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The Pyrite and Marcasite Electrodes

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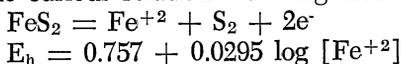Harvey Diehl
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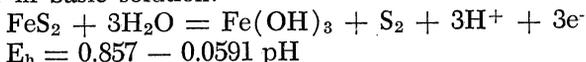
David L. Pringle and Harvey Diehl

Abstract. Pyrite and marcasite may be used as the indicating electrode in neutralization reactions. In acid solution the pyrite and marcasite electrodes behave almost identically with the platinum electrode with differences arising (1) in the presence of strong oxidizing agents where the attack on the pyrite and marcasite alters the potential, and (2) long standing where changes result from the dissolution of a little pyrite even under non-oxidizing conditions. Pyrite and marcasite can thus be used as indicator electrodes in oxidation-reduction titrations. A pyrite-platinum pair gives a differential titration curve. In alkaline solution pyrite, marcasite and platinum respond almost identically to changes in the concentration of sulfide, the single electrode potentials being shifted 120 mv. negative for each ten-fold increase in sulfide concentration.

Our attention was directed to pyrite by the geologists who regard as unsolved the geochemistry of the copper sulfide beds of northern Michigan where apparently pyrite has been converted to chalcocite by percolating waters. Oxidation-reduction is certainly involved here, quite possible under anaerobic conditions, and the electrical and electrochemical properties of the sulfide minerals make it conceivable that electrochemical cells could be formed and the oxidation-reduction reactions effected at a distance as well as by direct contact. The exact nature of the half-cell reaction of pyrite in contact with aqueous solutions becomes of fundamental importance.

Observations on the pyrite electrode have been reported at intervals during the past seventy years by workrs interested in its characteristics or its uses as electrode material for the manufacture of chemicals (1, 2, 3, 4, 5, 6). On the basis of its single electrode potential it has been arranged with other metal sulfides in an "electrochemical series of ore minerals" (7). It has been used as an indicator electrode in the potentiometric titration of heavy metals with sodium sulfide (8). The half-cell reaction, however, never seems to have been satisfactorily established. Sato (9), as late as 1960, wrote for the half-cell reaction the curious relation involving elemental sulfur:

$$FeS_2 = Fe^{+2} + S_2 + 2e^-$$
$$E_h = 0.757 + 0.0295 \log [Fe^{+2}]$$

or in basic solution:

$$FeS_2 + 3H_2O = Fe(OH)_3 + S_2 + 3H^+ + 3e^-$$
$$E_h = 0.857 - 0.0591 \, pH$$

where E_h is the potential with respect to the hydrogen electrode.

This work was directed first to learning the general response

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of the pyrite electrode to ions present in solutions with which
it has contact, and in particular to the hydrogen, the ferric, the
ferrous, and the sulfide ions. Identical measurements were made
at the same time with marcasite which has the same chemical
composition as pyrite, FeS_2, but has a different crystal structure,
pyrite being isometric, marcasite orthorhombic.

Apparatus. Construction of Electrodes. A pyrite bar, 4.5 cm
x 1.5 cm x 0.6 cm, was cut from a large twinned crystal of pyrite.
Electrical contact and suspension of the electrode were made
simply with an alligator clamp. Aqueous solutions did not creep
up the pyrite, the contact remained dry, and stable readings of
electrical potential were obtained.

A marcasite bar, 6 cm x 1 cm x 1 cm, was cut from a large
spherical piece of massive marcasite. It too was simply suspended
in the solutions studied by an alligator clamp.

The platinum electrode used was a piece of foil, 2 cm square,
welded to a platinum wire sealed into the end of a glass tube;
the tube was filled with mercury, and electrical contact was
made wtih an iron wire inserted through a rubber policeman
used to cap the open end of the glass tube.

Reagents. Analytical reagent chemicals were used without
further purification.

Potential Measurements. All potential measurements were
made with a Leeds and Northrup 7401 Stabilized pH Indicator.
The measurements were made against a commercial saturated
calomel reference electrode and converted to the hydrogen scale
using as the value of the saturated calomel electrode +0.246 v.
toward the normal hydrogen electrode.

Temperature and Atmosphere. Before potential measurements
were made, all solutions were allowed to equilibrate in a tem-
perature bath kept at 25.7°C. Equilibration and readings were
made under an atmosphere of nitrogen. Oxygen was removed
from the cylinder nitrogen used by passing the nitrogen through
a solution of vanadyl sulfate. Potentials remained constant for an
hour or more to within 2 mv.

Response to Hydrogen Ion. The potential of the pyrite elec-
trode was found to vary with the hydrogen ion concentration
of the solution into which it was dipped: $E = + 0.481$ v.
(hydrogen scale) at pH 4.0, +0.252 v. at pH 10.0. The pyrite
electrode can in fact be used as a hydrogen ion indicator elec-
trode, see titration curve (Figure 1).
Obviously when working with other ions, close control of the
hydrogen ion concentration is necessary.

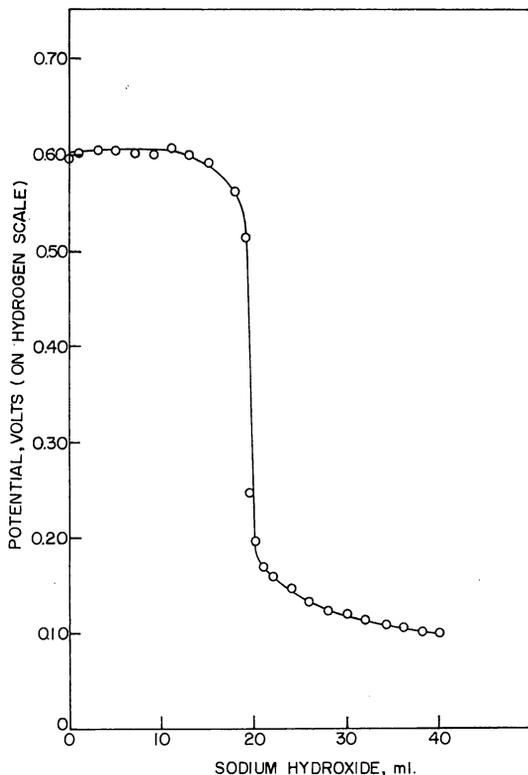*Response to Ferrous Iron.* The potential was measured of the

Figure 1. Titration curve of 20 ml. hydrochloric acid with sodium hydroxide using pyrite as indicator electrode. Concentration of acid and base, 0.09593 N and 0.1014 N, respectively. Potential measured against a saturated calomel electrode

pyrite electrode dipping into solutions varying in ferrous sulfate concentration from 0.001 M to 0.1 M, all solutions 1 M in hydrochloric acid. At all concentrations the potential was near +0.556 v. (hydrogen scale).

Response to Ferric Iron. The potential of the pyrite electrode did change with varying concentrations of ferric chloride over the range 0.001 M to 0.1 M all solutions being 1 M in hydrochloric acid. The potential varied linearly with the logarithm of the concentration of ferric iron (Figure 2). The slope was somewhat less than the 0.060 v. per 10-fold change expected. A platinum electrode gave the same response, all potentials being 75 mv. more positive. The marcasite electrode also gave the same response, all potentials being 50 mv. more negative than the corresponding potentials with the pyrite electrode.

Response to the Ferric-Ferrous Couple. Because the potential readings for ferrous sulfate were located at the lower end of the
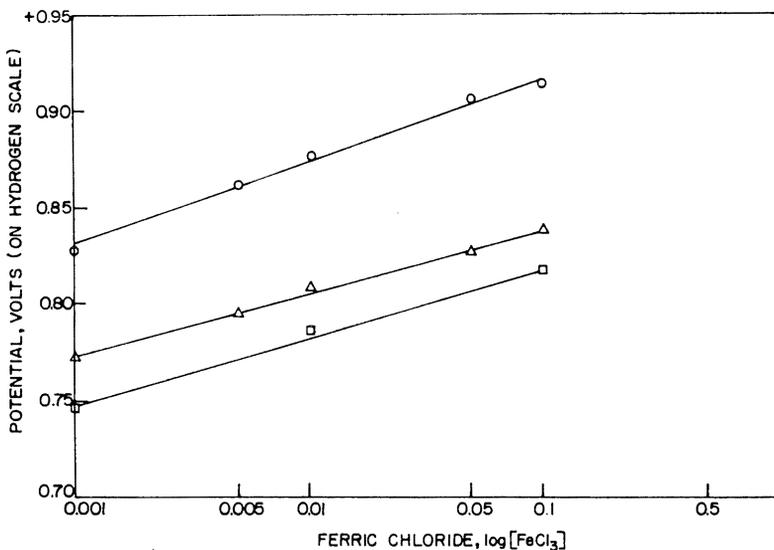
Figure 2. Potential of the pyrite and platinum electrodes with varying ferric iron concentration. Saturated calomel references electrode; o platinum electrode, △ pyrite electrode, □ platinum electrode after equilibration with powdered pyrite.

range of potential of the ferric-ferrous couple ($E° = +0.771$ v.) and that the potentials for ferric chloride were at the upper end of the range, it appeared possible that the potential measured was actually that of the ferric-ferrous couple. That this was the case was shown by following a titration of ferrous sulfate with sulfatoceric acid with a pyrite electrode. The curve obtained showed remarkable similarity to that obtained in the same titration with a platinum electrode (Figure 3). The curves were identical up to the end-point. Beyond the end-point, the pyrite electrode was apparently attacked by the excess oxidizing agent present. Similar results were obtained with the marcasite electrode.

As a further check, ferrous sulfate was titrated with sulatoceric acid and the reaction followed with a pyrite-platinum electrode pair. The titration curve (Figure 4) is exactly that expected for a differential titration with one attackable electrode. That is, the curve is the difference of the individual titration curves using the pyrite and platinum alone (Figure 3).

Except in the presence of a strong oxidizing agent, therefore, the pyrite and marcasite electrodes serve as inert electrodes responding like the platinum and other inert electrodes to the oxidation-reduction level of the solution.

Solubility of Pyrite and Marcasite. The observed potentials of the pyrite and marcasite electrodes in ferric chloride solutions

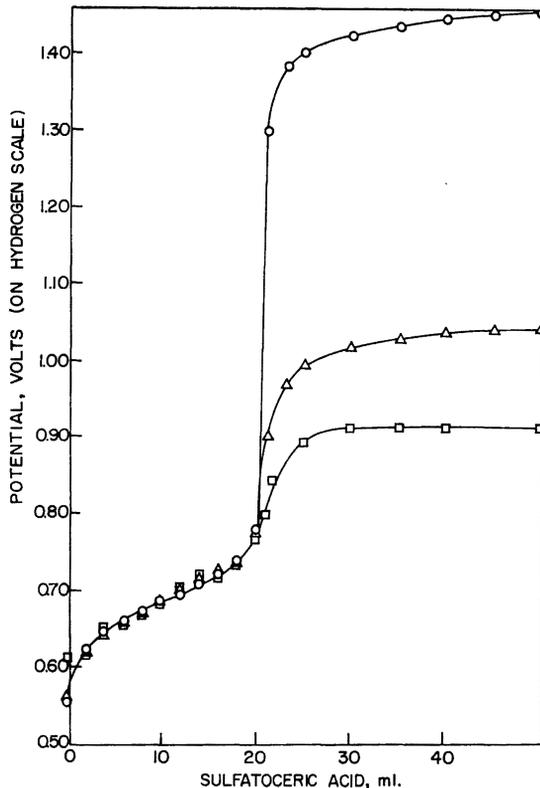were more negative than those of the platinum electrode in the

Figure 3.   Titration of ferrous sulfate with sulfatoceric acid using platinum, pyrite, and marcasite as indicator electrodes. Saturated calomel reference electrode; o platinum electrode, △ pyrite electrode, □ marcasite electrode.

same solutions. This difference is in the direction expected if some ferrous iron were present as a result of the dissolution of the pyrite or marcasite. Two experiments were performed which confirmed that pyrite and marcasite do dissolve in 1 M hydrochloric acid in the absence of oxygen.

A small amount of powdered pyrite was equilibrated with 1 M hydrochloric acid under anerobic conditions. At intervals over a twenty-four hour period, pairs of aliquots were withdrawn. To each aliquot was added sodium acetate sufficient to buffer the solution, to one was added hydroxylammonium chloride, and then to both was added 1,10-phenanthroline; the solutions were then diluted to the same volume and the absorbance measured at 510 mμ. In each pair the absorbance was the same showing that iron was present and that it was all in the plus two state.

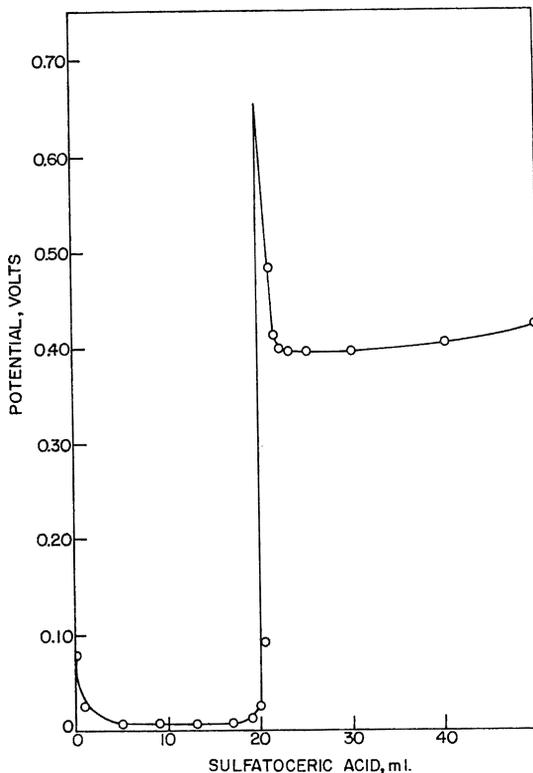In the second experiment, powdered pyrite was equilibrated

Figure 4. Differential titration of ferrous sulfate with sufatoceric acid with a pyrite-platinum electrode pair.

for 24 hours with solutions varying in concentration from 0.001 M to 0.1 M in ferric chloride and all 1 M in hydrochloric acid. The potential of the platinum electrode in each solution was then measured. In each solution the potential was more negative than found for the corresponding solution without the powdered pyrite, Figure 2, indicating the presence of ferrous iron.

Both experiments were repeated with powdered marcasite. The results were the same.

Response to Sodium Sulfide. The potentials were measured of pyrite and platinum electrodes dipping into solutions varying in sodium sulfide concentration from 0.001 M to 0.1 M, all 0.1 M in sodium hydroxide. The potentials varied markedly with sulfide content and the potentials of the pyrite were just slightly more positive than those of the platinum. A plot was made of the potential against the logarithm of the concentration of sulfide (Figure 5). The slope is -120 mv. per 10-fold change in concentration. Similar results were obtained with marcasite, the

potentials of the marcasite being also slightly more positive than the platinum.
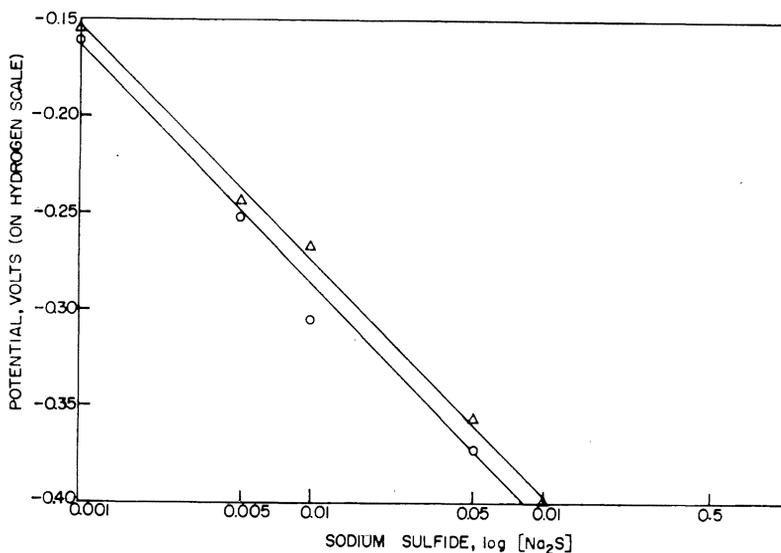

Figure 5. Potential of pyrite and platinum electrodes as a function of the concentration of sodium sulfide in 0.1 M sodium hydroxide. Saturated calomel reference electrode; o platinum electrode, △ pyrite electrode

It is apparent from these results that pyrite and marcasite in alkaline sulfide solutions behave essentially as inert electrodes and like platinum respond to the oxidation-reduction level of the couple in solution. Because the slope of the curve of potential versus the logarithm of sulfide concentration is negative, the sulfide is apparently the reduced form of the couple. The value of 120 mv. per 10-fold change in concentration indicates that the number of electrons involved in the couple must be half the number of sulfide ions involved:

$$E = E° + \frac{nF}{2.3\ RT} \log \text{[Oxidized Form]} + \frac{2.3\ RT}{nF} \log \frac{1}{[S^{-2}]^{2n}}$$

For a one-electron reduction, the oxidized form must then be the ion S_2^{-3} in which the oxidation number of the sulfur is -1½. The couple and the electrode potential equation then are

$$S_2^{-3} + e^- = 2S^{-2}$$
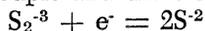
$$E = E° + \frac{2.3RT}{F} \log \frac{[S_2^{-3}]}{[S^{-2}]^2}$$

Presumably a small amount of the oxidized form, Na_3S_2, is present in the sodium sulfide used as a result of air oxidation or incomplete reduction during manufacture.

Conclusions. The pyrite and marcasite electrodes respond to changes in hydrogen ion concentration and can be used as hydrogen ion indicating electrodes in neutralization reactions.

The pyrite and marcasite electrodes in acid solution behave almost identically with the platinum electrode with differences arising in two situations: 1) in the presence of strong oxidizing agents where the attack on the pyrite and marcasite alters the potenial, and 2) long standing where the changes result from the dissolution of a little of the pyrite and marcasite even under non-oxidizing conditions. Pyrite and marcasite can thus be used as indicator electrodes in oxidation-reduction titrations, for example, in the titration of ferrous iron with sulfatoceric acid. A pyrite-platinum pair gives a differential type titration curve.

Pyrite, marcasite, and platinum electrodes respond almost identically to changes in concentration of sulfide in alkaline solution. The plot of potential versus logarithm of the sulfide concentration was found to be linear the change being -120 mv. per 10-fold increase in concentration. Polysulfides are probably involved in the oxidation-reduction couple being measured.

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