

## BACTERIOELECTRIC DEASHING OF COALS

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The premise that a combination of electric current and bacterial action would remove metals from coal more effectively than either of the factors acting alone, stemmed from earlier observations of enhanced pyritic ore leaching and iron corrosion by suspensions of *Thiobacillus ferrooxidans* in galvanic cells. Although sulfide minerals are oxidized more slowly than native metals under acid abiotic conditions, like metals their oxidation can be greatly accelerated by an imposed voltage in a galvanic cell. The consequent release of metal ions from pyritic substrates as the result of electrooxidations is analogous to the solubilization of minerals by the action of chemolithotrophic microorganisms which catalyze the transport of electrons from oxidizable cations or sulfide ligands to oxygen.

When metals are placed at the anode of a galvanic cell, the liberation of ionic species by electro-oxidation is dependent upon provision of a polarizing voltage and the presence of electron acceptors that promote current flow by cathode depolarization. While a metal in elementary form can be electrolytically oxidized to form a soluble cation, the insoluble metal in a sulfide mineral is already in cationic form complexed with a sulfur anion. If a sulfide mineral species conducts electricity, its cations can be released by electro-oxidation of the reduced sulfur ligands to produce elementary sulfur. The knowledge that pyritic minerals are good electrical conductors (Decker, R. F., 1986) as well as substrates for oxidation by thiobacilli, implied that the two phenomena could operate synergistically. It was visualized that the Fe(II) released electrolytically would be oxidized by chemolithotrophic iron oxidizing bacteria and that the soluble Fe(III) produced in an acid environment would oxidize pyritic sites insulated from electro-oxidation.

Conceptually, a suitable electrical potential, would liberate Fe(II) cations by oxidizing reduced sulfur anions of pyritic minerals. Electric current would flow from the source as the cathode is depolarized by hydrogen ions of the acid lixiviant and Fe(II) cations move into solution toward the cathode. In dilute sulfuric acid solution, as the Fe(II) is oxidized by iron oxidizing thiobacilli, the resultant Fe(III) sulfato complex would have the possibility of participating in several different reactions depending upon the conditions existing in the galvanic cell (Figure 1). These include: (1) aggregation (polymerization) to an insoluble amorphous hydrated Fe(III) sulfate; (2) reduction at the cathode forming additional substrate for bacterial iron oxidation in the bulk phase of solution; (3) reduction, after recirculation to non-anodic sites on pyritic surfaces, liberating oxidized sulfur species and Fe(II) from the pyrite; (4) alkaline precipitation; when proton consumption by cathode reactions occurs to the extent that the environment of the cathode becomes basic, the Fe(III) sulfato complex decomposes and iron is precipitated in the form of Fe(III) oxides and oxyhydroxides. The proton concentration in this system is also dependent upon the activities of thiobacilli which oxidize

sulfides, polythionates and elementary sulfur derived from the oxidation of pyritic minerals. Acidity produced from those activities counteracts proton consumption from cathode depolarization reactions and the reduction of  $O_2$  by chemolithotrophic oxidation of Fe(II). At low pH the iron sediments formed are those typical of chemolithotrophic iron oxidation, amorphous hydrated Fe(III) sulfate and jarosites. Consequently, cleaning coal by ordinary bacterial leaching may leave iron sediments remaining on the coal that contain sulfur in iron sulfato complexes. However, in a galvanic cell the iron and sulfur of the sulfato-complexes appear to be transported together to the cathode and remain undissociated under acid conditions. Therefore, this means of sulfatic sulfur removal represents further benefit to be gained from cleaning coal by a combined bacterial and electrolytic leaching process.

The following account describes an exploratory investigation of the feasibility of using the bacterioelectric phenomenon for metal removal and recovery from different coals.

#### Materials and Methods

Bulk leaching was carried out in magnetically stirred glass beakers equipped with glass cathode and anode chambers fitted with platinum electrodes as shown in Figure 2. Initially, approximately 0.4 g of a powdered coal sample was placed at the anode either wrapped in ashless filter paper, such as Whatman 41, or placed within a cellulose extraction thimble. The powdered coal was compressed around the platinum foil of the electrode by inserting the wrapped combination into the tightly fitting perforated glass tube that served as anode chamber. The leaching system was filled with a lixiviant of pH 2.5 sulfuric acid or some experimental modification thereof. The bacteria that were used, consisted of suspensions of the Leathen strain of *Thiobacillus ferrooxidans* prepared as previously described (Lazaroff, et al. 1982). The electric current and voltage were monitored by provision of individual integrated circuits for each bacterioelectric unit. These employed National Semiconductor LM117 voltage regulators as shown in Figure 2. In subsequent experiments powdered coal was rapidly circulated around an anode with a magnetic stirrer and the cathode was inserted in a medium porosity "alundum" extraction thimble. Usually the cathode chamber sediments were collected in centrifuge tubes, then washed by sedimentation and decantation; first in pH 2.5  $H_2SO_4$ , then distilled water. Prior to analysis washed sediment or coal samples were dried overnight at 85°C in a forced draft oven. The pre-weighed coal samples were ashed in tared porcelain crucibles in an electric furnace kept at 850°C overnight.

Energy Dispersive X-Ray analysis were used to identify and measure relative amounts of the different metals in sediments collected from the cathode chamber, as coatings on the platinum cathodes and from drying the bulk lixiviant to recover solubilized metals. Conventional methods were used to examine the IR spectra of sediments prepared in KBr discs (Lazaroff et al. 1982).

A laboratory scale continuous bacterioelectric reactor was constructed that utilized a porous alundum cathode chamber contained in a horizontal air-lift device that impinges a rapidly stirred coal slurry on a platinum anode. The system shown in Figures 3 and 4 allows periodic recovery of processed coal and electrically separated metals, while adding the feedstock coal.

## Results

The metals deposited on the cathode or in the cathode chamber following galvanic treatment of coal qualitatively reflect the metal composition of the heterogeneous starting material. While iron is most abundant in cathode sediments from pyritic coals, significant amounts of sodium, potassium, rubidium, magnesium, calcium, strontium, aluminum, titanium, copper, manganese, zinc, lead, nickel and chromium have also been recovered there, depending upon the coal sample studied. Although the univalent cations, sodium and potassium are found in the cathode sediments, often larger quantities are found in soluble form in the acid lixiviant along with much aluminum, calcium and magnesium as well as smaller amounts of heavier metals such as iron. In some coal samples, the rarer elements, lutecium, ytterbium, lanthanum and neodymium were found usually by inspection of localized deposits on the platinum cathodes with scanning electron microscopy and ED x-ray analysis (Lazaroff and Dugan, 1989). The non-metallic elements found at the cathode, presumably complexed with cations, include sulfur, phosphorous, silicon and less frequently chlorine. One coal sample yielded significant amounts of bromine. Not all of the metals leaching from coal samples deposited at the cathodes of the galvanic systems.

PSOC 667, a sub-bituminous Iowa coal containing approximately 6% pyrite, was found to be particularly suitable for studying bacterioelectric deashing. Earlier studies had shown that bacterial presence during galvanic treatment resulted in more complete removal of metals from the slurried coal compacted at a platinum anode (Lazaroff and Dugan, 1989). Table 1 compares the results of deashing in the presence of bacteria or by increasing the conductivity of the galvanic cell through addition of  $10^{-3}M Li_2SO_4$ . The enhancement of conductivity alone, resulted in removal of as much as 75% of the ash from the PSOC 667 coal in 20 hrs treatment. It was found that comparable results could be obtained with dispersed stirred coal particles at the anode if the lithium solute was present or with slower rates of deashing in the presence of bacteria in the absence of lithium sulfate. With protracted bacterioelectric leaching of stirred PSOC 667 coal slurries, over 90% of ash has been removed (Table 2).

Examination of the leachability of other coals by the bacterioelectric system indicated that most pyritic bituminous and subbituminous coals were susceptible to galvanic deashing but with considerable variation in efficiency of metal removal. The lignites investigated were not enhanced in deashing by the presence of bacteria which was possibly correlated with the absence of Pyrite (Table 1).

Although pyritic coals show the effect of bacterial enhancement of metal removal, there is no clear indication that the only metals removed from the coal are associated with pyritic inclusions. A good example of this is observed with PSOC 1322, an Illinois #6 high volatile bituminous coal. The presence of bacteria significantly contribute to metal removal. The cathode chamber deposit is mainly iron when the iron oxidizing bacteria are present but copper, calcium, silicon, manganese and aluminum are present as well. Without the additional iron oxidizing thiobacilli, the smaller cathode accumulation is qualitatively similar in metal composition but is predominantly calcium with comparatively little iron. The calcium is removed from the coal in large amounts without the added bacteria but it is found in

soluble form in the lixiviant rather than precipitated at the cathode (Figure 5). Figures 6 and 7 are ED-X-ray spectra of additional pyritic bituminous coals presented in Table 1 (PSOC 1316 and IBCSP #2) that further illustrate the removal of metals by the bacterioelectric effect.

An interesting aspect of this fractionation of metals in different phases of the system undergoing deashing is shown in Figure 8. As with the PSOC 1322 coal, the cathode chamber sediment from bacterioelectric leaching is largely iron while the comparable sediment from galvanic leaching without bacteria is mainly calcium. However, the calcium can be collected as a solid phase separate from the main cathode sediment or the dissolved solutes of the lixiviant by placing a membrane filter over the cathode chamber port. The calcium then deposits almost exclusively on the filter along with iron, and very little calcium enters through the porous membrane to deposit in the cathode chamber. This does not occur in the absence of added iron oxidizing bacteria suggesting that the Fe(III) sulfato-complex produced by chemolithotrophic iron oxidation is in some way responsible for co-precipitation of iron and calcium on the membrane.

The encouraging results obtained from deashing subbituminous coal galvanically in dispersed suspension, in the presence of bacteria or lithium sulfate led to construction of a system which allows re-use of the lixiviant and bacteria in a continuously fed laboratory scale reactor (Figures 3 and 4). In limited trials, so far, it appears possible to use the horizontal air-lift flowing system to remove 80 to 90% of ash from bacterially pre-treated Iowa subbituminous or Illinois #6 bituminous coal.

#### Summary

1. Metals can be removed from bituminous and sub-bituminous coals in galvanic cells at low voltages and currents. Originally this involved compressing powdered coal at an inert anode in a stirred dilute sulfuric lixiviant.
2. Pyritic coals may be simultaneously oxidized by acidic iron formed by iron oxidizing thiobacilli. This results in some coals yielding enhanced metal deposition at galvanic cathodes.
3. More complete deashing of a sub-bituminous coal was accomplished at high current densities in systems containing  $10^{-3}$  -  $10^{-2}$  M  $\text{Li}_2\text{SO}_4$  in the sulfuric lixiviant. 74% of ash removal has been accomplished.
4. The galvanic deashing can be carried out with dispersed-suspended coal particles in the  $\text{Li}_2\text{SO}_4$  lixiviant or in systems containing cells of *Thiobacillus ferrooxidans* or with coal slurries pre-treated with *Thiobacillus ferrooxidans*.
5. A continuous laboratory-scale system for bacterioelectric deashing of pyritic coals has been developed.

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### References

Decker, R. F. 1986. Metall. Trans A, 17:5-30.

Lazaroff, N., Sigal, W., and Wassenman, A. ,1982. Appl. and Env. Microbiol. 43:924-938.

Lazaroff, N. and Dugan, P. R. 1989. Proceedings, Bioprocessing of Fossil Fuels Workshop. Tyson's Corner, VA. pp. 79-104 (CONF-890884) available from NTIS U.S. Dept. Commerce, Springfield, VA 22161.

TABLE 1. ELECTROBACTERIAL DEASHING OF COAL SAMPLES

Coal Sample	Treatment	Ash (% by wt.)
<u>HBV</u> PSOC 1322 1.98% pyrite S	None	12.13
	46 hrs 8V, 2mA + Bact.	9.92
	46 hrs 8V, 2mA - Bact.	10.92
	Bact. pre-treat 56 hrs. 10V, 5 mA	6.99
<u>HBCB</u> PSOC 1316 1.47% pyrite S	None	11.06
	91 hrs 16V, 5mA + Bact.	10.86
	91 hrs 16V, 5mA - Bact.	11.16
<u>PSOC 551</u> 4.68% pyrite S	None	14.74
	43 hrs 16V, 5mA + Bact.	11.10
	43 hrs 11V, 5mA - Bact.	4.24
<u>IBCSP 2</u> 2.34% pyrite S	None	5.70
	90 hrs 15V, 5mA + Bact.	4.17
	90 hrs 15V, 5mA - Bact.	4.19
<u>Sub-bit. A</u> PSOC 667 6.0% pyrite S	None (as rec.)	18.73
	Bact. pre-treat + 45 hrs 7V, 2mA ave	7.04
	None (dry basis)	21.23
	in thimble, 20 hrs 12V, 5mA	13.04
	in thimble, 20 hrs 12V, 35mA + Li <sub>2</sub> SO <sub>4</sub> dispersed, 14 hrs, 12V, 38mA	4.80 7.96
<u>Sub-bit. C</u> PSOC 637 0.64% pyrite S	None	10.41
	Bact. Pre-treat + 67V, 3mA ave	4.79
<u>Lignite</u> PSOC 1489 0.02% pyrite S	None	6.90
	41 hrs 17V, 5.0mA + Bact.	3.60
	41 hrs 15V, 5.0mA - Bact.	3.20
Spanish Lignite	None	12.48
	66 hrs 10V, 2mA - Bact.	9.46
<u>Lignite A</u> PSOC 245 0.22% pyrite S	None	8.89
	90 hrs 10V, 2.5mA + Bact.	7.14
	90 hrs 13V, 2.5mA - Bact.	6.69

TABLE 2. BACTERIOELECTRIC DEASHING	
	Ash %
Iowa 667 Subbituminous Coal H <sub>2</sub> SO <sub>4</sub> pH 2.5	
	10 volts, 8.75 ma
Untreated control	21.23%
72 hrs	4.72%
140 hrs	1.22%
	10 volts, 21.82 ma
24 hrs	12.72%
96 hrs	7.74%
	5 volts, 7.70 ma
24 hrs	15.92%
96 hrs	5.53%
Illinois #6 Coal Argonne ID 301	
	10 volts, 12.5 ma
Untreated control	25.5%
72 hrs	15.5%
96 hrs	10.68%
168 hrs	10.70%
With $1 \times 10^{-3}M$ Li <sub>2</sub> SO <sub>4</sub>	
168 hrs	8.50%

SOLUBILIZATION OF PYRITE AND FORMATION OF OXIDIZED IRON SEDIMENTS IN A GALVANIC CELL WITH AN IMPOSED E.M.F., IRON OXIDIZING THIOBACILLI AND  $\text{H}_2\text{SO}_4$  pH 2.5

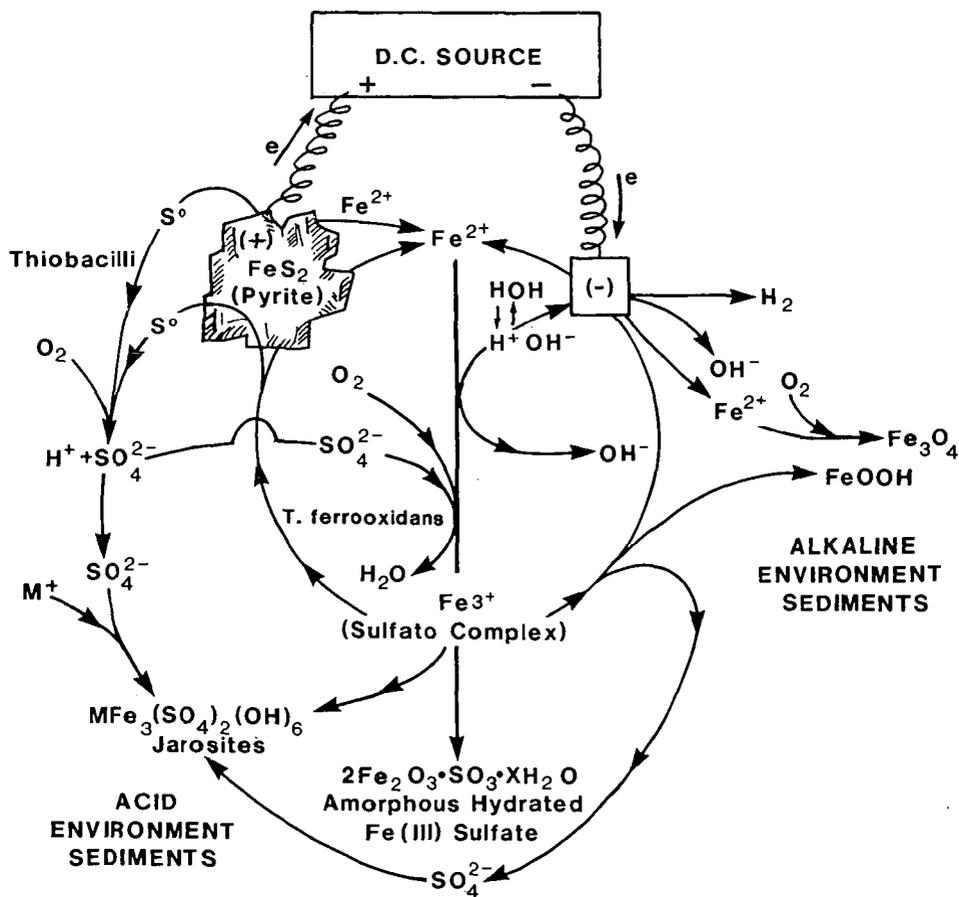


FIG. 1

LAB SET-UP of D.C. POWER SUPPLY WITH VOLTAGE REGULATOR  
and VOLTAGE, CURRENT MEASUREMENT

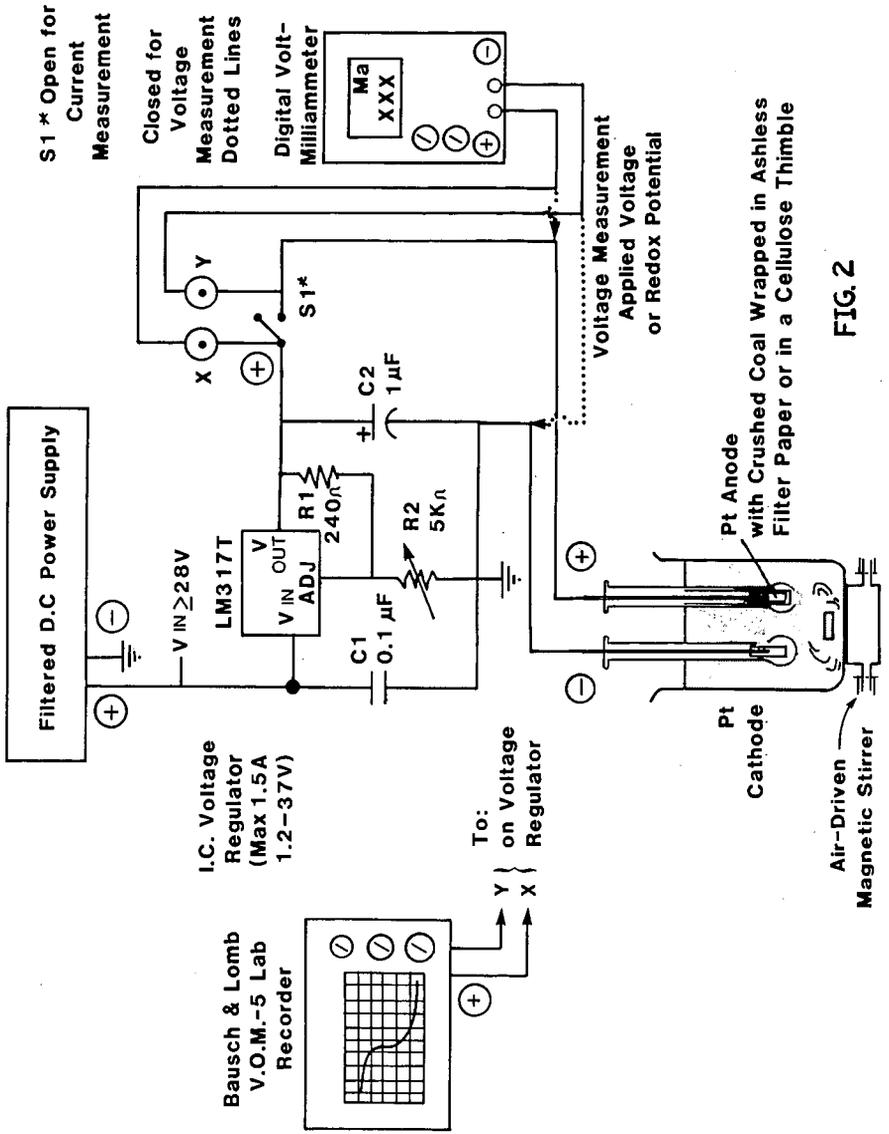


FIG. 2

LABORATORY SYSTEM for CONTINUOUS  
BACTERIO-ELECTRIC REMOVAL of METALS FROM COAL

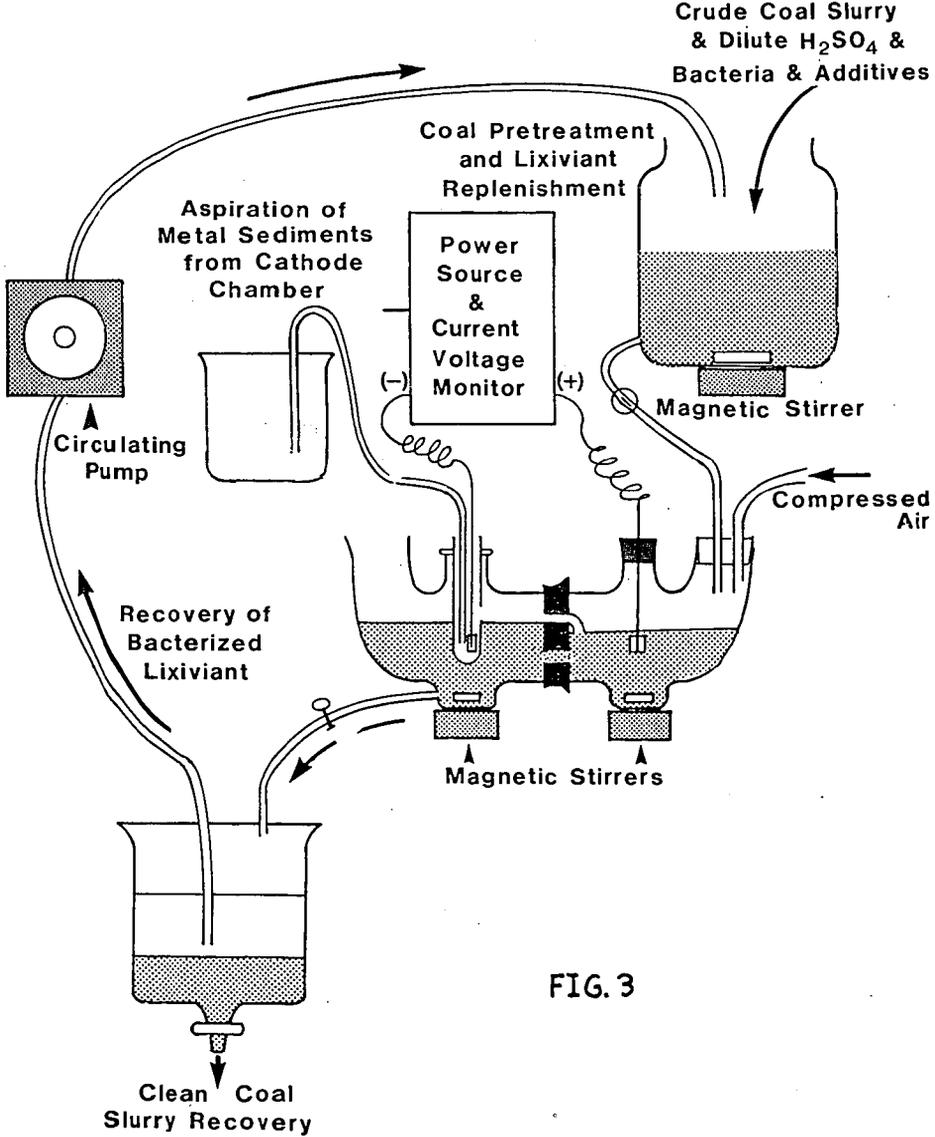


FIG. 3

HORIZONTAL AIRLIFT BACTERIO-ELECTRIC LEACHING CHAMBER

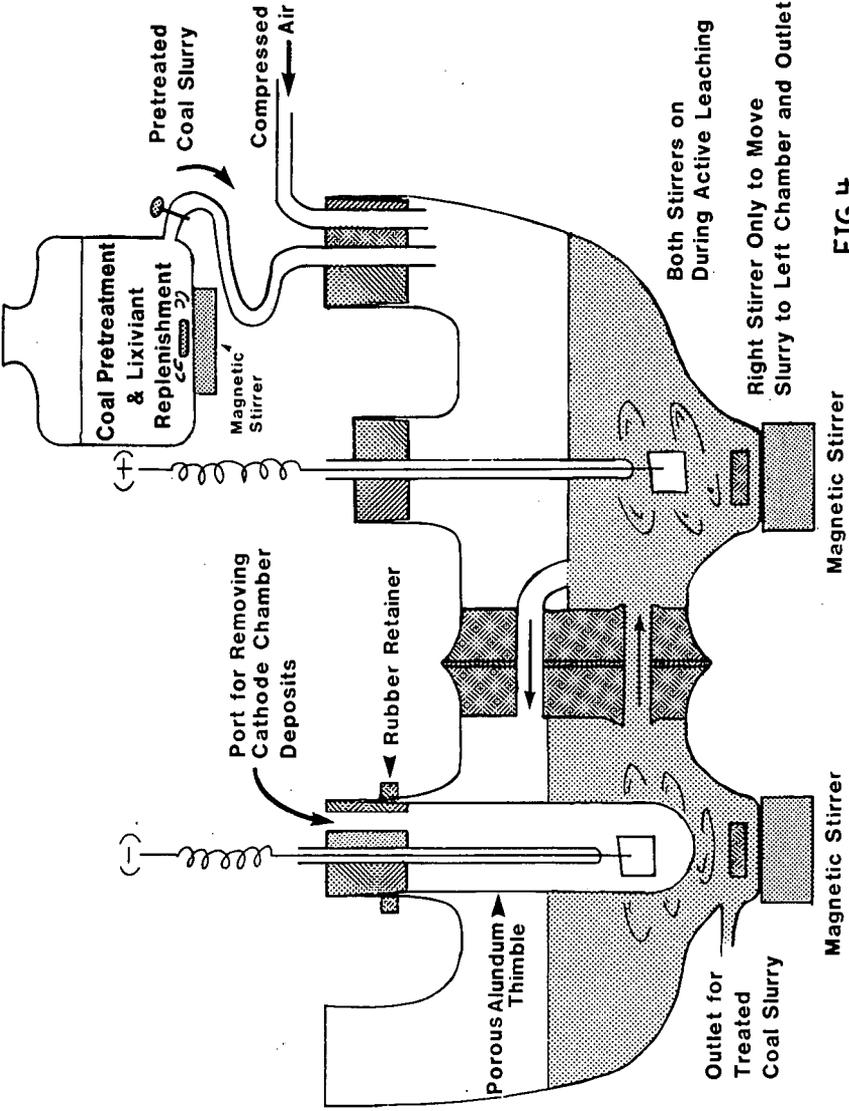


FIG. 4

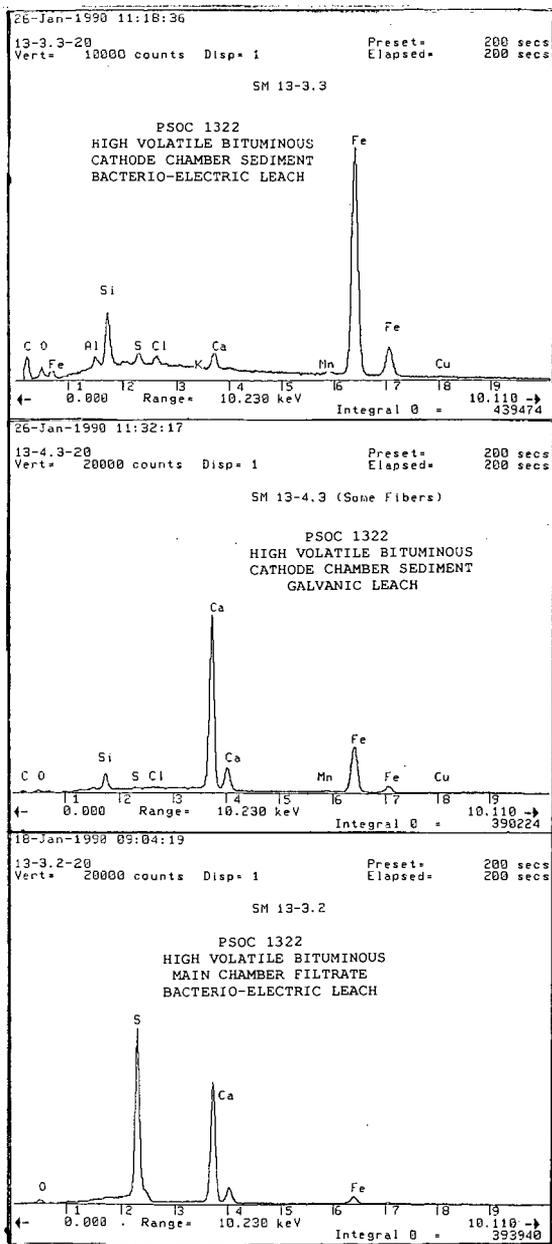


FIG. 5

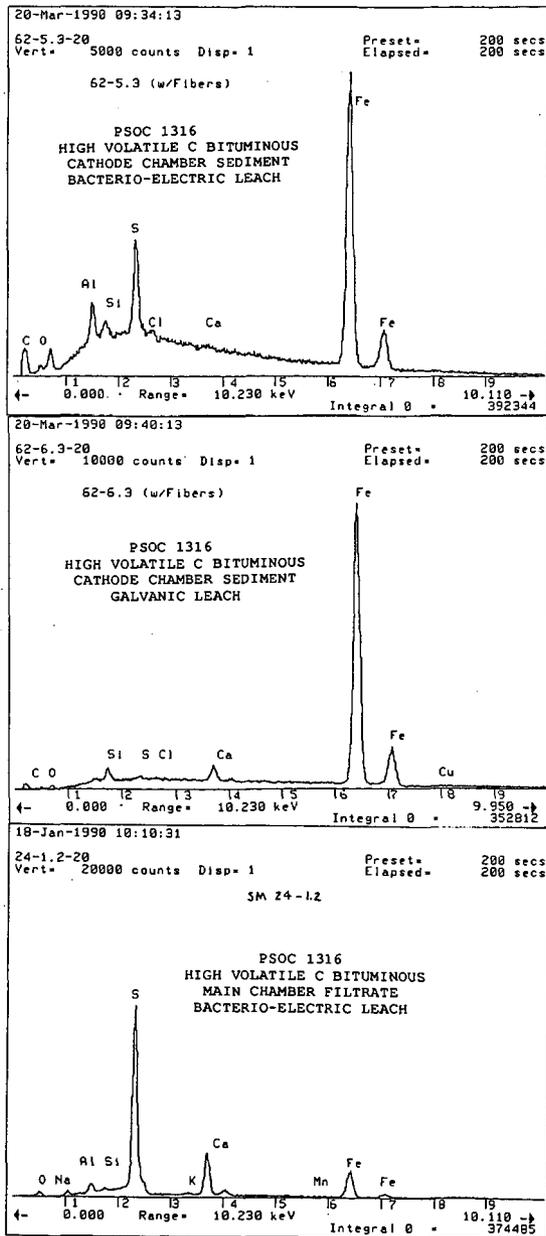


FIG. 6

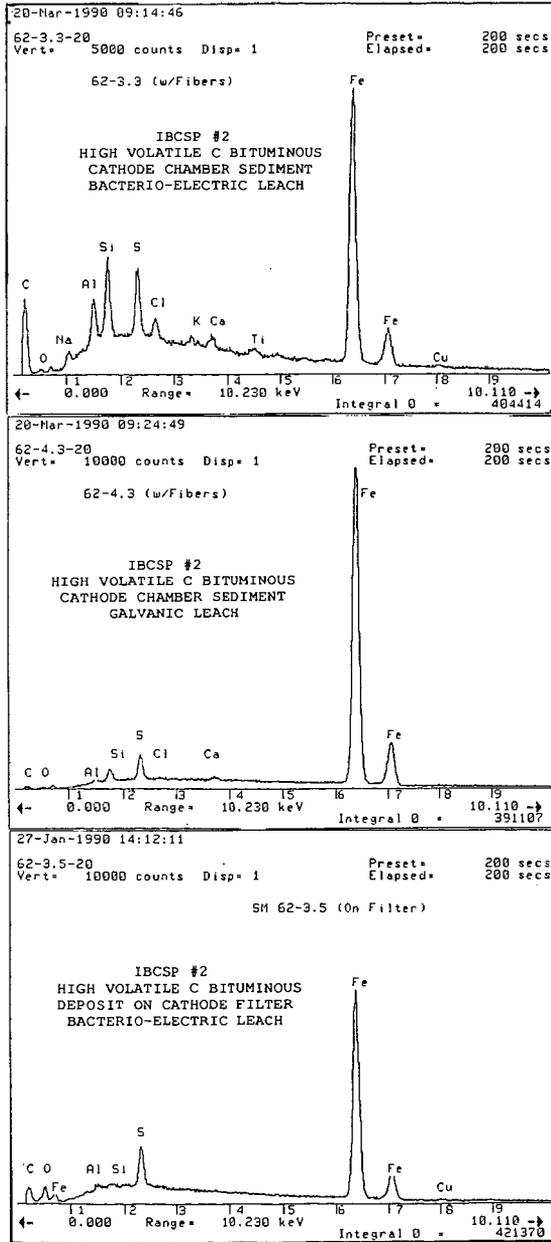


FIG. 7

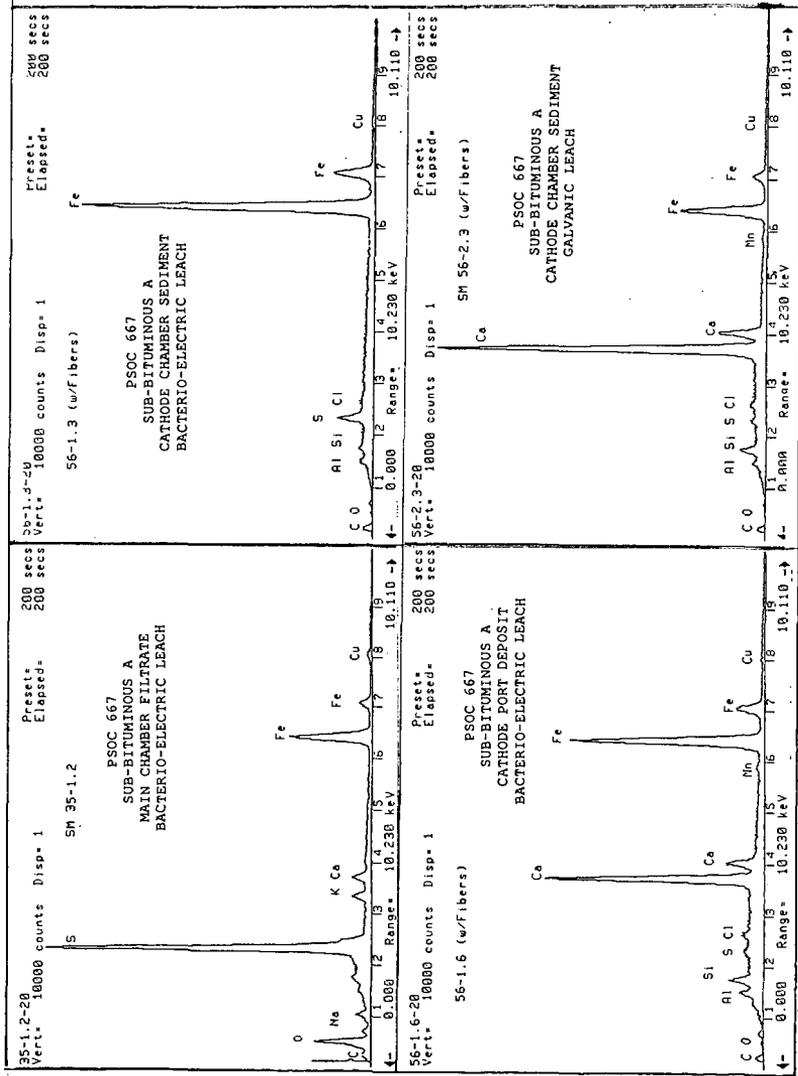


FIG. 8

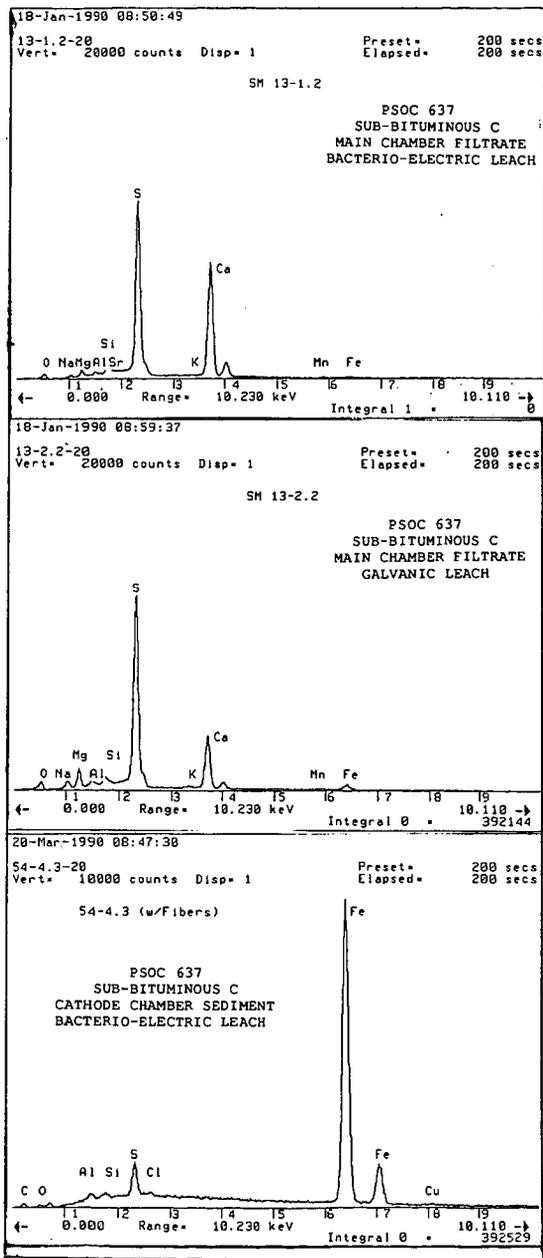


FIG. 9

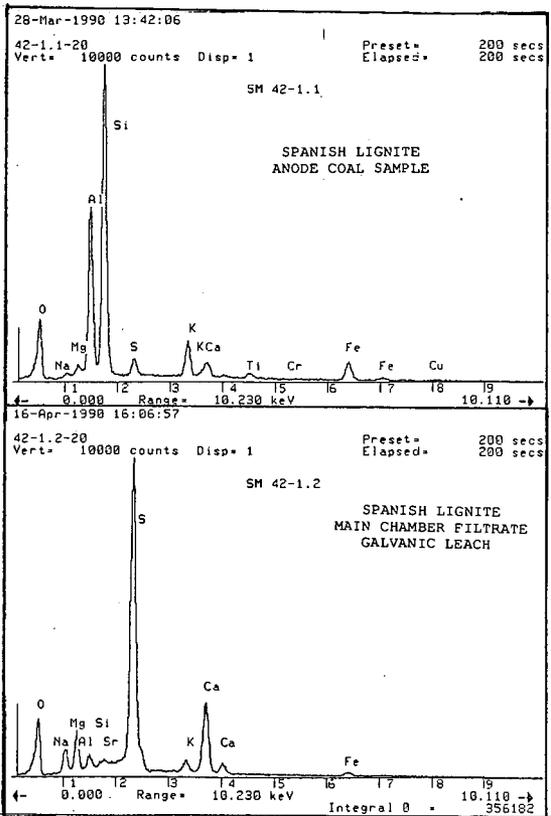


FIG 10

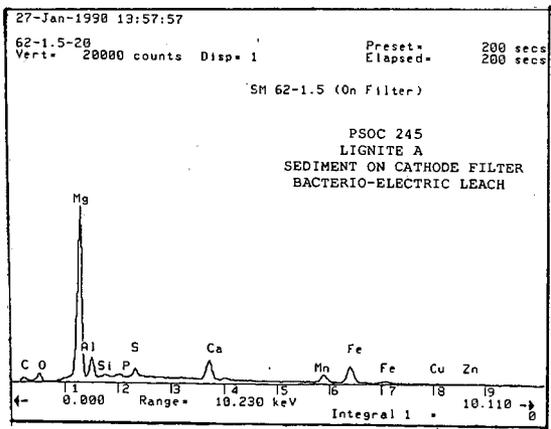


FIG 11