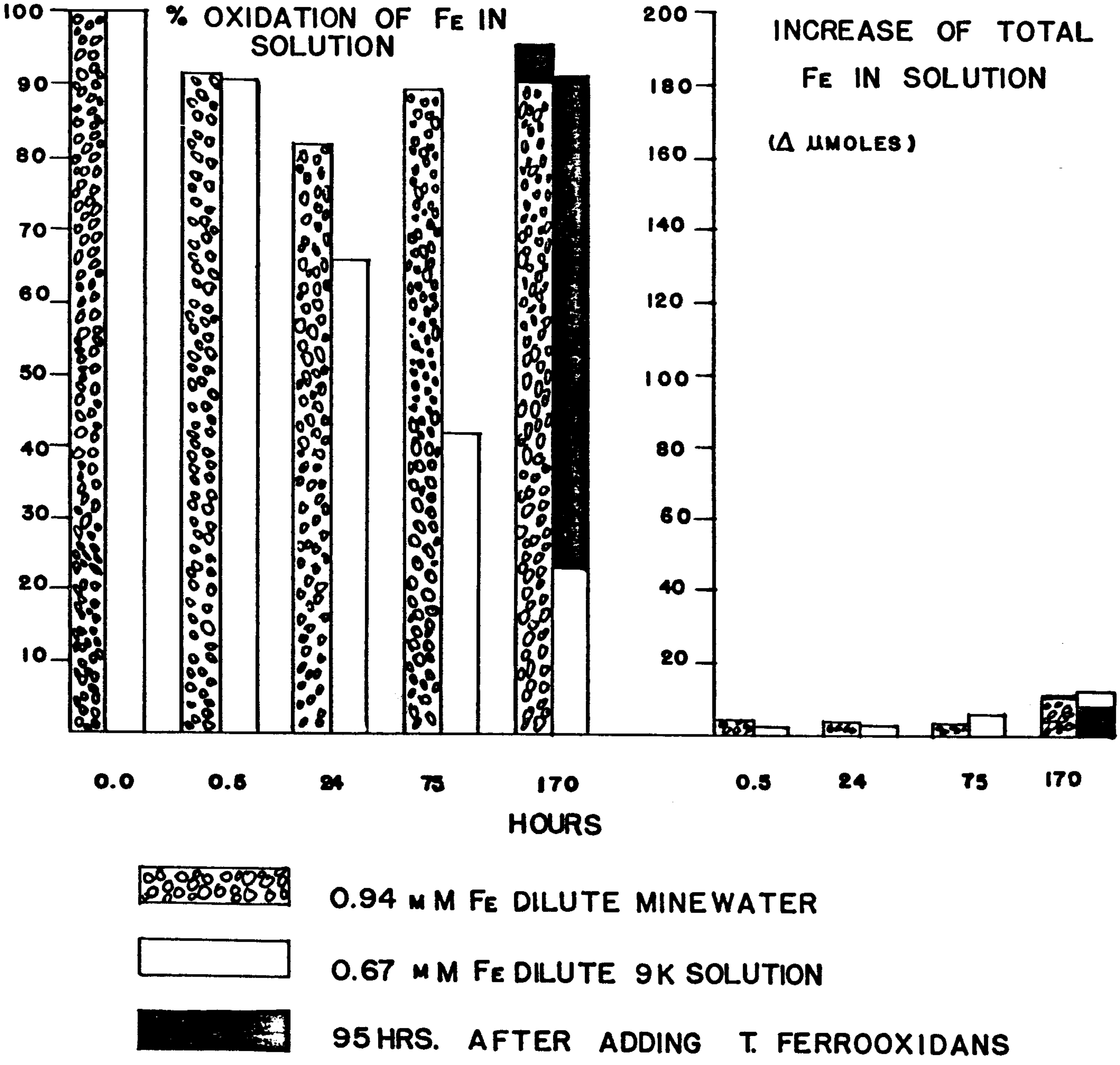


Figure 5

GREFF COAL (FIRECLAY)

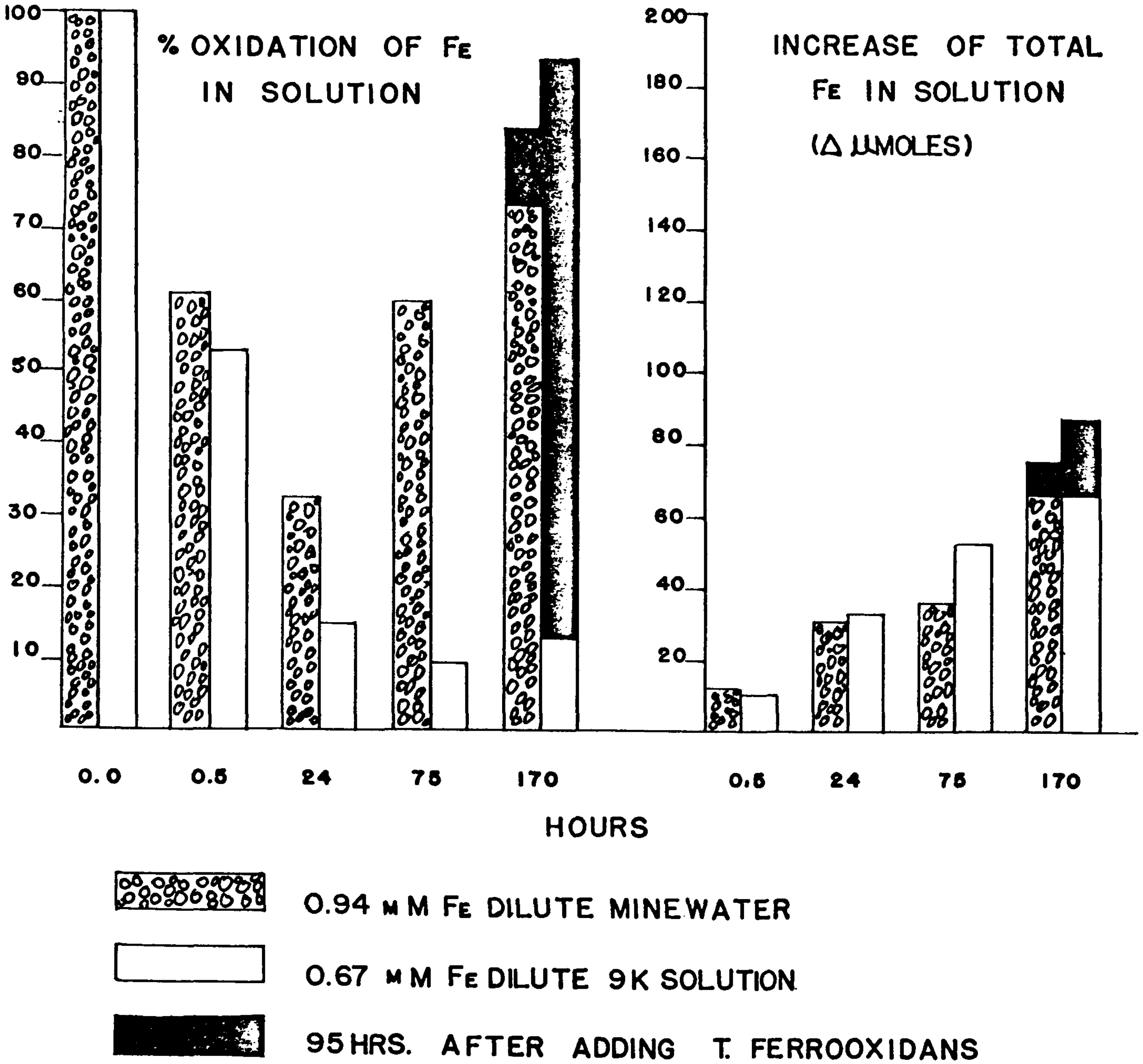


Figure 6

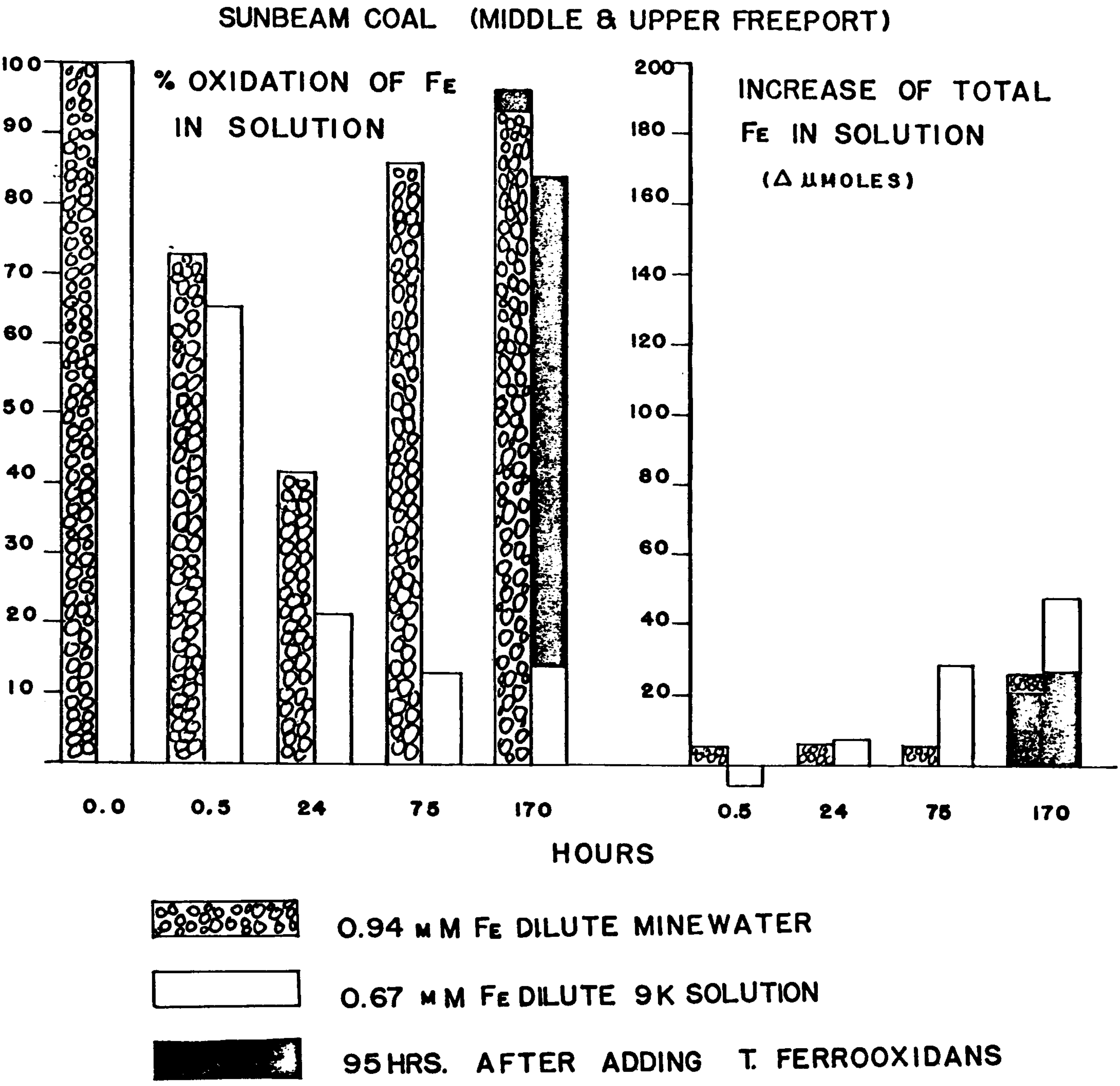
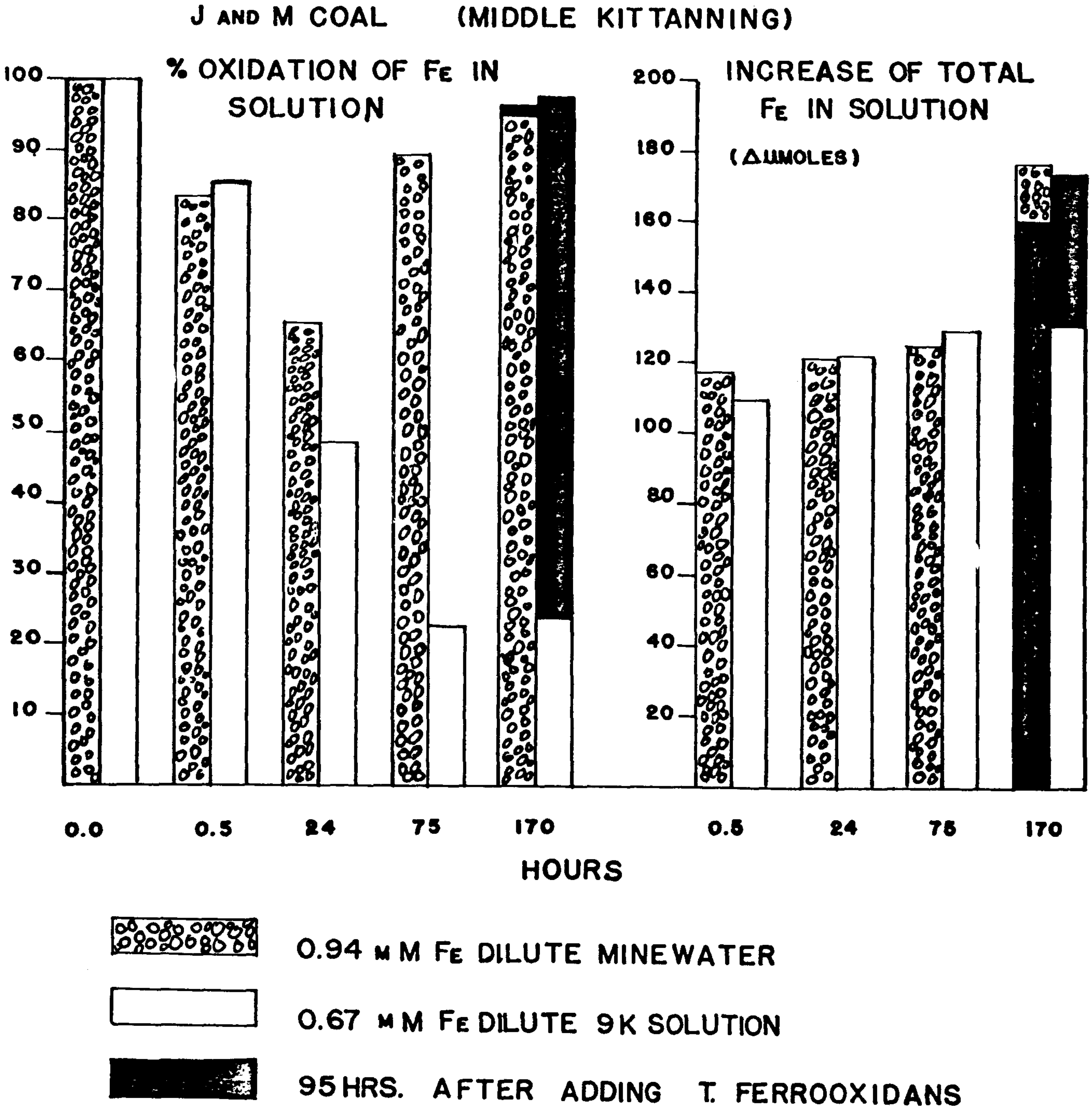

SUNBEAM COAL (MIDDLE & UPPER FREEPORT)
% OXIDATION OF FE IN SOLUTION
100
90
80
70
60
50
40
30
20
10
0.0
0.5
24
75
170
INCREASE OF TOTAL FE IN SOLUTION
(Δ μMOLES)
200
180
160
140
120
100
80
60
40
20
0.5
24
75
170
HOURS
0.94 mM FE DILUTE MINEWATER
0.67 mM FE DILUTE 9K SOLUTION
95 HRS. AFTER ADDING T. FERROOXIDANS

Figure 7


J AND M COAL (MIDDLE KITTANNING)
% OXIDATION OF Fe IN SOLUTION
INCREASE OF TOTAL Fe IN SOLUTION
(ΔμMOLES)
100
90
80
70
60
50
40
30
20
10
200
180
160
140
120
100
80
60
40
20
0.0
0.5
24
75
170
0.5
24
75
170
HOURS
0.94 mM Fe DILUTE MINEWATER
0.67 mM Fe DILUTE 9K SOLUTION
95 HRS. AFTER ADDING T. FERROOXIDANS

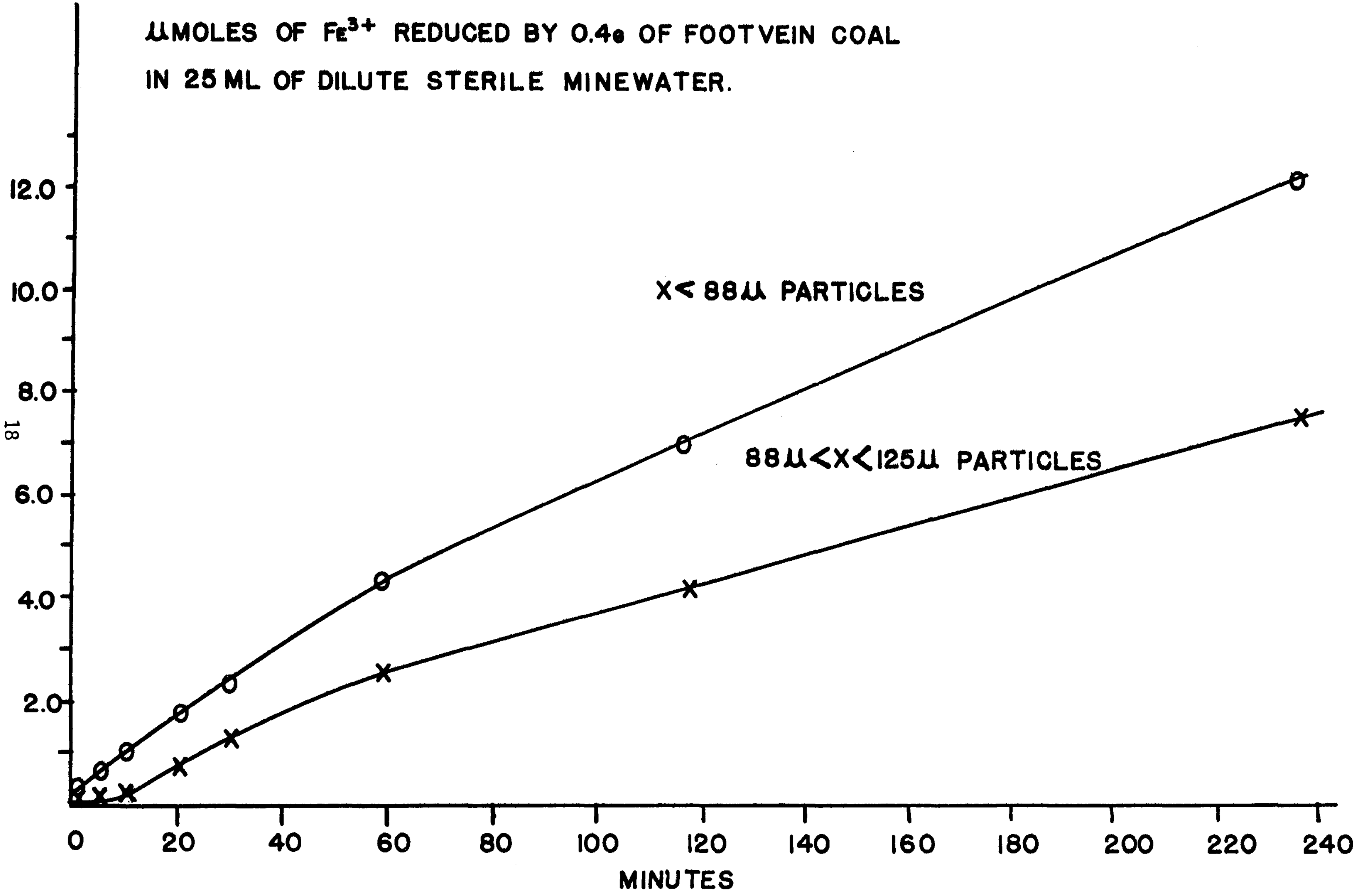

µMOLES OF FE³⁺ REDUCED BY 0.4g OF FOOTVEIN COAL
IN 25 ML OF DILUTE STERILE MINEWATER.
12.0
10.0
8.0
6.0
4.0
2.0
X< 88µ PARTICLES
88µ<X<125µ PARTICLES
0
20
40
60
80
100
120
140
160
180
200
220
240
MINUTES

Figure 8

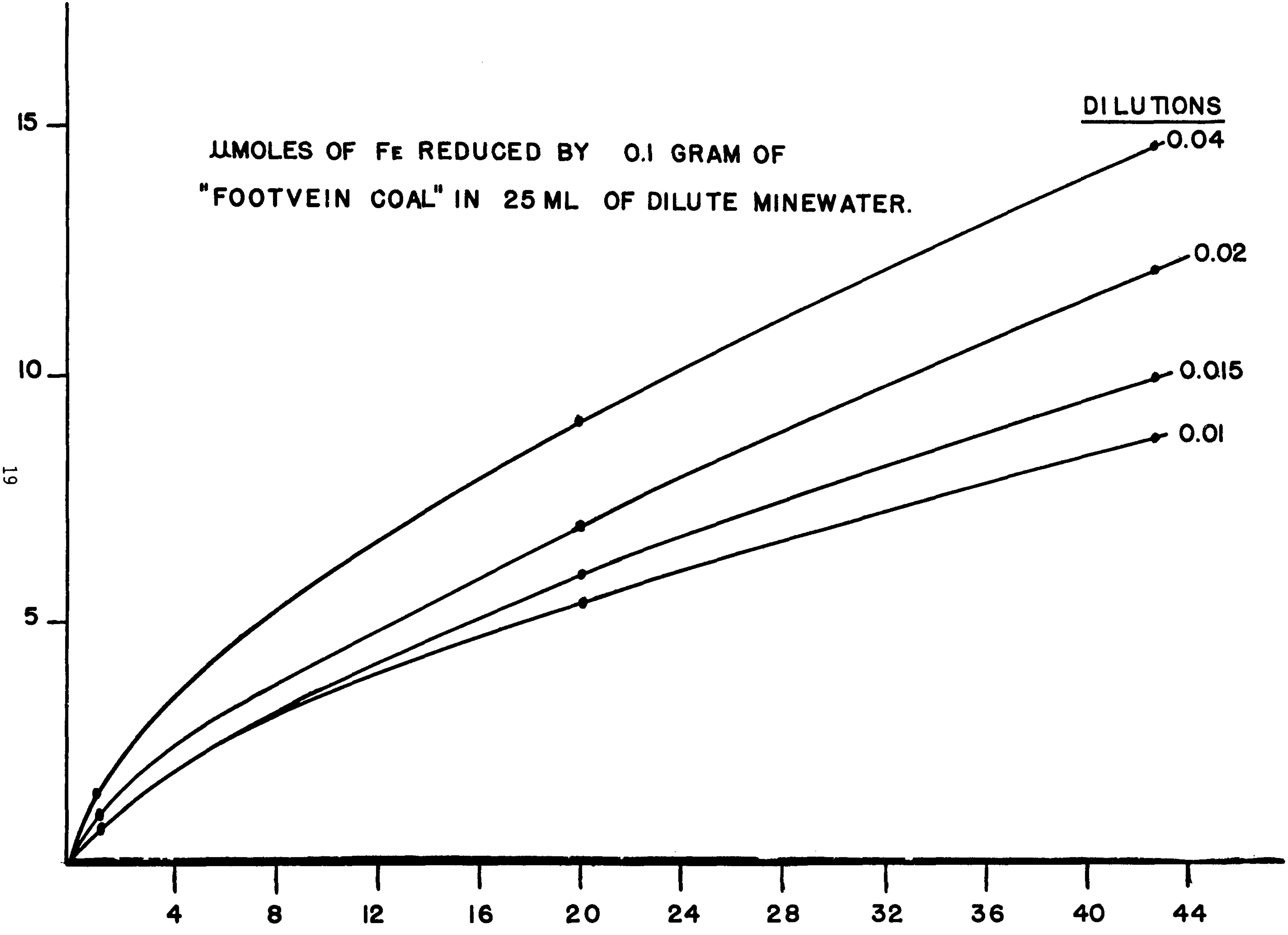
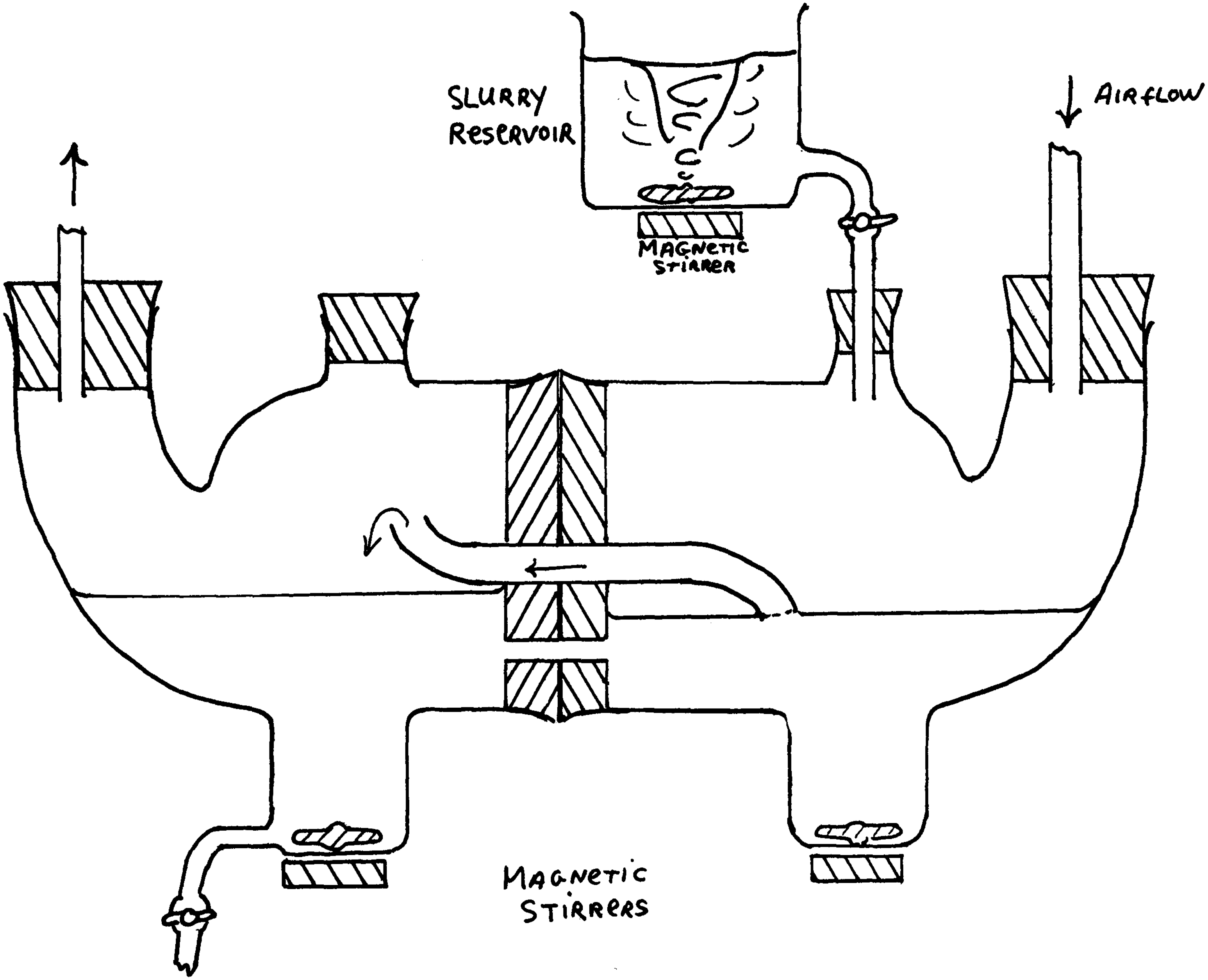

µMOLES OF FE REDUCED BY 0.1 GRAM OF
"FOOTVEIN COAL" IN 25 ML OF DILUTE MINEWATER.
DILUTIONS
0.04
0.02
0.015
0.01
15
10
5
4
8
12
16
20
24
28
32
36
40
44
HOURS

Figure 9



DOUBLE STIRRED AIR-LIFT LEACHER

Figure 10

LEGENDS AND INFRA-RED BAND ASSIGNMENTS FOR FIGURES 11-15

Fig. 11

A - Jarosite, formed by bacterial oxidation at pH 2.5 in the absence of added monovalent cations. (mainly hydronium jarosite)

B - Jarosite, formed by bacterial oxidation at pH 2.5 in the presence of $(NH_4)_2SO_4$. (mainly ammonium jarosite)

C - Jarosite, formed by bacterial oxidation at pH 2.5 in the presence of K_2SO_4. (spectrum of potassium jarosite)

D - Jarosite, formed by bacterial oxidation at pH 2.5 in the presence of Na_2SO_4. (spectrum of sodium jarosite)

Figs. 12-15

A - Jarosite, formed by bacterial oxidation.

B - Ferric precipitate, formed by slow spontaneous oxidation at pH 6.0.

C - Ferric precipitate, formed by oxidation with H_2O_2 at pH 2.5.

D - Ferric precipitate, formed by rapid spontaneous oxidation at pH 9.0.

INFRA-RED ASSIGNMENTS (ALL FIGURES) - Ref. M.M. Shokaarev et al 1972, Russian Journal of Inorganic Chemistry 17, 1293-1296

1. - OH^- Stretch
2. - H_3O^+
3. - NH_4^+
4. - SO_4^{2-} Stretch
5. - SO_4^{2-}
6. - SO_4^{2-}
7. - SO_4^{2-}
8. - OH^- Librational
9. - OH^- Librational
10. - SO_4^{2-}
11. - OH^- Translational
12. - ?, Characteristic of hydronium jarosite

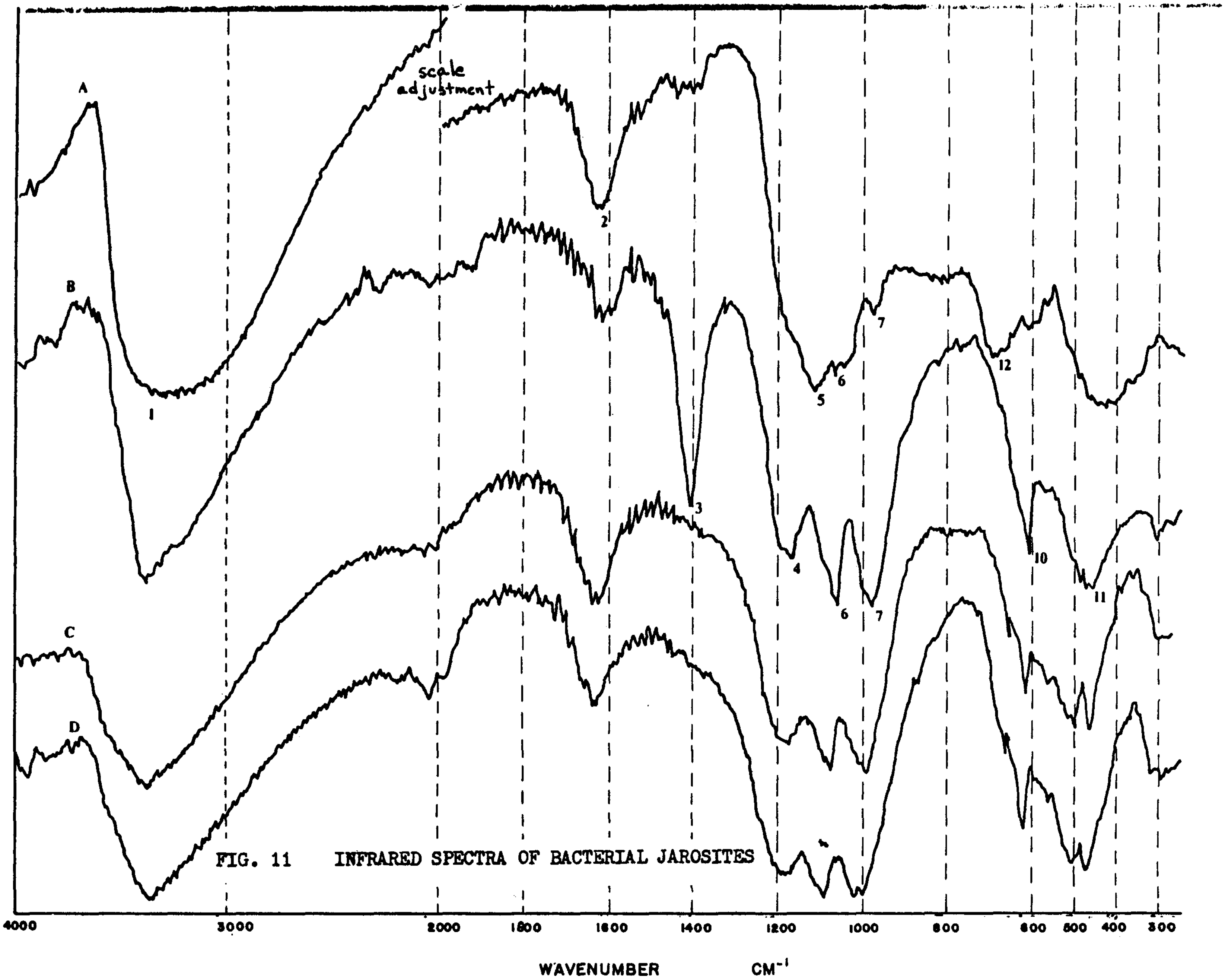


FIG. 11 INFRARED SPECTRA OF BACTERIAL JAROSITES

Figure 11

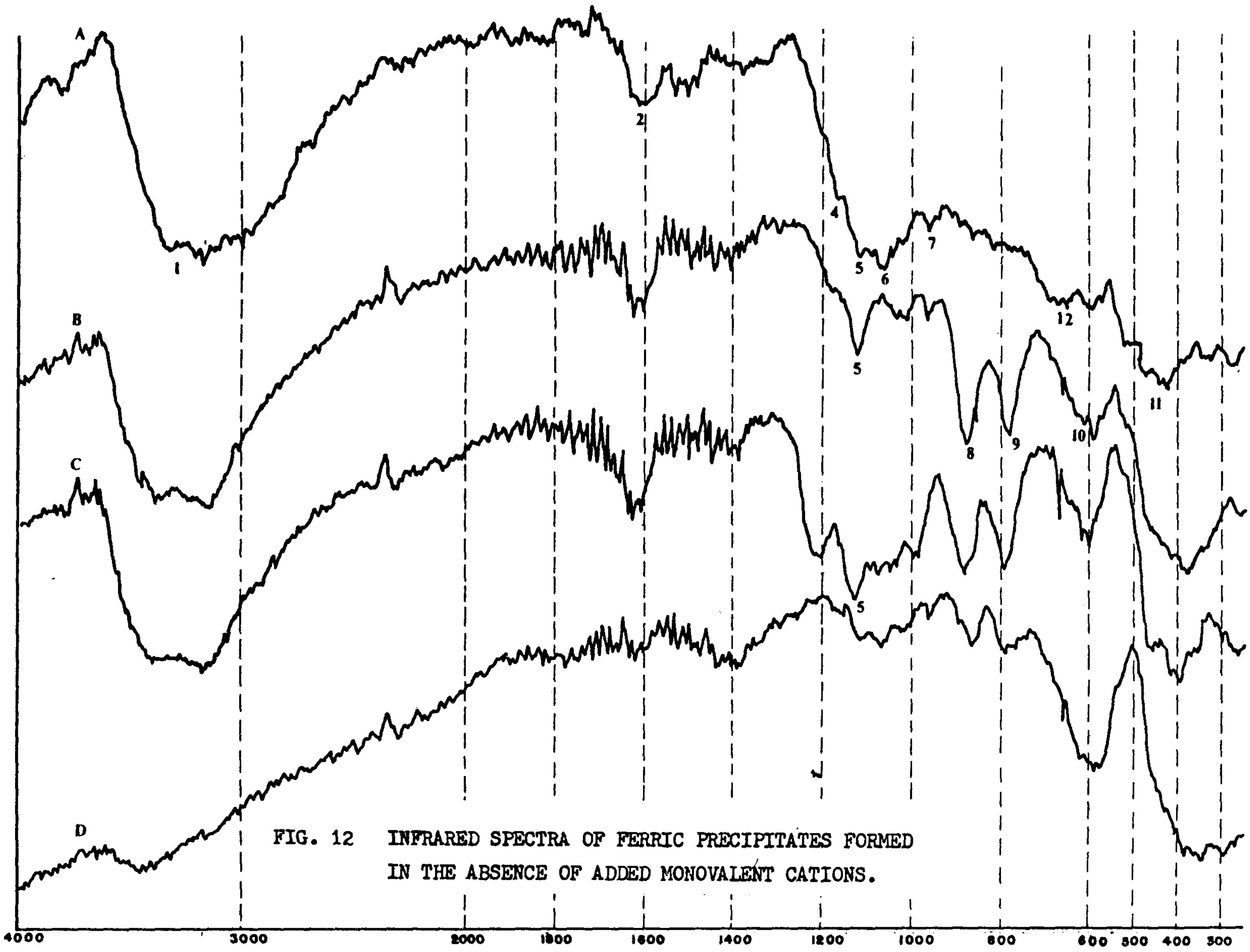


FIG. 12 INFRARED SPECTRA OF FERRIC PRECIPITATES FORMED IN THE ABSENCE OF ADDED MONOVALENT CATIONS.

Figure 12

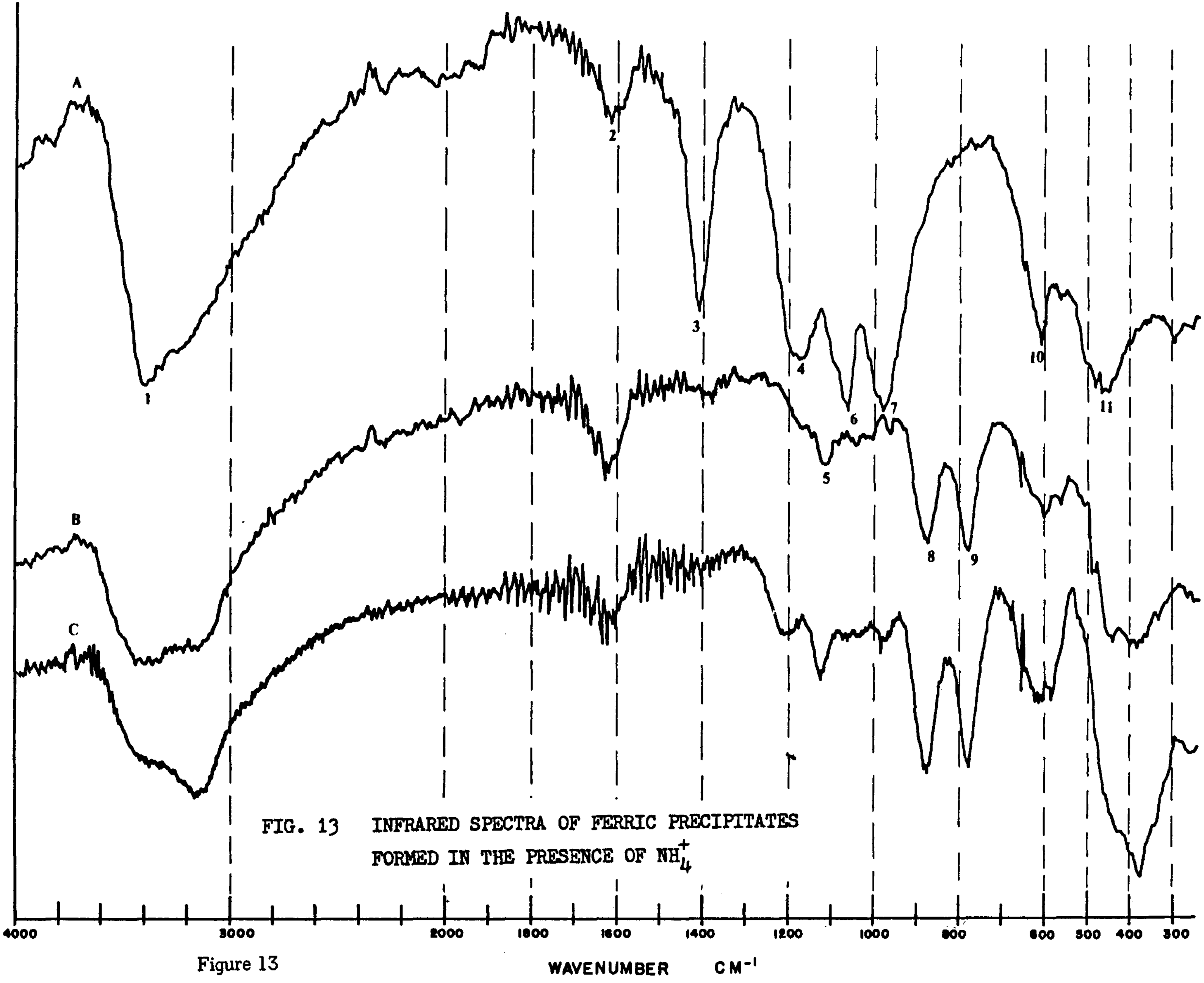


FIG. 13 INFRARED SPECTRA OF FERRIC PRECIPITATES FORMED IN THE PRESENCE OF NH_4^+

Figure 13

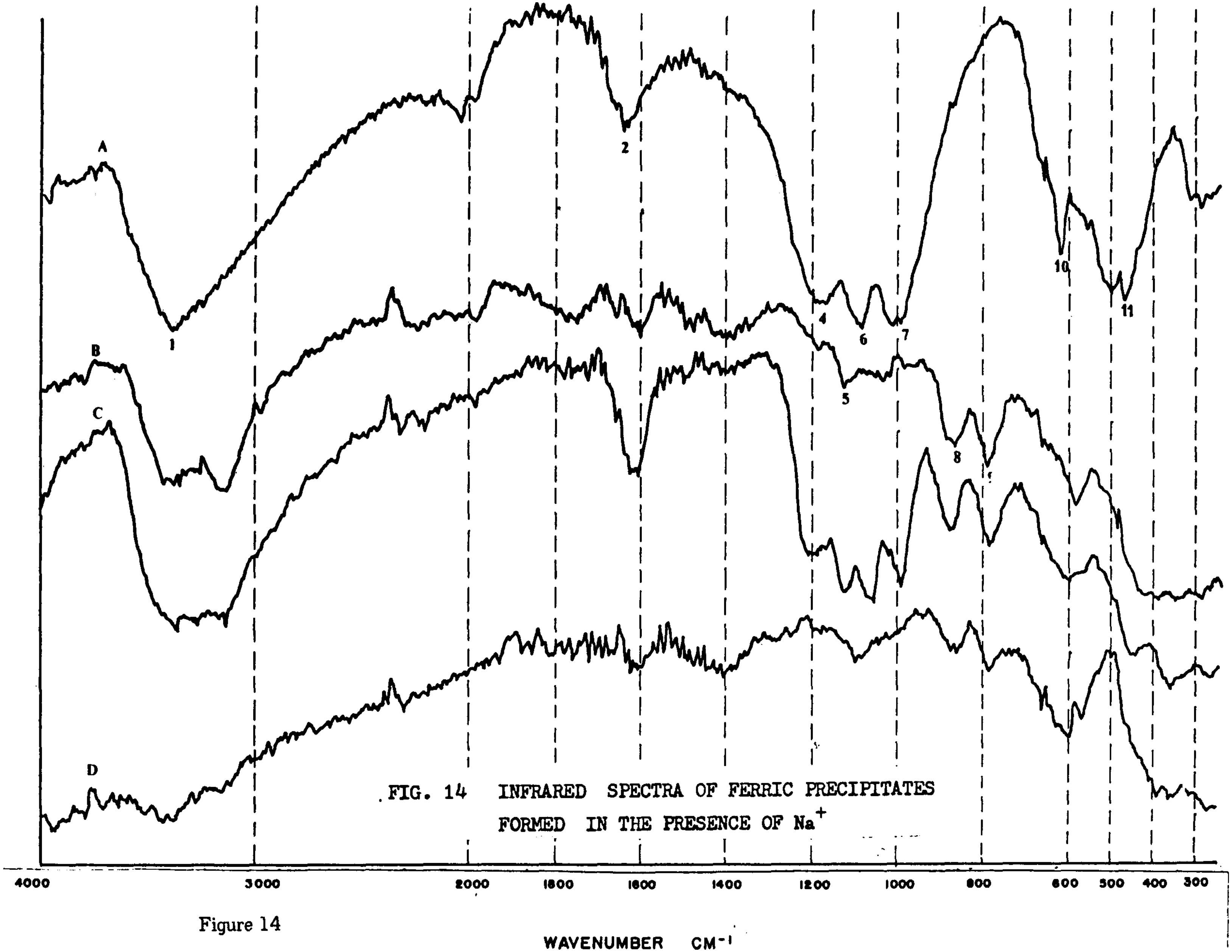


FIG. 14 INFRARED SPECTRA OF FERRIC PRECIPITATES FORMED IN THE PRESENCE OF Na^+

Figure 14

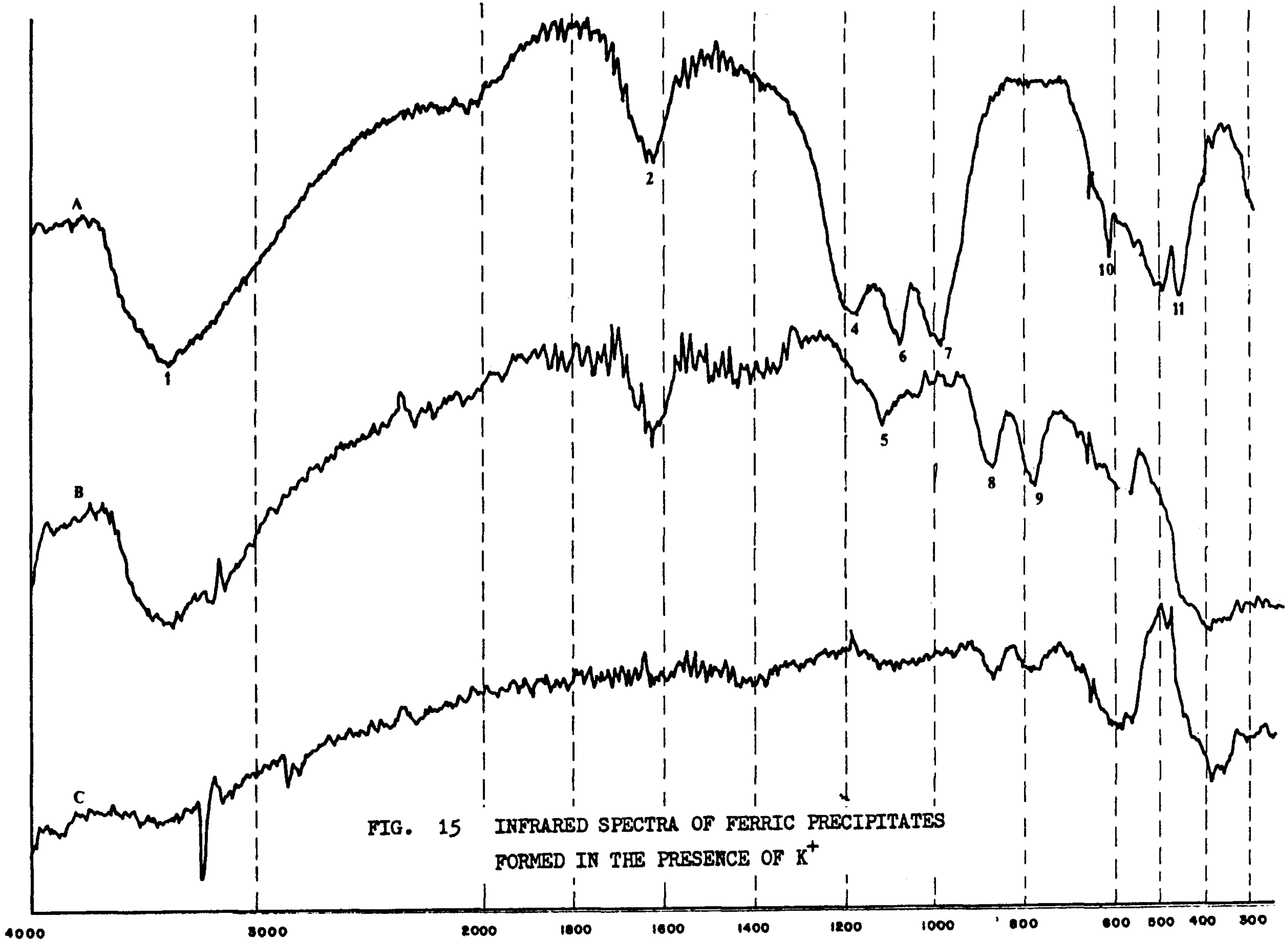


FIG. 15 INFRARED SPECTRA OF FERRIC PRECIPITATES FORMED IN THE PRESENCE OF K^+

Figure 15

Table 1

Relationship of Fe^{2+} Oxidized To Iron And Sulfur Solubilized In Leaching Powdered Coal Samples With Oxidized Dilute 9K Solution (0.67 mM Fe^{3+}).

		$\frac{\Delta Fe^{2+}-\Delta Fe}{\Delta Fe}$			$\frac{\Delta Fe^{2+}\ \text{(Calc. 170 hrs)}}{\Delta S\ \text{Total}}$	$\frac{\Delta Fe^{2+}-\Delta Fe}{\Delta S\ \text{Total}}$
COAL (<125µ)		24 hrs	75 hrs	170 hrs		
"Footvein"		4.18	2.27	0.94	0.27	0.06
Champion		2.4	1.92	0.84	2.77	0.79
Maidsville		32.21	11.72	4.54	1.63	0.24
Greff		1.11	0.69	0.41	0.98	0.37
Sunbeam		1.82	1.17	0.61	10.93	1.66
J & M		4.13	5.52	4.98	0.29	0.35
	$\lvert\overline{x}\rvert$	7.64	3.88	2.05	2.81	0.58
	$s_{\overline{x}}$	± 12.09	± 4.20	±2.11	±4.09	±0.58
Excluding Maidsville	$\lvert\overline{x}\rvert$	2.73	2.31	1.56		
"	$s_{\overline{x}}$	±2.23	±1.90	± 1.92		

Table 2

LEACHING OF SHAKEN SAMPLES OF POWDERED COALS (88 μ SIX - 7 DAYS)

Coal	% S (By Wt.)	μmoles S Removed	% of Total S Removed	% of Pyritic S Removed	μmoles S Removed / μmoles Fe Solubilized
Footvein	8.50 (Total)				
	7.34 (Pyritic)				
M.W.		914	22.96	26.57	12.63
M.W. + T.f.		1,355	34.04	39.39	10.95
9K		755	18.97	21.95	13.84
9K + T.f.		1,121	28.17	32.59	7.24
Champion	1.90 (Total)				
	1.02 (Pyritic)				
M.W.		131	14.72	27.41	2.62
M.W. + T.f.		145	16.29	30.33	2.83
9K		32	3.60	6.69	0.95
9K + T.f.		84	9.44	17.57	1.41
Maidsville	2.41 (Total)				
	0.91 (Pyritic)				
M.W.		184	16.14	42.79	15.15
M.W. + T.f.		221	19.39	51.40	17.93
9K		184	16.14	42.79	14.41
9K + T.f.		231	20.26	53.72	24.31
Greff	1.86 (Total)				
	1.23 (Pyritic)				
M.W.		134	15.40	23.30	2.01
M.W. + T.f.		167	19.20	29.04	2.22
9K		64	7.36	11.13	0.96
9K + T.f.		186	21.38	32.34	2.13
Sunbeam	1.10 (Total)				
	0.60 (Pyritic)				
M.W.		28	5.38	9.86	1.05
M.W. + T.f.		38	7.31	13.38	1.82
9K		9	1.73	3.17	0.19
9K + T.f.		9	1.73	3.17	0.33
J and M	1.99 (Total)				
	1.29 (Pyritic)				
M.W.		349	37.53	57.88	1.97
M.W. + T.f.		372	40.00	61.69	2.33
9K		297	31.94	49.25	2.27
9K + T.f.		339	36.45	56.22	1.94

Table 3

VARIANCE OF $\frac{S_{\text{removed}}}{Fe_{\text{solubilized}}}$, $\left(\frac{S_R}{\Delta Fe}\right)$ FOR SIX COALS AFTER FOUR LEACHING TREATMENTS

A. Comparison of Mean Variances for $\frac{S_R}{\Delta Fe}$; Different Treatments vs Different Coals.

Treatments	$\bar{x}$	$s^2_{\bar{x}}$
M.W.	5.91	39.19
M.W. + T.f.	6.35	44.22
9K	5.44	45.83
9K + T.f.	6.23	84.27
	av. =	53.38

Coals	$\bar{x}$	$s^2_{\bar{x}}$
"Foot-vein"	11.17	8.24
Champion	1.95	0.85
Maidsville	17.95	20.25
Greff	1.83	0.35
Sunbeam	0.85	0.56
J & M	2.13	0.04
	av.=	5.05

B. Analysis of Variance (Log Transformation)

The mean variances shown above suggest the possibility that greater variance is associated with higher means due to multiplicative effects. Accordingly, values were converted to logarithms, for analysis of variance, in order to minimize such effects of the mean on variance.

	S.S.	D^{o}f	M.S.
Total	7.06	23	0.307
Treatments	0.33	5	0.066
Coals	6.13	3	2.04

$$F\ \frac{(\text{Coals})}{(\text{Treatments})} = \frac{2.04_{(5)}}{0.066_{(3)}} = 30.91$$

The variance of average $\frac{S_R}{\Delta Fe}$ is significantly greater for coals than for treatments.

C. $(SS_{total} - SS_{treatments} - SS_{coals}) = SS_{interaction}$

$7.06 - 0.33 - 6.13 = 0.60$

$M.S. = \frac{S.S.}{n^{o}f} = 0.04$

Significance of variance between coals

$$F \frac{(Coals)}{(Interaction)} = \frac{2.04_{(3)}}{0.04_{(15)}} = 51$$

The averages of $\frac{S_R}{\Delta Fe}$ for coals are significantly different.

Significance of variance between treatments

$$F \frac{(Treatments)}{(Interaction)} = \frac{0.066_{(5)}}{0.04_{(15)}} = 1.65$$

The averages of $\frac{S_R}{\Delta Fe}$ for treatments are <u>NOT</u> significantly different.

Table 4

Leaching Index

Iron reduced per mole of iron solubilized, compared for coal suspensions, with or without the addition of iron oxidizing bacteria. In leaching systems during a 95 hour period.

Lixiviant	Coal	further treatment	$\frac{\Delta Fe^{2+} - \Delta Fe}{\Delta Fe}$	(A-B)	$(A-B)^2$
Dilute Minewater	"Footvein"	(A) ----	- 1.06	-0.08	0.0064
Dilute Minewater		(B) +Bact.	- 0.98		
Dilute Minewater	Champion	----	- 1.04	+0.19	0.0361
Dilute Minewater		+Bact.	- 1.23		
Dilute Minewater	Maidsville	----	- 1.27	+0.36	0.1296
Dilute Minewater		+Bact	- 1.63		
Dilute Minewater	Greff	----	- 1.44	+0.21	0.0441
Dilute Minewater		+Bact.	- 1.65		
Dilute Minewater	Sunbeam	----	- 1.27	+0.33	0.1089
Dilute Minewater		+Bact.	- 1.60		
Dilute Minewater	J & M	----	-1.23	+0.16	0.0256
Dilute Minewater		+Bact.	-1.39		
Dilute 9K	"Footvein"	----	-0.18	+1.33	1.769
Dilute 9K		+Bact.	-1.51		
Dilute 9K	Champion	----	-0.65	+2.09	4.368
Dilute 9K		+Bact.	-2.74		
Dilute 9K	Maidsville	----	+1.64	+12.20	148.84
Dilute 9K		+Bact.	-10.56		
Dilute 9K	Greff	----	-0.42	+3.4	11.56
Dilute 9K		+Bact.	-3.82		
Dilute 9K	Sunbeam	----	-0.20	-42.3	1789.29
Dilute 9K		+Bact.	+42.10		
Dilute 9k	J & M	-----	-1.66	+2.52	6.35
Dilute 9K		+Bact.	-4.18		

Table 5

Standard Deviations of Leaching Indices

	Treatment and Leaching Intervals				
Coal Samples	0-24 hrs. (MW-9K)	24-75 hrs. (MW-9K)	75-170 hrs. (MW-9K)	75-170 hrs. M.W. (A-B)*	75-170 hrs. 9K (A-B)*
"Footvein"	-0.52	-1.71	-0.876	-0.08	+1.33
Champion	+1.63	-4.01	-0.39	+0.19	+2.09
Maidsville	+929.79	+13.16	-2.91	+0.36	+12.20
Greff	+0.18	-7.26	-1.02	+0.21	+3.40
Sunbeam	+35.98	+125.56	-1.07	+0.33	-42.30
J & M	+5.01	-18.85	+0.43	+0.16	+2.52
$\lvert\bar{x}\rvert$	162.19	28.43	1.12	0.22	10.64
$s_{\bar{x}}$	±376.3	±48.00	±0.94	±0.11	±16.02

* Difference between $\frac{\Delta Fe^{2+} - \Delta Fe}{\Delta Fe}$ of A (uninoculated) and B (inoculated) leaching systems 75 hrs after leaching was initiated.

TABLE 6

LEACHING OF FOOT VEIN COAL IN DOUBLE STIRRED, AIR LIFT LEACHER

Time (Days)	% S	(Fe^{3+})	Sample
0	6.39	3.9×10^{-2} M	Susp.
2	5.38		"
6	4.47		"
12	3.95		"
15	2.97	3.4×10^{-2} M	"
19	6.71	4.1×10^{-2} M	Settled

540 ml Minewater, J & B Strip Mine, Fallbrook, Pa.
20 g Foot Vein Coal > 120 µ, 0.5 ml Dilute Triton X-100

TABLE 7

HCL SOLUBLE IRON IN LEACHED AND UNLEACHED FOOT VEIN COAL. LEACHING FOR 8 DAYS, 1/100 DIL. J & B MINEWATER

Sample Treatment			m Moles HCl Soluble Fe/g Coal
x < 88 µ		Leached	.74
"	Inoc. T. ferrooxidans		1.12
x < 1,500 µ			.38
"	Inoc. T. ferrooxidans		2.30
x < 88 µ	Untreated		0.06
x < 1,500 µ			0.05

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