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Control of Pyrite Surface Chemistry in Physical Coal Cleaning

by

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ABSTRACT

One of the most difficult separations in minerals processing involves the differential flotation of pyrite and coal. Under practical flotation conditions, they are both hydrophobic and no cost-effective method has been developed to efficiently reject the pyrite. The problem arises from inherent floatability of coal and pyrite. Coal is naturally hydrophobic and remains so under practical flotation. Although pyrite is believed to be naturally hydrophilic under practical flotation conditions it undergoes a relatively rapid incipient oxidation reaction that causes "self-induced" flotation. The oxidation product responsible for "self-induced" flotation is believed to be a metal polysulfide, excess sulfur in the lattice, or in some cases elemental sulfur. It is believed that if incipient oxidation of pyrite could be prevented, good pyrite rejection could be obtained.

In order to gain a better understanding of how pyrite oxidizes, a new method of preparing fresh, unoxidized pyrite surfaces and a new method of studying pyrite oxidation have been developed this reporting period.

OBJECTIVE

The overall objective of this research is to obtain a sufficient fundamental understanding of the surface properties of coal-pyrite to foster the development of advanced physical coal cleaning (APCC) processes. This objective is being met by: 1) investigating the mechanisms responsible for the inefficient rejection of coal-pyrite, and 2) developing schemes for improving the rejection of coal-pyrite based on information gathered from part 1).

The specific objectives of the research this quarter were to develop a technique to (1) produce fresh, or completely unoxidized, surfaces of pyrite to allow the initial stage of pyrite oxidation to be studied and (2) evaluate the use of photoelectrochemistry to study the initial stage of pyrite oxidation. It is believed that the best way to prevent the "self-induced" flotation of pyrite is to prevent the incipient oxidation reactions that produce a hydrophobic surface on pyrite. It should be noted that nearly all electrochemical studies on pyrite have utilized polished electrodes, which are inadvertently oxidized during polishing. Therefore there has been no way to study, in situ, the very first stages of pyrite oxidation.

The preparation of fresh, unoxidized pyrite surfaces is accomplished by fracturing electrodes in situ in an electrochemical cell. This technique was developed earlier by one of the PI's for studying galena oxidation. Currently the incipient oxidation of pyrite is being studied on the freshly fractured surfaces using the photocurrents generated by chopped illumination.

EXPERIMENTAL

Initial studies have been conducted on well-crystallized mineral pyrite samples from Peru. Samples of approximate dimensions of 3mmX3mmX10mm were cut with a slow speed diamond saw, taking care to orient the saw cuts parallel to the external crystal faces of the samples. Silver epoxy was used to attach an electrical lead to one of the 3mmX3mm surfaces (back surface). Approximately one-half of the sample was then encapsulated using a non-conducting epoxy (Torr seal, manufactured by Varian), with the epoxy carefully applied to define the fracture surface. The sample was then mounted on a glass tube with the same epoxy, with the

tube serving as both a sample support and a container for the conducting wire to the sample. The glass tube was inserted into the electrochemical cell using an O-ring seal. Fracture was accomplished by inserting a glass rod through a separate cell port, resting the rod on the projecting epoxy-free part of the sample, and sharply tapping the rod with a piece of wood or plastic. Fracture usually occurred such that the new surface was flush with the epoxy, i.e., virtually the entire surface of the mounted portion of the sample after fracture was composed of the new unoxidized surface.

Photocurrents were generated using illumination from an 80-watt tungsten-halogen projector lamp, and a lab-built chopper operating at about 80 Hz. The photocurrents were measured using a PAR 5208 lock-in amplifier and strip chart recorder. A PAR 273 potentiostat was used to control and/or measure the electrode potentials before, during, and after fracture and to conduct routine cyclic voltammetry studies on the electrodes.

RESULTS AND DISCUSSIONS

It is well-known that the electrode potential assumed by mineral sulfides in solutions, without added redox couples, represents a mixed corrosion-type potential. The sample undergoes anodic oxidation while simultaneously dissolved oxygen is reduced to maintain overall charge neutrality. The initial stages of the mixed potential reactions are believed to produce the excess sulfur, polysulfides or elemental sulfur on pyrite that renders it hydrophobic.

When a pyrite electrode is fractured in solution at pH 9.2, the potential immediately drops by about 300 mV, instantaneously going from the usual mixed potential of about -0.1 V(SCE) to approximately -0.4 V(SCE). The freshly produced surface then oxidizes, with a

subsequent rise in potential to the usual steady state mixed potential. Illustrated in Figure 1, this behavior is characteristic of approximately 20 samples from this source that have been produced by in situ fracture.

In order to maintain an unoxidized surface after fracture, electrodes have been fractured while potentiostating near the fracture potential. It is difficult to determine the exact fracture potential a given electrode will reach at breakage. Between electrodes there may also be slight variations in the fracture potential reached. However, the value of all of the electrodes has been near -0.4 V(SCE). Potentiostating during electrode fracture is a means of preventing oxidation of the electrodes through the usual mixed potential mechanism. For example, electrodes held at -0.425 V(SCE) during fracture exhibit a small cathodic current, while electrodes held near -0.375 V(SCE) exhibit a small anodic current.

Figure 2 (bottom curve) shows the second cyclic voltammetry curve on a freshly fractured surface. The oxidation peak at -0.1 V(SCE) is known to represent the formation of ferric hydroxide and either polysulfides or excess lattice sulfur; the reduction wave at -0.55 V(SCE) the reduction of Fe(III) to Fe(II) hydroxides. At a potential of -1.0 V(SCE) pyrite is cathodically decomposed and the sulfur content of the surface is reduced by formation of the hydrosulfide ion. When the first sweep on a freshly fractured surface is from the fracture potential of -0.4 to -1.0 V(SCE), the reduction process at -0.55 V(SCE) is not observed.

Figure 2 (top curve) shows the photocurrent (in arbitrary units) obtained simultaneously with the cyclic voltammetry curve. It should be noted that (1) the photocurrent is the peak transient response of pyrite to chopped illumination, (2) no photocurrents are observed with steady illumination for the potential ranges used in Figure 2, (3) the maximum magnitude of the

photocurrent is approximately 10 to 15 percent of the maximum dark current observed on the voltammetry curve, (4) the instantaneous photocurrent produced by sudden illumination is always anodic, (5) the spikes observed on the cyclic voltammetry curve are due to the chopped illumination, but are somewhat random because of the asynchronism between the digital measurement rate of the PAR 273 potentiostat and the chopped light, and (6) polishing the electrodes at 600 grit reduces the photocurrent by more than an order of magnitude.

The anodic photocurrents indicate that the energy bands (valence and conduction bands) just beneath the surface of pyrite are bent upwards. The absence of cathodic photocurrents indicates that the bands do not bend downwards, even under strong cathodic potentials. This suggests that the pyrite used in this work is highly n-type.

The upward band bending corresponds to a positive space charge layer that is depleted in electrons and enriched in holes. The electrode potential where a zero photocurrent is observed is an indication of the flat band potential, i.e., the electrode potential where there is no space charge layer. The surface chemical analogue of the flat band potential is the zero point of charge. A zero photocurrent is observed only when pyrite is held at -1.0 V(SCE) for one or two minutes or the potential is swept to potentials lower than -1.0 V(SCE). As mentioned previously, as pyrite undergoes cathodic decomposition at the lower potentials, sulfur is removed from the lattice.

The anodic peak in the photocurrent observed at about -0.5 V(SCE) corresponds with the cathodic peak on the voltammetry curve representing the reduction of ferric- to ferrous-hydroxide. The reduction process occurs in the dark and involves the capture of the majority carriers (electrons) from the conduction band. The reduction reaction produces a relatively high

concentration of the reduced form of the Fe(II)/Fe(III) couple at the surface. It is believed that the photocurrent peak associated with this process represents the re-oxidation of the ferrous hydroxide by the minority carriers (holes) generated in the valence band during each light pulse.

Polishing has a dramatic effect on the photocurrent. Polishing obviously introduces localized electronic states at the surface and probably throughout the space charge region. These localized states have two major effects. They act as recombination centers that greatly reduce the lifetimes of photogenerated carriers, thereby reducing the photoresponse by over an order of magnitude. They also act as centers that trap charge, or in other words that provide a new charge storage capability at the surface and in the space charge region. The additional charge storage capacity in the surface region may pin the Fermi energy at the surface, i.e., prevent polarization of the space charge region, limiting the amount of band bending. The change in electronic structure induced by polishing may also affect the oxidation of pyrite.

One important finding is that pyrite potentiostated near the fracture potential (during fracture) exhibits a finite anodic photocurrent. This indicates that, at the instant of fracture, a net negative charge already exists on pyrite (the positive space charge layer develops to compensate this negative charge). The negative surface charge must be due either to intrinsic surface states or to the extremely rapid adsorption of negative hydroxyl ions. Work at Penn State on pyrite has shown that surface states exist on pyrite in non-aqueous acetonitrile solutions. Therefore hydroxide ion adsorption may not be necessary in producing the negative charge; however, intrinsic surface states may be highly reactive and promote hydroxyl ion adsorption. Much more work remains to be done before the origin of the negative surface charge can be determined. However, both intrinsic surface states and extrinsic surface states produced by

hydroxyl ion adsorption will influence how the electrochemical potential at the pyrite-electrolyte interface is partitioned between the Helmholtz layer and the space charge layer. The exact partition of the interfacial potential is undoubtedly important in incipient pyrite oxidation. In conclusion, the photoresponse, possibly coupled with interfacial capacitance measurements, provides a method to study the early stages of oxidation and may suggest ways to prevent oxidation.

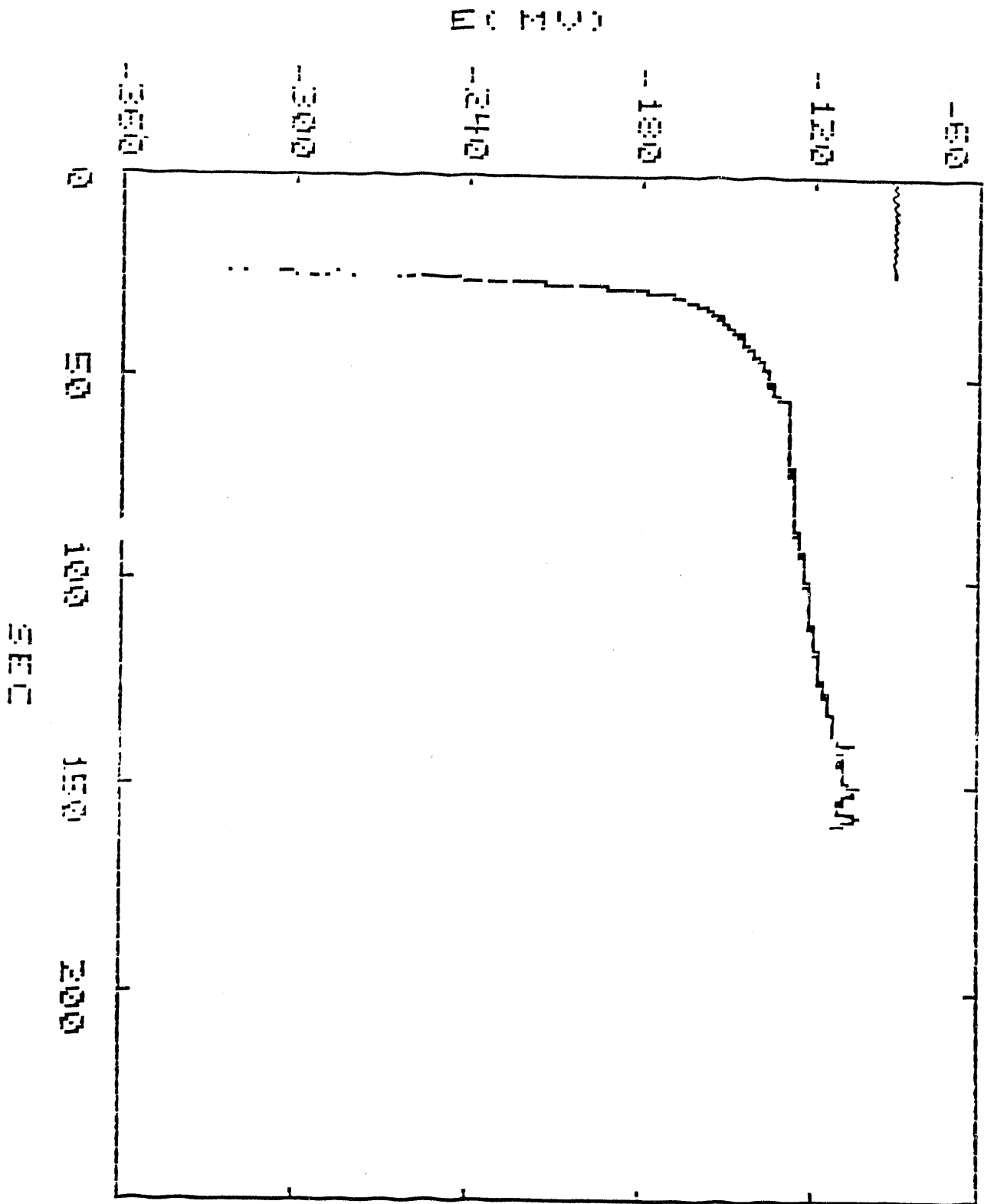


Figure 1. The electrode potential of freshly fractured pyrite electrodes at pH 9.2. At fracture the electrode potential decreases by approximately 300 mV, and then slowly increases by a mixed potential corrosion type reaction.

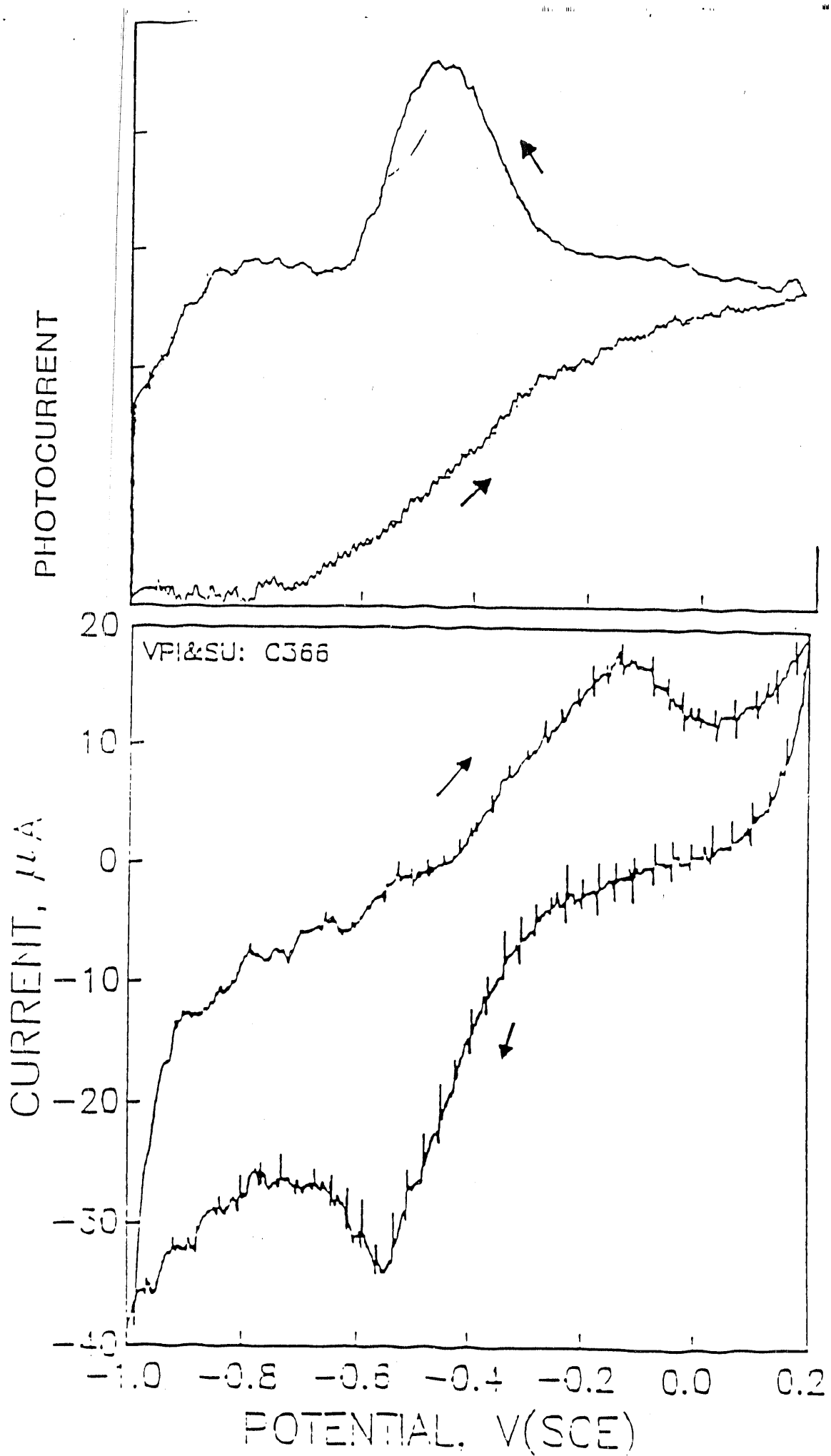


Figure 2. The Photocurrent (top) and cyclic voltammogram of fractured quiza at μM 0.2

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