#3.

Aqueous Biphasic Extraction for Processing of Fine Coal

Grant No. DE-FG22-96 PC96211

Semi-Annual Report

Reporting Period Start Date: 04/01/98

Reporting Period End Date: 10/01/98

Principal Author: K. Osseo-Asare, Professor of Metallurgy

Date Report was issued: 05/24/1998

DOE Award Number: DE-FG22-96 PC96211

**Submitting organization: Metals Science and Engineering Program
Department of Materials Science and Engineering
209 Steidle Building
Penn State University
University Park, PA 16802**

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Ever-stringent environmental constraints dictate that future coal cleaning technologies be compatible with micron-size particles. This research program seeks to develop an advanced coal cleaning technology uniquely suited to micron-size particles, i.e., aqueous biphasic extraction. The partitioning behavior of pyrite in aqueous biphasic systems and the effect of some surfactants were studied. The partition of pyrite was highly dependent upon the pH in the system; below pH 5, the particles transferred preferentially to the upper polymer-rich phase. Xanthate addition improved the yield of pyrite in the top phase at all pH values. On the other hand, addition of sodium dodecyl sulfate (SDS) or oleic acid had no effect.

TABLE OF CONTENTS

Abstract.....	3
List of Figures	5
List of Tables	6
Executive Summary	7
Introduction.....	7
Results and Discussion	9
Conclusions.....	11
References	11

LIST OF FIGURES

- Figure 1. Physicochemical basis of particle partitioning in aqueous biphasic systems.... 13
- Figure 2. Effect of pH on pyrite partitioning in the PEG-2000/Na₂SO₄/H₂O system.... 14
- Figure 3. Effect of pH on pyrite partitioning in the PEG-2000/Na₂SO₄/H₂O system in the presence of xanthate (1×10^{-3} M). 15
- Figure 4. Effects of SDS and oleic acid on the partition of pyrite in the PEG-2000/Na₂SO₄/H₂O system (SDS: 3.5×10^{-4} M, oleic acid: 1×10^{-4} M). 16

LIST OF TABLES

Table 1. Effect of xanthate on pyrite partitioning in the PEG-2000/ Na_2SO_4 / H_2O system.	17
--	----

EXECUTIVE SUMMARY

The objective of this research project is to develop an aqueous biphasic extraction process for the treatment of fine coals. Aqueous biphasic extraction is an advanced separation technology and it relies on the ability of an aqueous system consisting of a water-soluble organic polymer and an inorganic salt to separate into two immiscible aqueous phases. Differences in the hydrophobic/hydrophilic properties of particulates can then be exploited to effect selective transfers to either the top polymer-rich phase, or the bottom salt-rich phase. The goal of this experimental program is to identify process conditions that optimize the selective transfer of coal into the top phase while retaining the mineral matter in the bottom phase. An additional goal is to develop an improved coal-pyrite separation technique based on aqueous biphasic extraction.

The partitioning behavior of pyrite in aqueous biphasic systems was studied, including the effects of some surfactants. The partition of pyrite was highly dependent upon pH, with preferential transfer to the top polymer-rich phase below pH 5. Xanthate addition improved the yield of pyrite in the top phase under all pH conditions. However, sodium dodecylsulfate (SDS) and oleic acid had no effect on the partitioning behavior of pyrite.

INTRODUCTION

Coal represents the largest source of fossil energy in the U.S. This resource also represents the most readily accessible and socially acceptable substitute for oil and natural gas. In response to the stipulations of the Clean Air Act (1), advanced coal cleaning technologies are needed in order to more efficiently eliminate unacceptable levels of ash and sulfur from the run-of-mine coal prior to combustion. The ability to achieve mineral matter liberation from coal is fundamental to all separation techniques that seek to produce super-clean coal. It has been concluded from the microscopic examination of a wide variety of U.S. coals that, in many cases, grinding to 10 μm or below may be necessary in order to achieve the necessary liberation (2). It is clear, therefore, that future advanced coal cleaning technologies must be capable of accommodating micron size particles.

Large quantities of fine coals already exist in the rejects discharged into waste ponds. These fine coals are a result of the current highly mechanized production practices of continuous and longwall mining. As a result of the nonselectivity of cutting machines and the exploitation of higher ash/sulfur seams, these coal fines are characterized by high contents of mineral matter. These coal fines must therefore be cleaned in order to produce a salable product. Unfortunately, conventional coal cleaning techniques are not

effective in treating such fine coals. The result is that large amounts of fine coals are discharged into refuse ponds, even though this material represents a potential source of energy. The proliferation of such waste ponds is no longer environmentally acceptable.

This project seeks to investigate the feasibility of separating pyrite and mineral materials from fine coal by using aqueous biphasic extraction. Although aqueous biphasic systems have been known for more than 100 years, it was only in the mid 1950s that their potential use as separation media was recognized. Albertsson who pioneered the separation of microbial cells, cell organelles, and virus (3) performed the initial work. In recent years, interest in aqueous biphasic extraction has broadened to applications in the commercial-scale separation of proteins (5), as well as separation of metal ions (6), ultrafine particles (7), and organics (8). Chaiko et al. used aqueous biphasic extraction to remove radioactive residue from soil (4, 9).

It is possible to form a two-phase system in certain polymer/inorganic salt/water mixtures. When the concentrations of the salt and polymer exceed certain limits, the aqueous system separates into two immiscible phases, in which the top phase is polymer-rich and the bottom phase is enriched in salt. Aqueous biphasic extraction is very similar to conventional solvent extraction. Just like the organic solvent/water two-phase systems, the top phase of the aqueous biphasic system is more hydrophobic, and the bottom phase is more hydrophilic. The hydrophobic/hydrophilic character of the particle surface determines the partitioning of the particles into either the top more hydrophobic phase or the bottom more hydrophilic phase. Thus, differences in the surface chemistry of particles can be exploited for selective separations. It can be expected that the partitioning behavior of particles in aqueous biphasic systems will also be significantly affected by surfactants because these reagents can change the surface properties of particles through adsorption.

Compared with conventional organic-solvent-based liquid-liquid extraction, aqueous biphasic extraction is especially attractive for waste treatment applications, because it avoids the use of an organic solvent which itself is a possible pollutant. In addition, the polymers used in aqueous biphasic systems are generally inexpensive, nontoxic, and biodegradable (7). The aqueous biphasic systems can be recycled with the effective separation of particulates and solution. For separation of colloid particles, this process possesses another advantage compared with traditional separation processes such as flotation and flocculation because it does not have a low limit of particle size; it can even be used to separate metal ions (6).

In order to separate fine particles by aqueous biphasic extraction, it is necessary to understand the partitioning behavior of particles in aqueous biphasic systems. Because this process is greatly dependent upon the surface properties of the particles, it is of interest to study the effects of surfactants, since these reagents can modify the surface

properties of particles. In this reporting period, we studied the partitioning behavior of pyrite in the PEG/sulfate/water aqueous biphasic system, with and without surfactant addition.

RESULTS AND DISCUSSION

Surface Energy and Particle Partition

The physicochemical basis for particle partitioning in an aqueous biphasic system can be understood by considering the interfacial energy between a solid particle and the surrounding aqueous phase, as shown in Figure 1 (1). In this diagram, γ_{P-L1} , γ_{P-L2} , and γ_{L1-L2} represent the interfacial energy of the solid particle/top phase (Phase 1), particle/bottom phase (Phase 2), and top phase/bottom phase, respectively. If the particle shows both hydrophilic and hydrophobic tendencies, which means that the difference between γ_{P-L1} and γ_{P-L2} is very small, then Equation 1 will be satisfied, and the particles will stay at the interface. Otherwise, the solid will transfer to either the top or bottom phase, depending upon the interfacial energy between the solid and the liquids, as shown in Figure 1.

$$\left| \frac{\gamma_{P-L1} - \gamma_{P-L2}}{\gamma_{L1-L2}} \right| \leq 1 \quad (1)$$

Effect of pH

In the PEG-2000/Na₂SO₄/H₂O system (Figure 2), almost all the pyrite stayed in the bottom phase for pH 9-13. For pH 5-8, practically all the solid particles distributed to the interface and there was little solid material in the top and bottom phases. Because the interface area for the aqueous biphasic system in the separatory funnel was too small to support all the pyrite (0.5 g) at the interface, some particles settled down along the glass wall and went into the bottom phase or stayed at the bottom of separatory funnel. In this case, for mass balancing, pyrite at the interface was combined with pyrite in the bottom phase. When the pH fell below 5, all pyrite went into the top phase and the bottom phase was very clear. For all pH conditions, there was always some pyrite at the interface.

It is well known that the oxidation of pyrite in aqueous solution depends on the oxidation condition and the pH of the solution. In alkaline solution, the oxidation of pyrite (10) is as expressed in Equation 2:

On the other hand, the oxidation reaction of pyrite in acidic media is suggested as (11):

After the pyrite surface is oxidized, the surface reaction products determine the resulting interfacial properties. Because $\text{Fe}_{1-x}\text{S}_2$ is Fe-deficient, it is more hydrophobic than FeS_2 , while FeOOH is more hydrophilic than FeS_2 . When the pH in the PEG/salt/ H_2O system exceeds pH 9, the FeOOH sites predominate over the $\text{Fe}_{1-x}\text{S}_2$ sites and the pyrite surface is more hydrophilic. The interfacial energy, $\gamma_{\text{P-L1}}$ increases when the surface becomes more hydrophilic and $\gamma_{\text{P-L2}}$ decreases at the same time. After 2 hours conditioning, the difference between $\gamma_{\text{P-L1}}$ and $\gamma_{\text{P-L2}}$ increases enough to make the particles go into the bottom phase. When pH is less than 5, after conditioning, the fraction of the $\text{Fe}_{1-x}\text{S}_2$ sites on the pyrite surface becomes relatively high and the surface increases in hydrophobicity. The interfacial energy $\gamma_{\text{P-L1}}$ is then less than $\gamma_{\text{P-L2}}$ and the condition $|\gamma_{\text{P-L1}} - \gamma_{\text{P-L2}}| > \gamma_{\text{L1-L2}}$ is satisfied, so that pyrite transfers to top phase. Between pH 5 and pH 9, the concentrations of both protons and hydroxide ions in the system are relatively low, which make the oxidation reaction of pyrite surface very slow. Although the pyrite surface changes, the values of $\gamma_{\text{P-L1}}$ and $\gamma_{\text{P-L2}}$ vary little and the difference between $\gamma_{\text{P-L1}}$ and $\gamma_{\text{P-L2}}$ is still lower than $\gamma_{\text{L1-L2}}$ so that pyrite stays at the interface.

Effect of Xanthate

The xanthates are the most widely used collectors in pyrite flotation. Xanthates adsorb on pyrite to form Fe(III) xanthate or Fe(III) dixanthate compounds which play an important role in controlling the flotation behavior. Theoretically calculations (12) indicate that different types of Fe(III) xanthate compounds can be formed in a broad range of pH values (e.g., pH 2-10). The partitioning behavior of pyrite in the PEG-2000/ Na_2SO_4 / H_2O system in the presence of ethyl xanthate is shown in Table 1 and Figure 3. It can be seen from Table 1 that, with 1×10^{-5} M xanthate and pH ~11.5, there was only a slight increase in pyrite transfer to the top phase. However, when xanthate concentration increased to 1×10^{-3} M, almost all pyrite went into the top phase.

These results indicate that, as in conventional flotation systems, ethyl xanthate is capable of adsorbing on pyrite in aqueous biphasic systems. The hydrophilic thio group of xanthate bonds with the Fe atoms on the pyrite surface, and the hydrophobic ethyl group extends into the surrounding solution. Through this process, the pyrite surface acquires a hydrophobic layer, with a resulting net increase in the hydrophobicity of the solid surface. Consequently, the interfacial energy, $\gamma_{\text{P-L1}}$ decreases while $\gamma_{\text{P-L2}}$ increases and the condition $|\gamma_{\text{P-L1}} - \gamma_{\text{P-L2}}| > \gamma_{\text{L1-L2}}$ is satisfied, so that pyrite goes into the top phase.

Effects of SDS and Oleate

Figure 4 illustrates the partitioning behavior of pyrite in the PEG-2000/Na₂SO₄/H₂O system in the presence of SDS (3.5×10^{-4} M) and oleic acid (1×10^{-4} M). Comparing this diagram with the results in Figure 2, it can be seen that addition of SDS or oleic acid had no effect on partitioning behavior. It is well known that SDS and oleic acid can only adsorb physically on the surface of pyrite in aqueous systems (13). Apparently, in aqueous biphasic systems, the ionic strength and the concentration of PEG are both so high that the adsorption of SDS and oleic acid on pyrite surface is prohibited. As a result, the surface of pyrite remains unchanged after addition of SDS and oleic acid; correspondingly, the partitioning behavior of pyrite stays the same.

CONCLUSIONS

The experimental results demonstrate that the partitioning of pyrite is highly dependent upon pH. Almost all the pyrite stayed in the bottom phase for pH 9-13 and in the bottom phase at pHs below 5. Between pH 5 and 8, almost all the pyrite distributed to the interface and there was little pyrite in the top and bottom phases. The presence of xanthate significantly enhanced pyrite transfer to the top phase. With 1×10^{-3} M xanthate, almost all pyrite went into the top phase, irrespective of the pH. The addition of SDS or oleic acid had no significant effect on the partitioning behavior of pyrite, a reflection of the physical nature of the adsorption of these reagents.

REFERENCES

1. Asst. Sec. Of State for Fossil Energy, *U. S. Department of Energy, Clean Coal Technology: The New Coal Era*, June, 1990
2. M. J. Mankosa, G. T. Adel, and R. H. Yoon, *Powder Tech.*, 1986, 49: 75
3. P. A. Albertsson, *Partition of Cell Particles and Macromolecules*, 3rd. ed., Wiley-Interscience: New York, 1986
4. D. J. Chaiko, R. Mensah-Biney, C. J. Mertz and A. Rollins, *Sep. Sci. Technol.*, 1993, 28: 765
5. H. Walter, D. E. Brooks and D. Fisher Eds., *Partitioning in Aqueous Two-Phase Systems*, Academic Press: New York, 1985
6. R. D. Rogers, A. H. Bord and C. B. Bauer, *Sep. Sci. Technol.*, 1993, 28(5): 1091
7. K. P. Ananthapadmanabhan and E. D. Goddard, *Process for the Separation of Solid Particulate Matters*, U. S. Patent 47,225,358, 1987
8. D. J. Chaiko et al., in *Proceeding 14th Annual Army Environmental R&D Symposium*, USATHAMA Report CETHA-TE-TR-90055, p. 305, 1989
9. D. J. Chaiko, Y. Vojta and M. Takenchi, *Sep. Sci. Technol.*, 1995, 30: 1123

10. V. S. T. Ciminell and K. Osseo-Asare, *Metall. Mater. Trans.*, **1995**, 26B: 209
11. D. Fornasiero, V. Eijt and J. Ralston, *Colloids and Surfaces*, **1992**, 62: 63
12. X.-H. Wang and K. S. E. Forssberg, *Int. J. Miner. Process.*, **1991**, 33:275
13. J. Leja, *Surface Chemistry of Flotation*, Plenum, New York, **1982**

Figure 1. Physicochemical basis of particle partitioning in aqueous biphasic systems

Fig. 2 Effect of pH on pyrite partitioning in the PEG-2000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system.

Fig 3 Effect of pH on pyrite partitioning in the PEG-2000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system in the presence of xanthate ($1 \times 10^{-3} \text{ M}$)

Fig. 4 Effects of SDS and oleic acid on the partition of pyrite in the PEG-2000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system (SDS: 3.5×10^{-4} M, oleic acid: 1×10^{-4} M).

Table 1 Effect of xanthate on pyrite partitioning in the PEG-2000/Na₂SO₄/H₂O system

#	pH	Xanthate conc. (M)	Y _t *	Y _b *
1	8.6	1×10 ⁻⁵	14.34	72.46
2	8.1	-	6.63	92.50
3	11.4	1×10 ⁻⁵	3.87	89.57
4	11.5	1×10 ⁻³	73.75	18.59
5	11.5	-	0.98	79.10

* Y_t: yield of pyrite in the top phase; Y_b: yield of pyrite in the bottom phase