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Control of Pyrite Surface Chemistry in Physical Coal Cleaning

by

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ABSTRACT

To better understand the surface chemical properties of coal and mineral pyrite, studies on the effect of flotation surfactants (frother and kerosene) on the degree of hydrophobicity have been conducted. The presence of either frother or kerosene enhanced the flotability of coal and mineral pyrite with a corresponding decrease in induction time over the pH range examined. In the presence of both frother and kerosene a synergistic effect is observed and the order of flotability is as follows: mineral pyrite > Pocahontas No. 3 coal pyrite > Pittsburgh No. 8 coal pyrite. Scanning electron microscopy (SEM) results indicate a correlation exists between the sample surface morphology and crystal structure and the observed hydrophobicity. Preliminary studies on the reduction/oxidation properties of coal and mineral pyrite indicate that Pocahontas No. 3 coal pyrite behaves more irreversibly towards surface oxidation and reduction than does mineral pyrite. As a result of the data obtained from the surface characterization studies, controlled surface oxidation was investigated as a possible pyrite rejection scheme in microbubble column flotation. The results obtained for a run of mine Pittsburgh No. 8 coal sample are promising and indicate that grinding and conditioning of the coal sample at alkaline pH results in a significant decrease in pyritic sulfur without loss of combustible recovery.

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INTRODUCTION

The primary objective of this research is to obtain fundamental knowledge concerning the surface properties of coal pyrite as they relate to advanced physical coal cleaning (APCC) processes. This goal will be achieved through a two-part program: (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 objectives of the research conducted during this reporting period were to determine the following: (1) the influence of commonly used flotation surfactants (i.e., frother and kerosene) on the hydrophobicity of coal and mineral pyrite samples as a function of pH, (2) the correlation between the observed hydrophobicity and changes in sample morphology using scanning electron microscopy (SEM), (3) the reduction/oxidation properties of the coal and mineral pyrite samples as a function of pH, and (4) the effect of controlled surface oxidation as a possible pyrite rejection scheme in microbubble column flotation.

EXPERIMENTAL PROCEDURE

Materials

An additional coal pyrite sample from the Pittsburgh No. 8 seam (Pennsylvania) was obtained in massive crystalline and run-of-mine (-6mm) form. The sample preparation for the hydrophobicity measurements was identical to the procedure outlined in the last quarterly report.

Induction Time and Microflotation

The induction time and microflotation measurements were conducted in similar fashion to those described in the previous report. The flotation surfactants used in these studies were Dowfroth 1012 and kerosene.

Spectroscopic Analysis

Scanning electron microscopy was employed to determine morphological changes. The samples examined were the 100 x 150 mesh float and sink products of microflotation tests at pH 6.8. The photomicrographs shown in this report were typical of the total pyrite sample under study.

Electrochemistry

Electrodes of hand-picked crystals of each pyrite sample were constructed by attaching a wire to one end of the crystal with a conducting epoxy and then sealing the crystal in a glass tube filled with a nonconducting epoxy. The exposed end of the crystal was roughly polished on successive grades of silicon carbide paper followed by a final polish using 0.3 and 0.05 micron alumina powder in deionized water.

A standard three electrode electrochemical cell was used, with the pyrite electrode as the working electrode, a platinum wire mesh as the counter electrode and a silver-silver chloride electrode as the reference electrode. All potentials are reported against the saturated hydrogen electrode (SHE).

Microbubble Column Flotation

The run-of-mine coal sample from the Pittsburgh No. 8 seam was determined to have a feed assay of 3.9% sulfur and 12% ash. Prior to flotation, the coal sample was dry pulverized in a laboratory hammermill to below 100 mesh. This was followed by wet grinding at 30% solids in a stirred ball mill using stainless steel balls while maintaining the desired pH. The sample was micronized for 15 minutes which resulted in a mean product diameter of approximately 5 microns. After micronizing, the sample was diluted to an appropriate solids content in a conditioning sump where the slurry pH was adjusted to maintain the desired pH during the conditioning phase prior to

flotation. The collector (kerosene) addition was made into the sump after the conditioning phase and was followed by an additional 5 minutes of conditioning.

The conditioned slurry was fed to a 5-cm diameter Plexiglas column with a length-to-diameter (L/D) ratio of 20 at a point approximately 45 cm below the froth overflow lip. Bubbles were generated externally and introduced at the bottom of the column. A summary of the operating conditions is shown in Tables I-III. The results presented in this report were obtained while the column was operating under steady-state conditions.

RESULTS AND DISCUSSION

SURFACE CHARACTERIZATION

Induction Time and Microflotation

Effect of surfactants:

The effects of frother and kerosene addition on the flotability and induction time of the three freshly-ground pyrite samples are shown in Figures 1-4. For all three pyrite samples, the addition of either frother or kerosene enhanced the flotation recovery and resulted in a corresponding decrease in the induction time. In the presence of frother alone, the flotation recovery of mineral pyrite (Fig. 1) is the highest followed by the Pocahontas No. 3 coal pyrite (Fig. 2) with the Pittsburgh No. 8 coal pyrite (Fig. 3) as the least flatable. Also, the induction time results for mineral pyrite and Pocahontas No. 3 coal pyrite are very similar while the Pittsburgh No. 8 coal pyrite displays a higher induction time. In the presence of kerosene alone, the mineral pyrite and the Pocahontas No. 3 coal pyrite exhibit similar flotability; however, the Pittsburgh No. 8 sample has comparable flotability

and induction time in acidic solution and lower flotability in neutral to alkaline solutions. When both frother and kerosene are added to the solution a synergistic effect is observed as shown in Figure 4. The flotation recovery of mineral pyrite is the highest over the entire pH range followed by a lower flotability and slightly longer induction time for the Pocahontas No. 3 coal pyrite at neutral and alkaline pH with the Pittsburgh No. 8 coal pyrite exhibiting even lower flotability and longer induction time in the neutral and alkaline solutions. These results suggest that frother alone is capable of improving the flotability of mineral pyrite and the Pocahontas No. 3 coal pyrite; however, kerosene is needed to improve the flotability of the Pittsburgh No. 8 coal pyrite.

The overall lower degree of hydrophobicity of the Pittsburgh No. 8 coal pyrite may be related to surface oxidation. The results from XPS measurements of a freshly-ground sample of the Pittsburgh No. 8 coal pyrite indicate a higher ratio of oxygen to sulfur on the surface as compared to the Pocahontas No. 3 coal pyrite, both of which have a higher oxygen to sulfur ratio than the mineral pyrite. The hydrophobicity and XPS measurements suggest that the Pittsburgh No. 8 coal pyrite undergoes rapid surface oxidation resulting in a hydrophilic surface requiring the adsorption of a collector, such as kerosene, to render it hydrophobic.

Morphology

Scanning electron microscopy (SEM) examination of coal and mineral pyrite particles was conducted in an attempt to correlate morphological differences with the observed degrees of hydrophobicity. Comparisons were made between the microflotation float products at pH 6.8 for the three pyrite samples and are shown in Figures 5-7. The photomicrographs indicate that the surfaces of mineral pyrite particles (Fig. 5) are relatively smooth and exhibit a euhedral

crystal form, often with striations. The Pittsburgh No. 8 pyrite particles (Fig. 7) are dramatically different in that they are comprised of spherical and granular masses having grain sizes of approximately 10 microns. The Pocahontas No. 3 pyrite particles (Fig. 6) do not show the well-formed crystal habit as do the mineral pyrite particles; however, the fracture surfaces are somewhat smooth. Studies by other researchers on the influence of morphology and crystal structure on the reaction rate of pyrite have resulted in the following reaction order: euhedral pyrite < framboidal pyrite < marcasite (most reactive). In light of this and the XPS results, there is very good agreement between the surface morphology of the three pyrite samples and their hydrophobicity. The lower degree of hydrophobicity observed for the Pittsburgh No. 8 coal pyrite is most likely a result of the more reactive nature of this pyrite source.

The SEM results of microflotation sink (reject) products for the three pyrite samples at pH 6.8 are very similar to the float products and did not provide any insight into the nature of the difference in hydrophobicity. XPS analysis of the three pyrite samples indicated similar amounts of oxidation products on the surfaces of both the float and sink products. These findings suggest that the differences in the hydrophobicity between the float and sink products are not very obvious and, at this time, are not clearly understood.

Electrochemistry

A preliminary investigation of the electrochemical behavior of pyrite samples from an ore and a coal source in alkaline borate solution (pH 9.2) has been carried out by cyclic voltammetry. Representative cycles from the first 10 oxidation/reduction cycles for mineral pyrite and the Pocahontas No. 3 coal pyrite are presented in Figures 8 and 9, respectively. The current densities for the two pyrite samples are very similar in addition to the shape of the

voltammograms. For both samples investigated, the first cathodic cycle differs substantially from the subsequent cycles and the current densities decrease with increasing number of cycles. The large reduction peak observed in the first cycle indicates the presence of oxidation product(s) on the pyrite surface. The oxidation product(s) are formed during the polishing of the pyrite electrodes prior to insertion into the electrochemical cell. The charge associated with the anodic process during the first anodic scan of each pyrite sample is considerably smaller than the cathodic charge passed during the initial cathodic scan. However, the anodic and cathodic charge passed during each subsequent cycle balances and decreases with increasing number of cycles. Moreover, the anodic and cathodic peak potential shifts to less anodic and cathodic values, respectively. From these findings it is believed that the surface oxidation product(s) formed during the sample polishing procedure are reduced leaving the product $\text{Fe}(\text{OH})_2$ on the first cathodic cycle which then oxidizes to $\text{Fe}(\text{OH})_3$ during the subsequent anodic scan. Upon repeated cycling of either the mineral pyrite or coal pyrite electrode the oxidation/reduction behavior of the surface product is very similar and tends to be less irreversible with increasing number of cycles. However, the coal pyrite exhibits a shift in the anodic and cathodic peak potentials of approximately 50mV as compared with the mineral pyrite. Thus, the Pocahontas No. 3 coal pyrite exhibits a higher degree of irreversibility because of the larger overpotential necessary to oxidize and reduce the surface product.

REJECTION SCHEME DEVELOPMENT

Microbubble Column Flotation

As a result of the information obtained from the surface characterization studies on mineral and coal pyrite, controlled surface oxidation was chosen as a possible pyrite rejection scheme in microbubble column flotation.

Preliminary results for a run-of-mine Pittsburgh No. 8 seam coal sample are shown in Figures 10-11 and Tables I-III. The effect of pH and conditioning time on the recovery-sulfur grade curve is illustrated in Figure 10. The recovery-grade curve shifts to a lower sulfur grade when the pH of the coal slurry during grinding is pH 9 as compared to pH 7. A further improvement in the sulfur grade-recovery curve occurs if the coal slurry is conditioned at pH 9 for five hours prior to flotation. The improvement in the pyritic sulfur rejection may be a result of pyrite oxidation to form more stable, hydrophilic surface products.

The effect of pH and conditioning time on the recovery-ash grade curve is shown in Figure 11. Similarly to the recovery-sulfur grade curve, the recovery-ash grade curve shifts to lower ash with increasing pH. The effect of conditioning time at pH 9 on the recovery-ash grade curve is minimal. These results suggest that the method of grinding and conditioning the coal sample at alkaline pH may have a two-fold effect: (1) formation of hydrophilic surface products on the coal pyrite and (2) increased dispersion of particles in the slurry, thus minimizing the likelihood of ash particle entrapment.

CONCLUSIONS AND FUTURE WORK

The results presented in this report indicate that surface oxidation plays an important role in the hydrophobicity of coal and mineral pyrite. The nature of the pyrite source is also important and further studies on the surface characterization of coal pyrite samples from several sources are planned. These studies will correlate the effect of hydrophobicity in the absence and presence of surfactants with sample source. Additional surface characterization measurements will be integrated into the existing testing

procedure. These measurements include electrochemistry coupled with spectroscopy (XPS and SEM), specular and diffuse reflectance fourier transform infrared spectroscopy (FTIR), and in-situ controlled potential contact angle. The incorporation of these measurements into the testing procedure will complement the existing methods as well as provide independent measures for correlating hydrophobicity with changes in surface properties. Continuation of pyrite rejection scheme development emphasizing controlled surface oxidation will focus on optimization of the parameters in microbubble column flotation for maximum pyrite rejection.

A problem that will develop is, what is happening to the coal while the pyrite is being oxidized. The key to success is to oxidize pyrite selectively. Although I know that the scope of this work doesn't include work with coal samples, it seems that for meaningful results to be arrived at, coal-pyrite mixtures must be assessed.

PERU PYRITE
DOWFROTH 1012 / KEROSENE
FLOTATION TIME = 2 min.

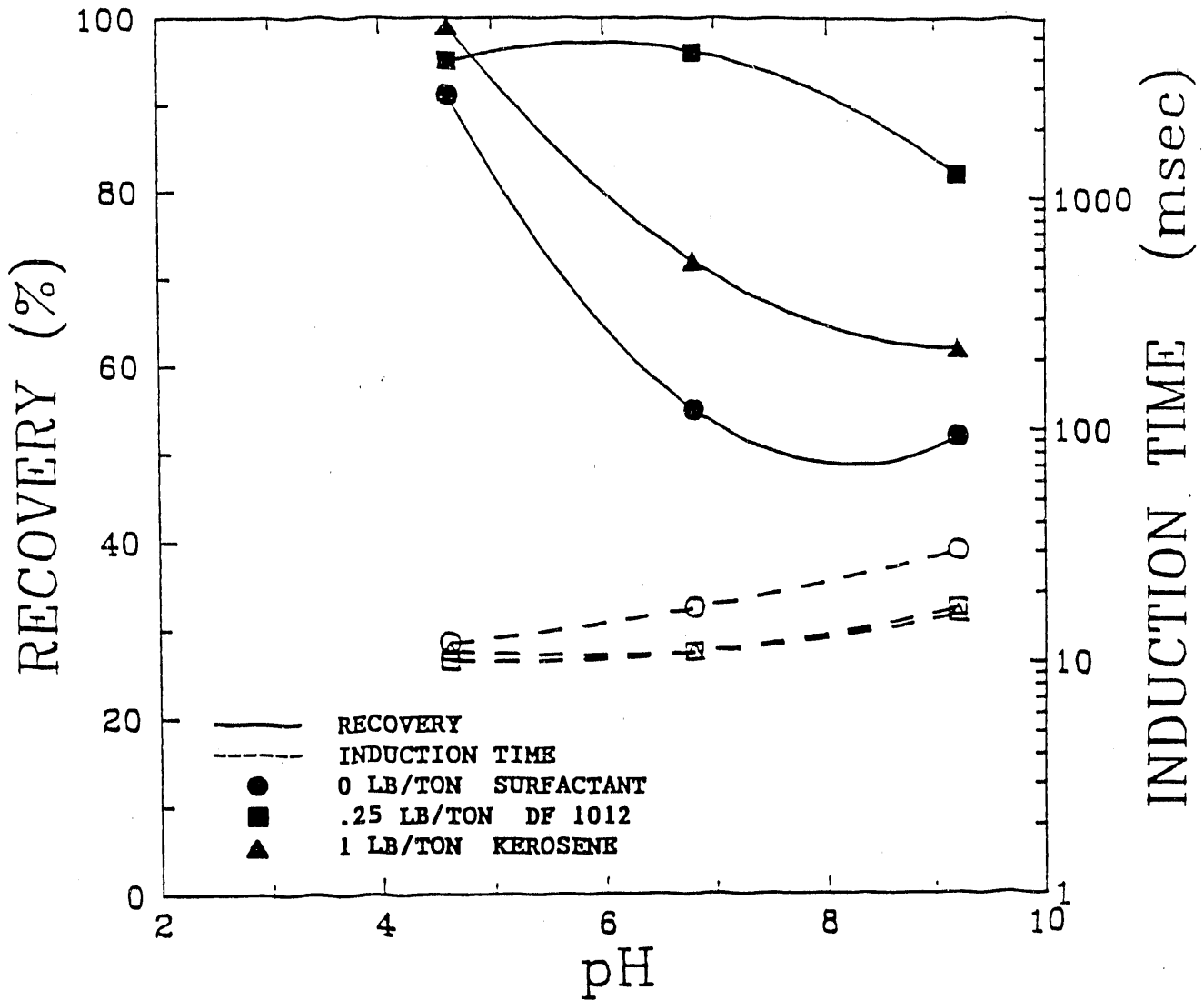


Figure 1. Microflotation recovery and induction time for Peru mineral pyrite in buffered solutions in the absence and presence of flotation surfactants. Flotation recovery: - - - -; Induction time: - - -; Surfactants: ●, ○ - none; ▲, △ - 1 lb/ton kerosene; ■, □ - 0.25 lb/ton Dowfroth 1012.

COAL PYRITE - POCAHONTAS No. 3
 DOWFROTH 1012 / KEROSENE
 FLOTATION TIME = 2 min.

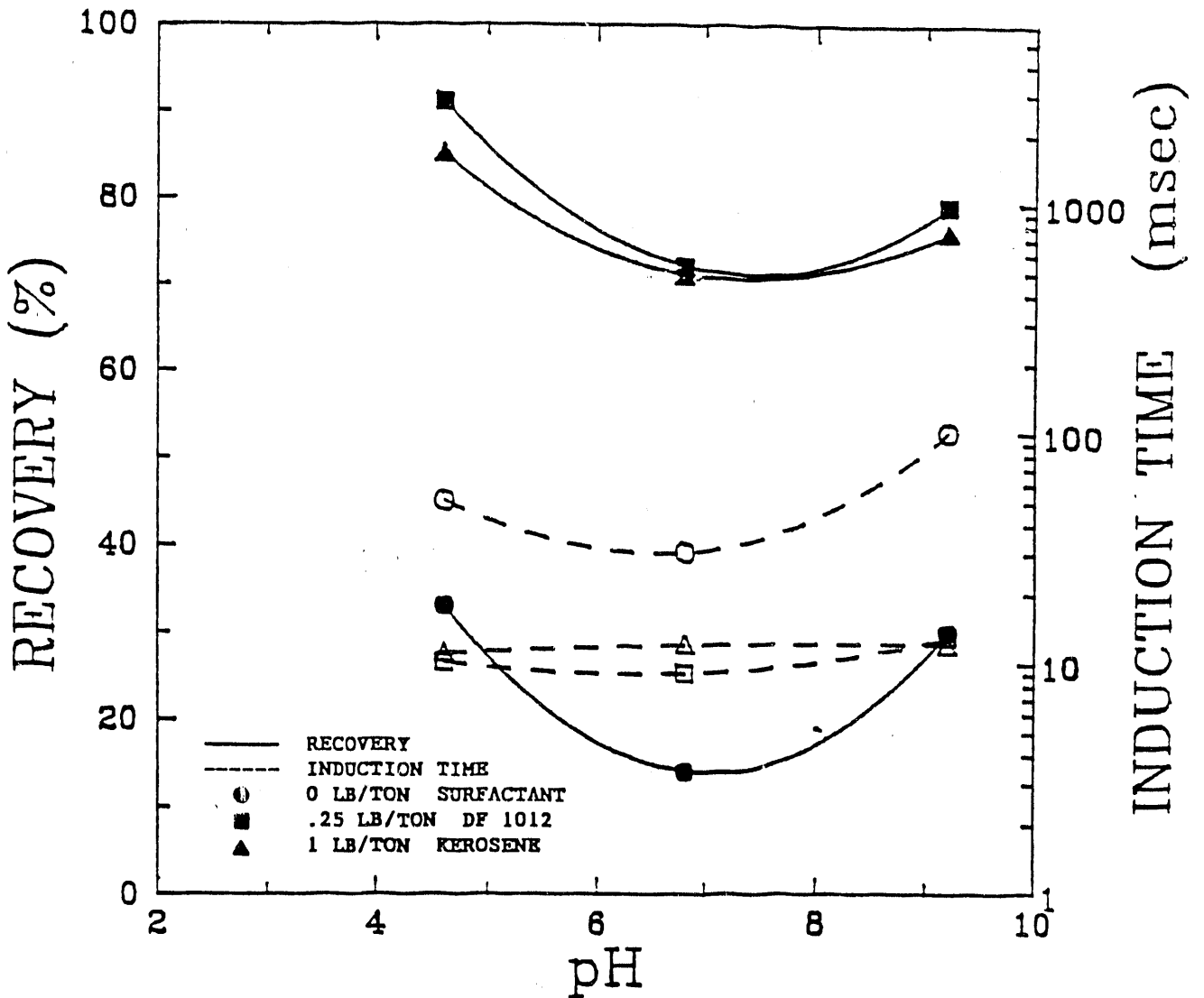


Figure 2. Microflotation recovery and induction for Pocahontas No. 3 coal pyrite in buffered solutions in the absence and presence of flotation surfactants. Flotation recovery: -----; Induction time: - - -; Surfactants: ●, ○ - none; ▲, △ - 1 lb/ton kerosene; ■, □ - 0.25 lb/ton Dowfroth 1012.

COAL PYRITE - PITTSBURGH NO. 8
 DOWFROTH 1012 / KEROSENE
 FLOTATION TIME = 2 min.

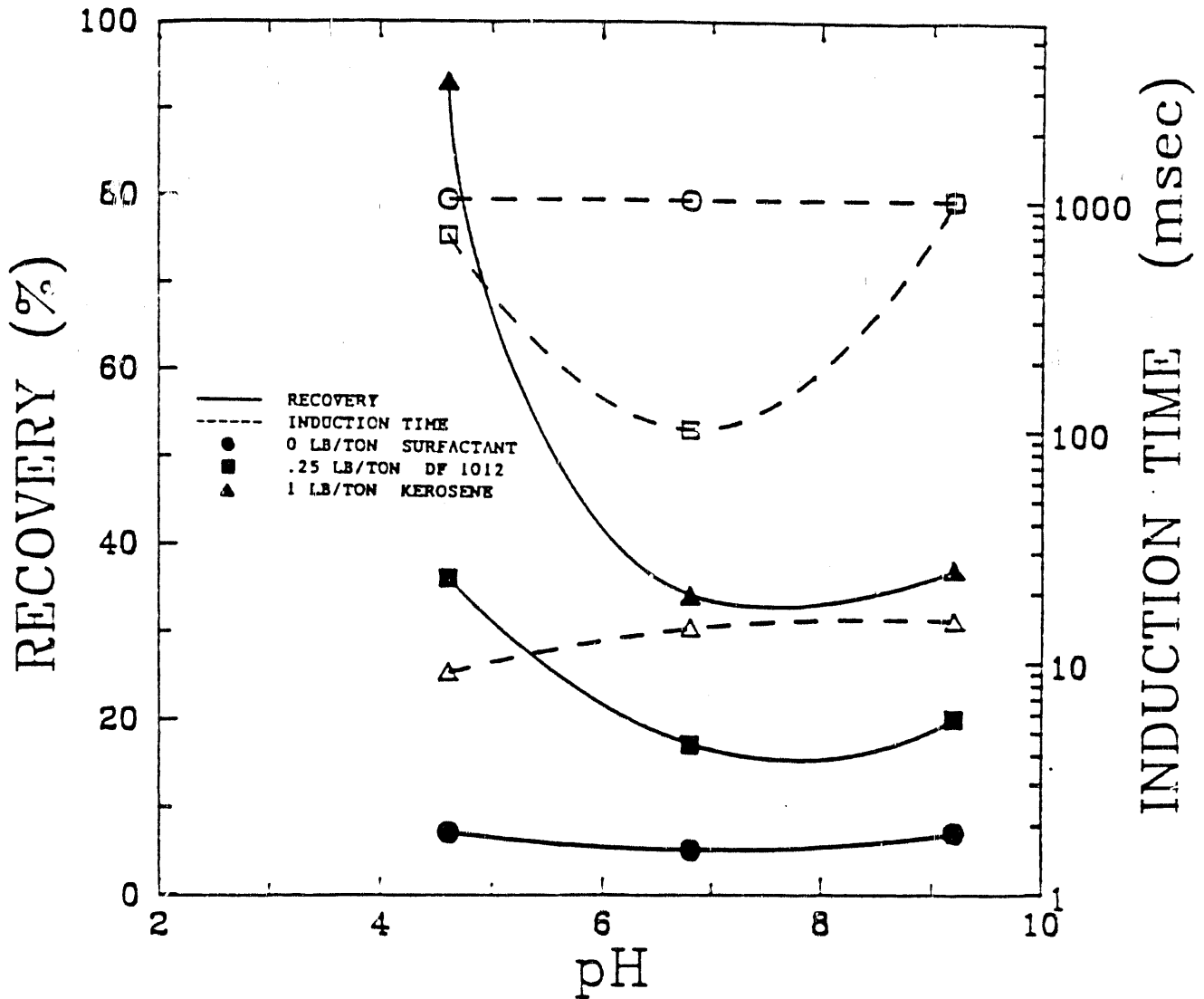


Figure 3. Microflotation recovery and induction time for Pittsburgh No. 8 coal pyrite in buffered solutions in the absence and presence of flotation surfactants. Flotation recovery: - - - -; Induction time: - - - -; Surfactants: ●, ○ - none; ▲, △ - 1 lb/ton kerosene; ■, □ - 0.25 lb/ton Dowfroth 1012.

COAL AND MINERAL PYRITE
 DOWFROTH 1012 + KEROSENE (.25 lb./ton)
 FLOTATION TIME = 2 min.

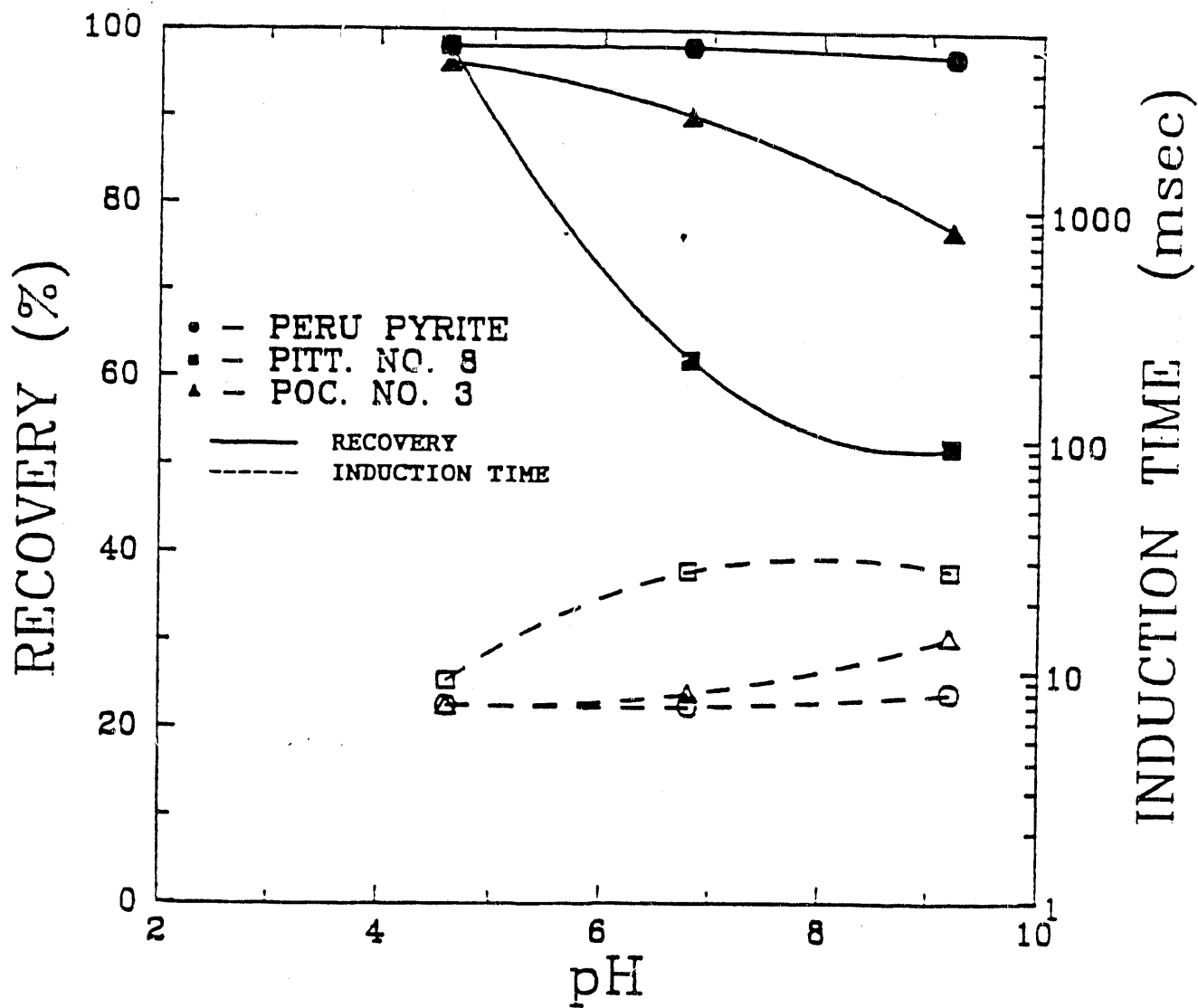


Figure 4. Various pyrite samples in buffered solutions containing 0.25 lb/ton kerosene and 0.25 lb/ton Dowfroth 1012. Flotation recovery: - - - - -; Induction time: - - -; Sample: O - Peru mineral pyrite; Δ - Pocahontas No. 3 coal pyrite; \square - Pittsburgh No. 8 coal pyrite.

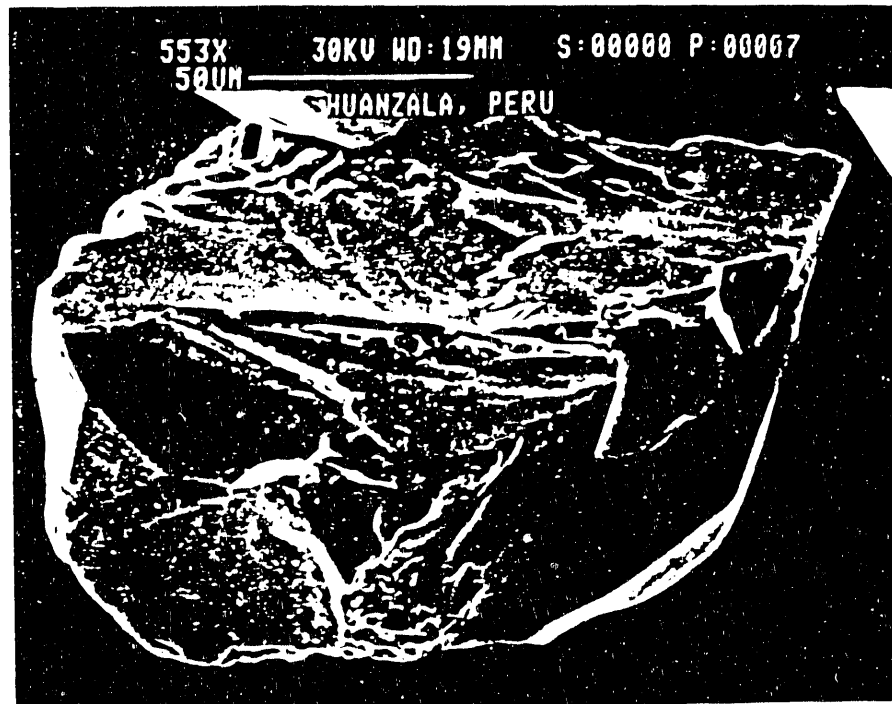
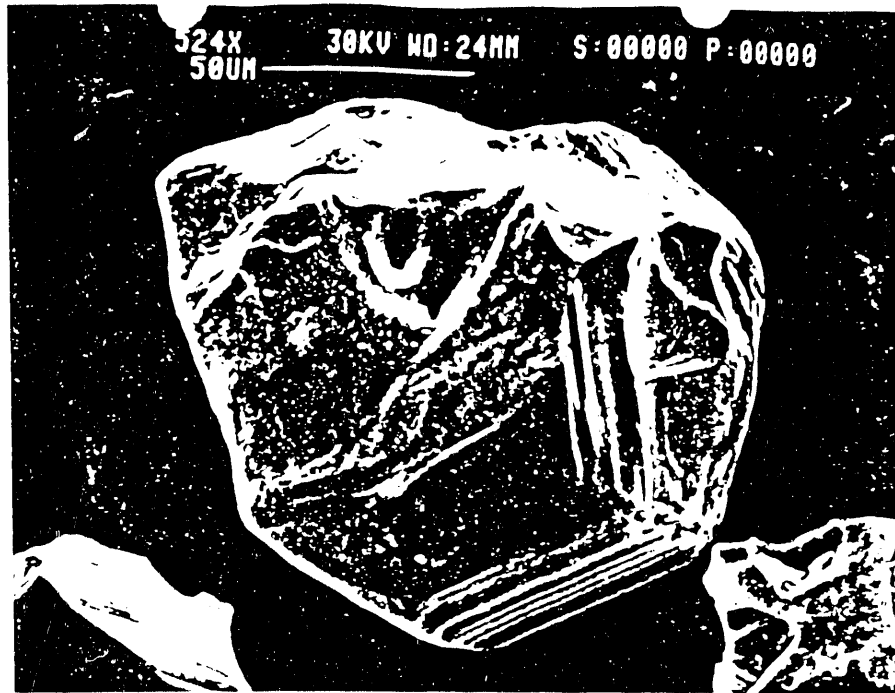


Figure 5. SEM photomicrographs of microflotation float product of Peruvian mineral pyrite.

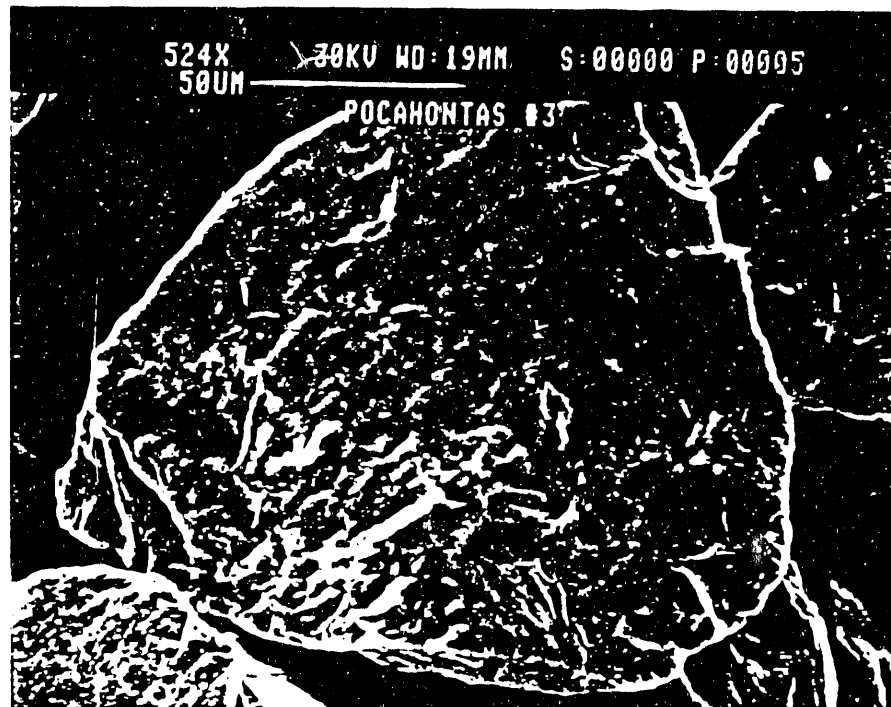
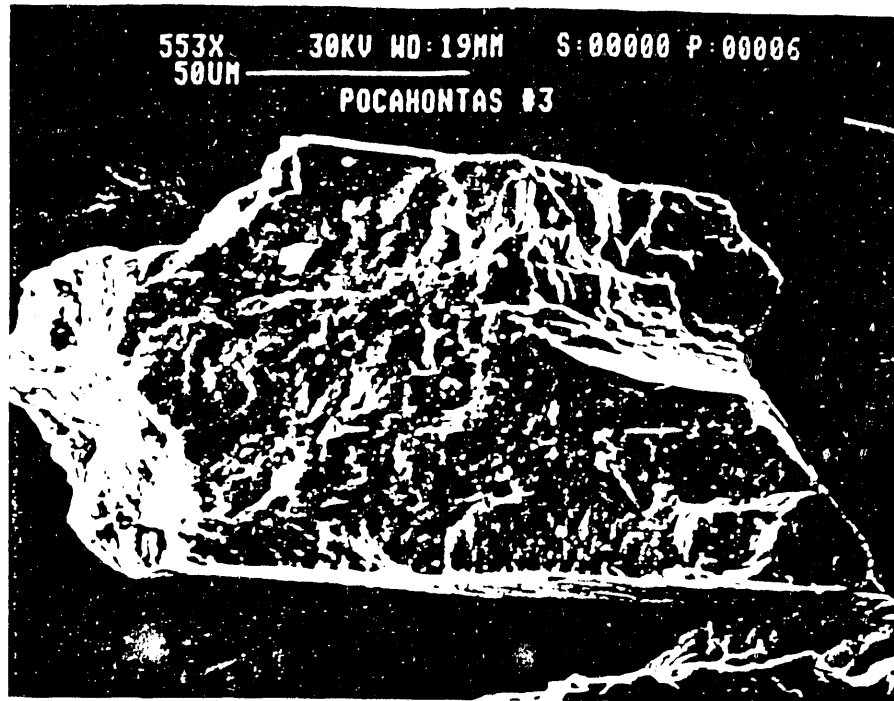


Figure 6. SEM photomicrographs of microflotation float product of Pocahontas No. 3 coal pyrite.

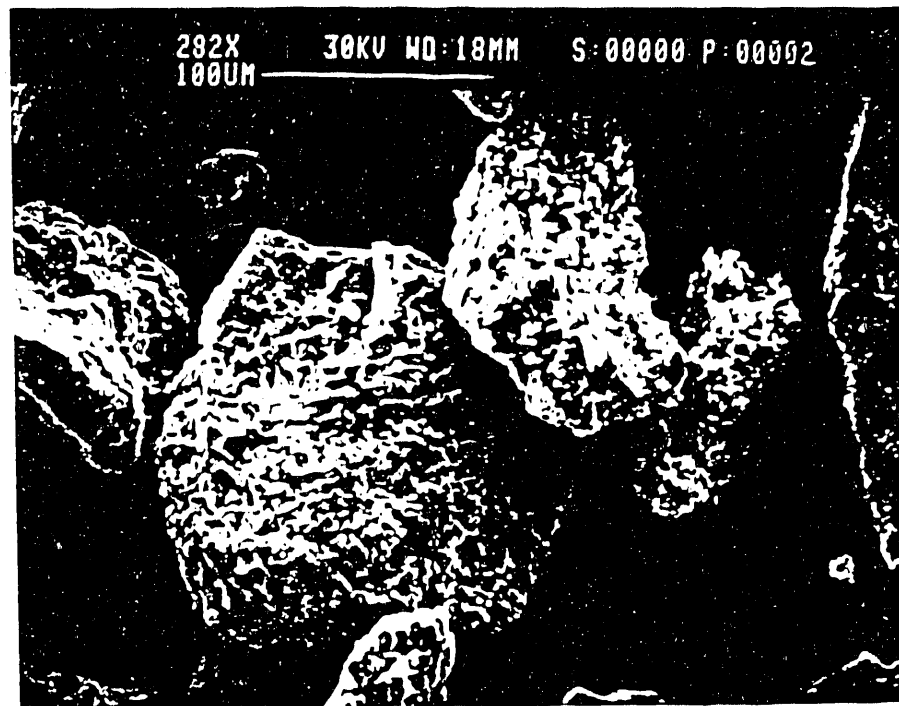
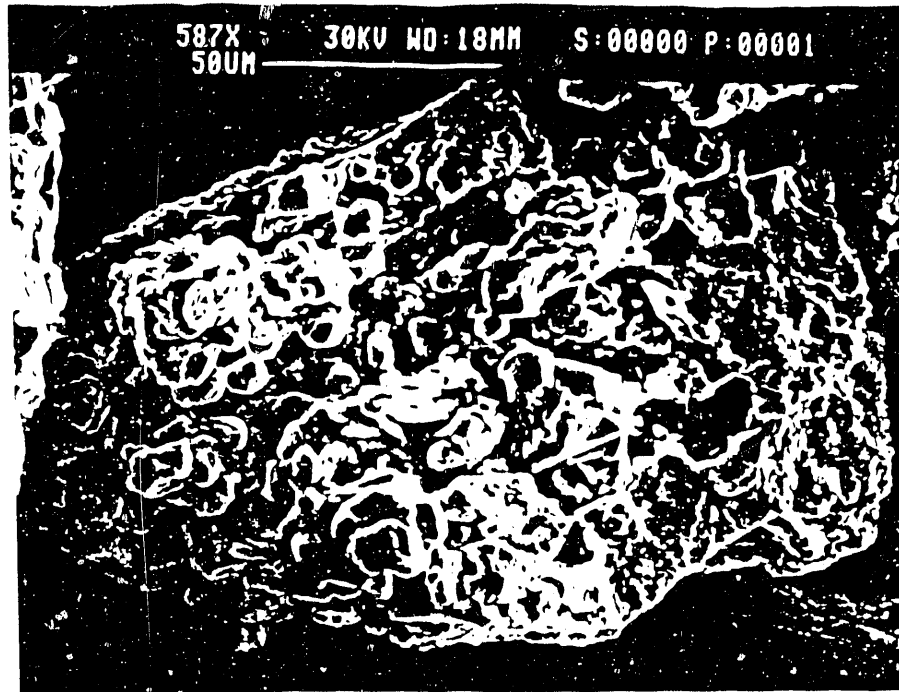


Figure 7. SEM photomicrographs of microflotation float product of Pittsburgh No. 8 coal pyrite.

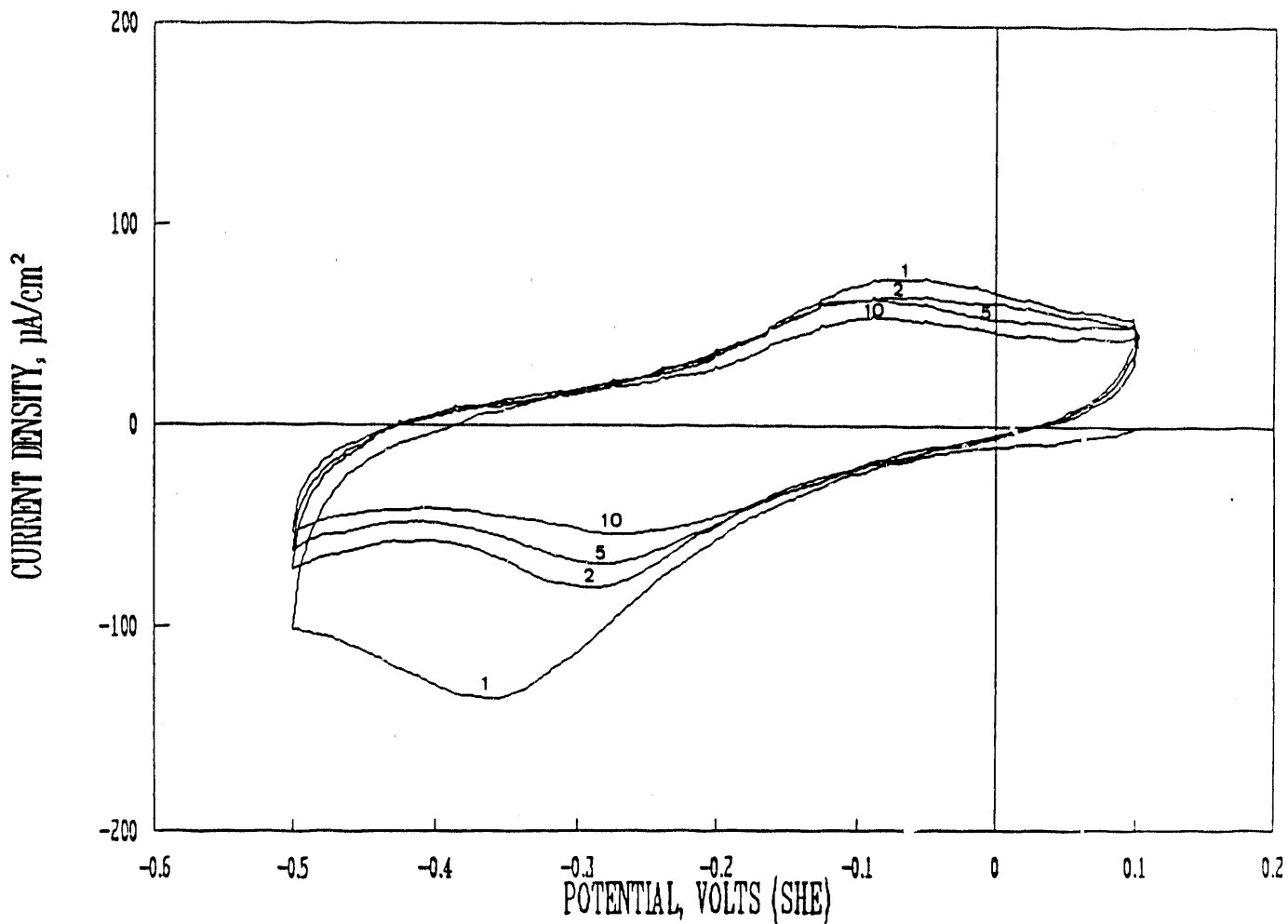


Figure 8. Cyclic voltammograms of a stationary Peruvian mineral pyrite electrode in pH 9.2 solution at 20mV/sec. Cycle number shown on the respective curve.

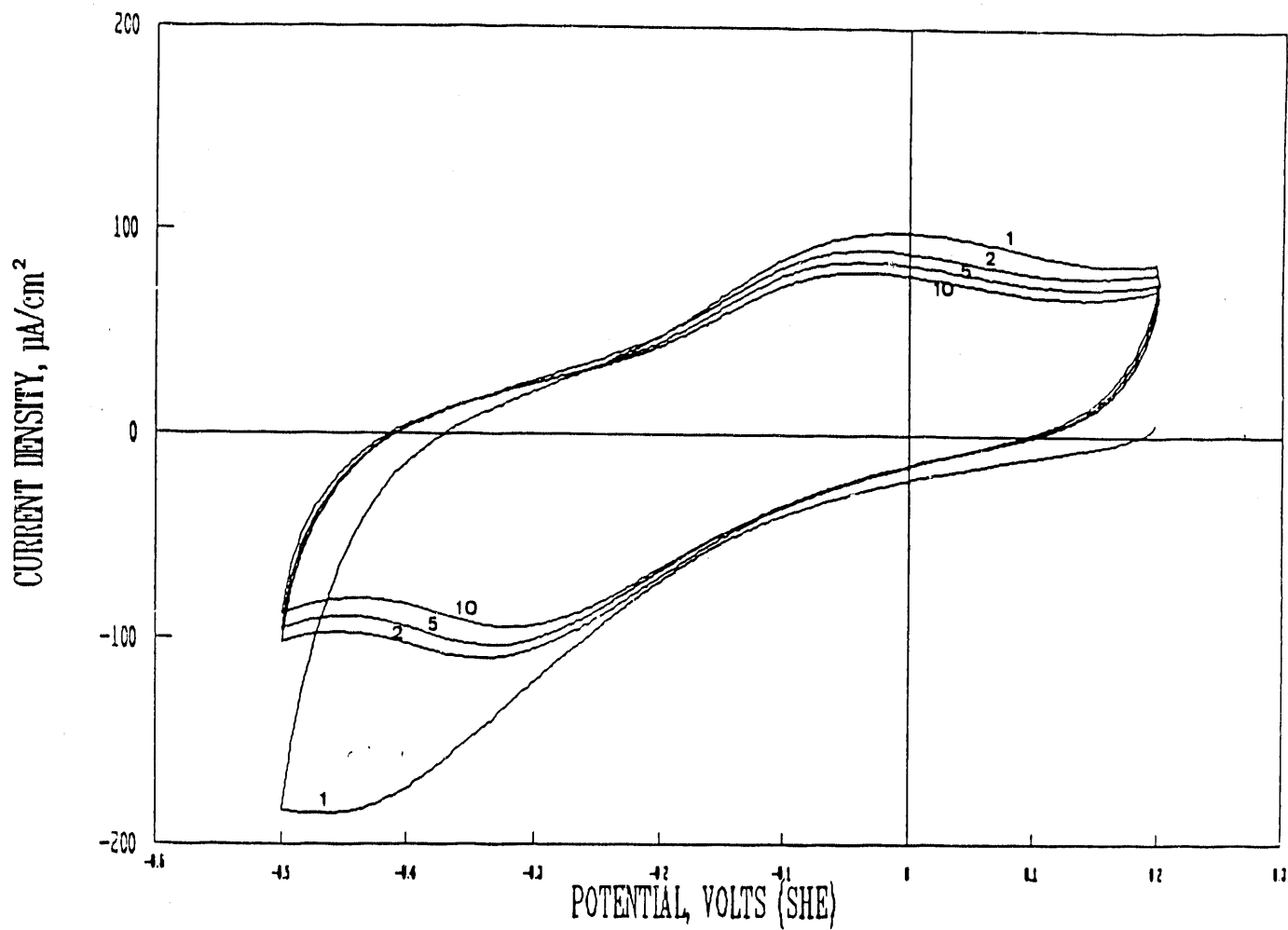


Figure 9. Cyclic voltammograms of a stationary Pocahontas No. 3 coal pyrite electrode in pH 9.2 solution at 20mV/sec. Cycle number shown on the respective curve.

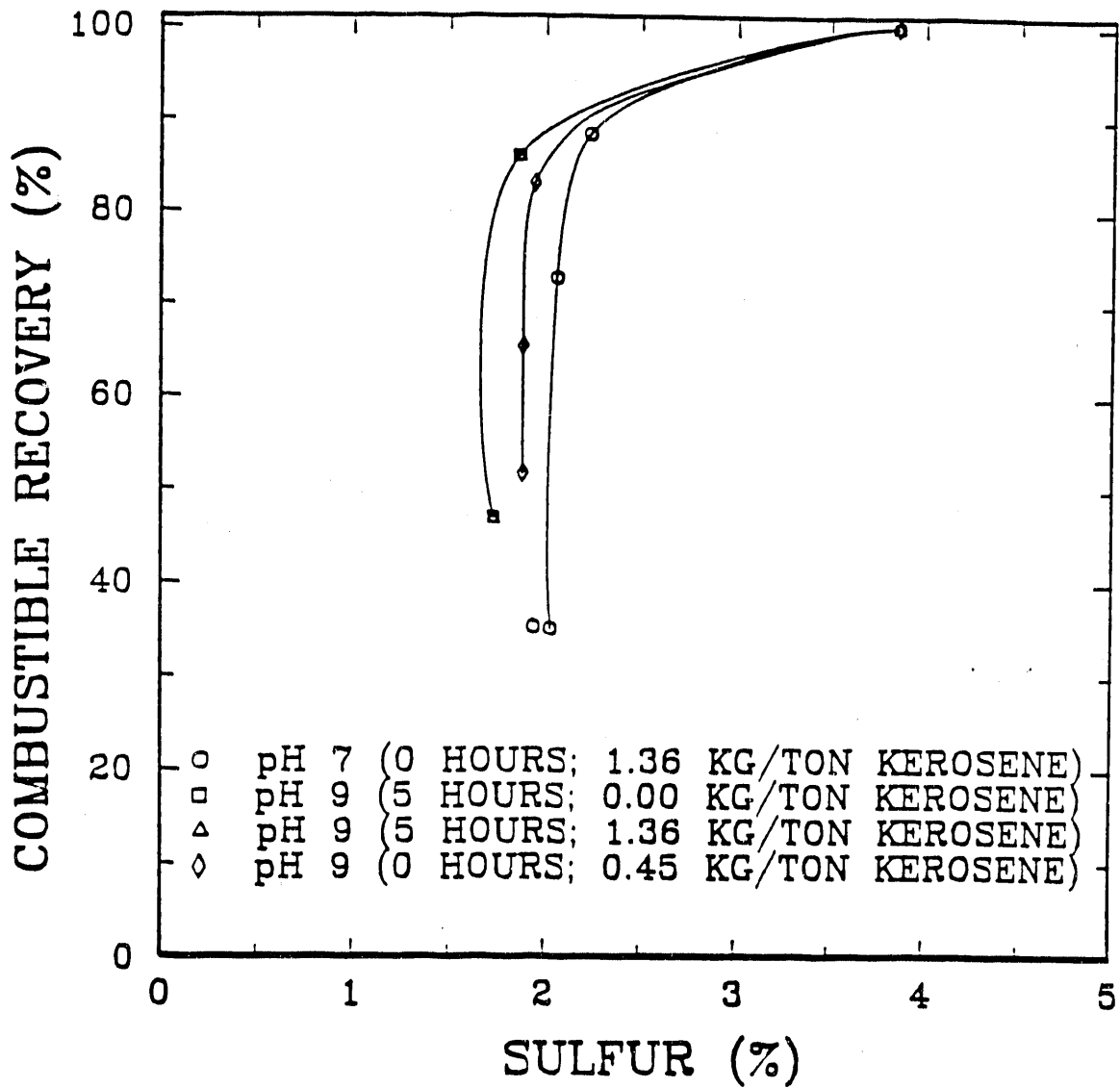


Figure 10. The effect of pH and conditioning time on the recovery-sulfur grade curve for a run-of-mine Pittsburgh No. 8 seam coal.

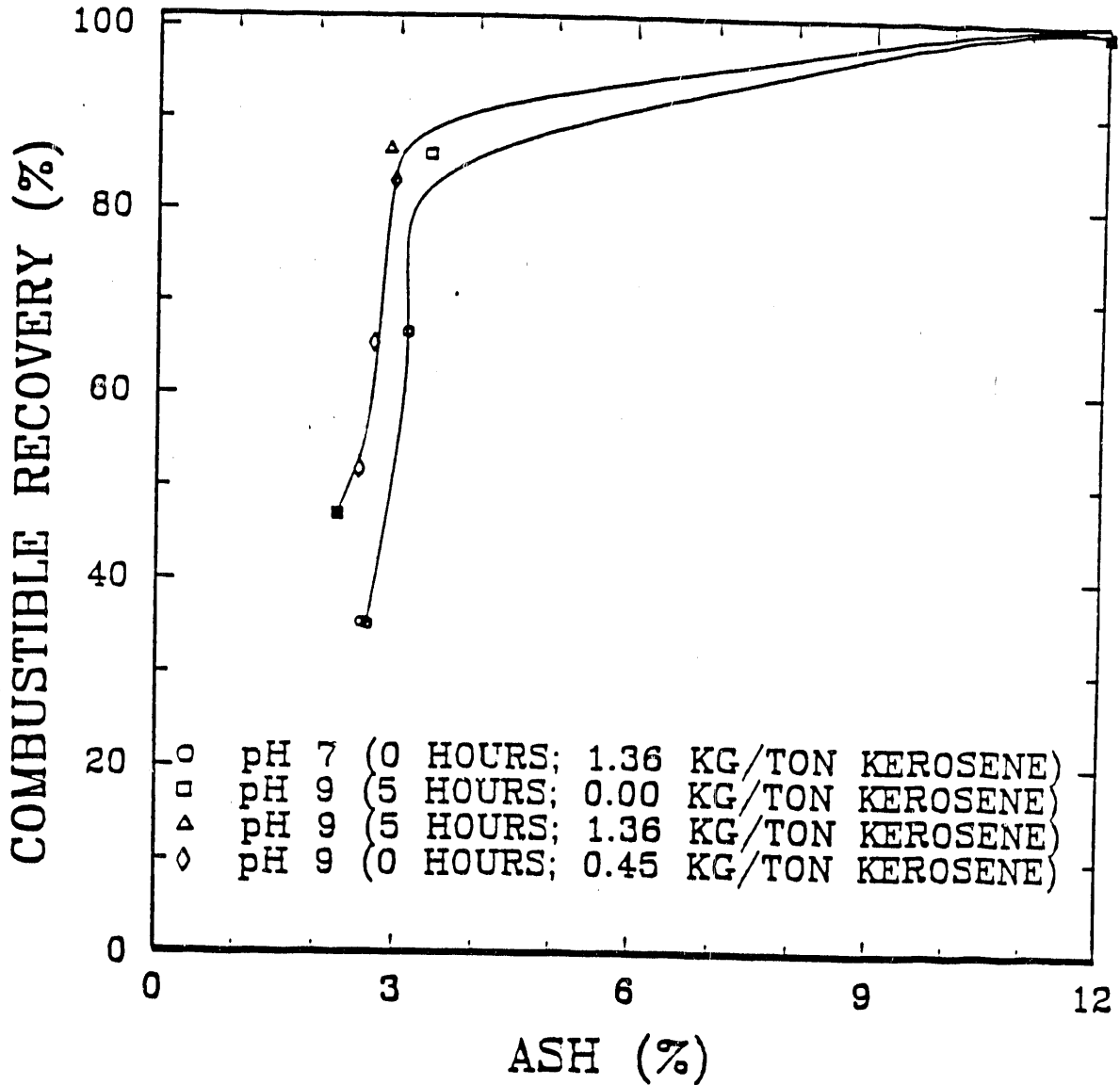


Figure 11. The effect of pH and conditioning time on the recovery-ash grade curve for a run-of-mine Pittsburgh No. 8 seam coal.

TABLE I. The effect of pH and conditioning time upon the recovery-grade curve for a run-of-mine Pittsburgh No. 8 seam coal.

Yield	31.83	31.91	66.60	81.24
Recovery	35.07	35.23	72.81	88.34
Product Ash	2.65	2.58	3.12	3.86
Reject Ash	15.84	16.05	27.88	45.05
Product Sulfur	2.03	1.94	2.06	2.23
Reject Sulfur	5.21	5.38	7.80	11.96
pH	7.0			
Conditioning Time	0.0 hours			

Feed Rate = 12, 22.5, 32, 12 gm/min

Wash Water Rate = 500 ml/min

Aeration Rate = 1300 cc/min

Frother Rate = 0.45 kg/ton

Kerosene Addition = 1.36 kg/ton

Residence Time was fixed at 5 minutes for all tests

Feed Size = -325 mesh

TABLE II. The effect of pH and conditioning time upon the recovery-grade curve for a run-of-mine Pittsburgh No. 8 seam coal.

Yield	76.24	59.48	46.94
Recovery	83.00	65.41	51.68
Product Ash	2.95	2.71	2.54
Reject Ash	36.21	24.48	19.40
Product Sulfur	1.94	1.88	1.88
Reject Sulfur	8.46	6.55	5.65
pH	9.0		
Conditioning Time	0.0 hours		

Feed Rate = 5.89, 12.51, 13 gm/min

Wash Water Rate = 500 ml/min

Aeration Rate = 1250 cc/min

Frother Rate = 1.71, 1.54, 1.48 kg/ton

Kerosene Addition = 0.45 kg/ton

Feed Size = -325 mesh

The sample was also ground at pH 9

TABLE III. The effect of pH and conditioning time upon the recovery-grade curve for a run-of-mine Pittsburgh No. 8 seam coal.

Yield	78.73	42.59	79.81	49.34
Recovery	86.00	46.91	86.64	53.60
Product Ash	3.39	2.27	2.89	2.56
Reject Ash	41.80	17.95	40.83	17.85
Product Sulfur	1.86	1.73	1.88	1.84
Reject Sulfur	9.63	4.97	9.33	5.02
pH	9.0	9.0	9.0	9.0
Conditioning Time (hours)	5.0	5.0	5.0	5.0
Kerosene Addition (kg/ton)	0.00	0.00	1.36	1.36

Feed Rate = 5.74, 15.73, 5.58, 22.05 gm/min

Wash Water Rate = 500 mL/min

Aeration Rate = 1200 cc/min

Frother Rate = 1.75, 1.31, 1.77, 0.61 kg/ton

Feed Size = -325 mesh

The sample was also ground at pH 9 prior to conditioning

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