

Aqueous Biphasic Extraction for Processing of Fine Coal

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ABSTRACT

Ever-stringent environmental constraints dictate that future coal cleaning technologies be compatible with micron-size particles. For super-clean coal production, the degree of liberation needed to separate coal from mineral matter, including pyrite, requires grinding to 10 μm or below. In addition, large amounts of fine coal are discharged to refuse ponds because current coal cleaning technology cannot adequately treat such finely divided materials. This research program seeks to develop an advanced coal cleaning technology uniquely suited to micron-size particles, i.e., aqueous biphasic extraction. This technique relies on the ability of an aqueous system consisting of a water-soluble organic polymer and an inorganic metal 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 upper polymer-rich phase, or the lower salt-rich phase. An experimental program is proposed involving phase diagram determination, phase separation rate measurements, partition measurements, and washing experiments.

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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 technique which relies on the ability of an aqueous system consisting of a water-soluble organic polymer and an inorganic metal 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 upper polymer-rich phase, or the lower salt-rich phase. The goal of this experimental program is to identify process conditions that optimize the selective transfer of coal into the upper polymer-rich phase while retaining the mineral matter in the lower salt-rich phase. An additional goal is to develop an improved coal-pyrite separation technique based on aqueous biphasic extraction. The experimental program involves phase diagram determination, phase separation rate measurements, partition measurements, and washing experiments.

Aqueous biphasic extraction is an advanced separation technique uniquely suited to the separation of micron-size particles. This method, which exploits differences in hydrophobicity and hydrophilicity, is also uniquely suited to coal separations from mineral matter since differences in the relative hydrophobicities of coal and mineral matter exist and can also be modified.

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 saleable 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.

Among the potential fine coal cleaning processes commonly cited in the literature are the following (3-6): (a) heavy media cyclone, (b) froth flotation, (c) selective flocculation, and (d) oil agglomeration. Froth flotation is the most well established of these techniques. This method is, however, not very responsive as particle size falls below 100 mesh (6). Recently, there has been a growing interest in selective oil agglomeration since, when applied to finely divided coals, this

technology appears to surpass the efficiency attainable with froth flotation (5,6). The oil agglomeration process has, however, been criticized for the need for heating (90-120°C, with heavy oils), the potential fire hazards (especially when the relatively volatile light oils are used), relatively high cost of oil, and the need for very high energy input (mixing) in order to effect phase separation (6). Finally, it has not yet been demonstrated that selective oil agglomeration can yield acceptable pyrite-coal separations (6). Thus, the search for efficient cleaning technologies for fine coals cannot be said to be over.

This research proposal seeks to investigate the feasibility of adapting for fine coal cleaning, a novel separation technique uniquely suited to micron size particles, i.e., aqueous biphasic extraction (ABE). This separation technique, initially developed in the mid 50s for microbial cell separations (7), has recently attracted considerable attention and is being investigated for a broad range of applications such as protein separations (7-9), metal ion separations (10), and separation of ultrafine inorganic particles (11). This technique relies on the ability of an aqueous system of an organic polymer and an inorganic salt to separate into two immiscible aqueous phases. The upper phase is enriched in the polymer whereas the lower phase is enriched in the inorganic salt; in each phase, the water content is in the 70-80 wt % range. This two-phase system has many of the characteristics of conventional solvent extraction oil/water systems. Thus, the extraction relies on the distribution of solutes or colloidal particles between the two immiscible phases. However, aqueous biphasic systems are especially attractive when considering waste treatment applications, since they avoid the use of an organic diluent, which is itself a possible source of pollution. Another attractive feature is that the water-soluble polymers that are utilized in aqueous biphasic formation are inexpensive, nontoxic, and biodegradable (11).

RESULTS AND DISCUSSION

Since selective aqueous biphasic extraction relies on differences in surface chemical properties, a major aspect of this work is to investigate the utility of promoters and depressants. Anticipating that the flotation and oil agglomeration literatures will provide valuable guidelines on potential candidate additives, a review of these literatures was initiated. Among the interesting candidate additives identified are organic polymers which serve as pyrite depressants, e.g., starches and dextrans. These polymers are characterized by the presence of a large number of polar functional groups in their molecular structures. These polar groups permit polymer adsorption on the solid surface; at the same time, the unattached hydrophilic groups are exposed to the aqueous phase. The net result is that the adsorption of starches and dextrans enhances the hydrophilicity of the solid surface and this results in flotation depression.

Oxidation, pH, dissolved mineral matter (Fe, Al, Mg, etc.), and humic acids can all influence the hydrophobicity/hydrophilicity of coal-mineral matter systems. Therefore an important aspect of this research will be to investigate the effects of these factors in aqueous biphasic extractions. Wettability techniques provide quantitative methods of assessing the hydrophobicity/hydrophilicity of surfaces. A contact angle goniometer system is being modified with a microsyringe attachment. A glass specimen cell, equipped with a flat optical wall has already been designed and built.

Batch partition experiments are to be conducted in order to assess the effects of: (a) biphasic composition, (b) solids pretreatment, (c) solids concentration, (d) solids particle size, and (e) temperature. The following types of solid materials will be utilized: model oxides (e.g.,

Fe₂O₃, Al₂O₃), silicates and clays (e.g., kaolinite), mineral pyrite, and coal. Mineral pyrite of high purity has been purchased. A portion of this material has been ground in preparation for these experiments.

Future work will involve four main types of experiments: (a) Phase diagram determinations, (b) Phase separation rate measurements, (c) Partition measurements, and (d) Washing experiments. These four types of experiments are fundamental to any attempt to develop a practical biphasic separation process. This is because: (a) In order to conduct a biphasic extraction, it is necessary to have a two phase system; (b) the rate of phase separation directly will control the throughput attainable with a practical continuous operation; (c) the particulate materials of interest must exhibit preferential partition between the two conjugate aqueous phase, otherwise no separation is possible; and (d) for economic reasons, excessive reagent losses must be avoided.

CONCLUSION

The review of the flotation and oil agglomeration literatures has revealed that candidate additives are available which may be judiciously exploited to control surface properties in aqueous biphasic systems. The stage is now set to commence systematic experiments.

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.*, **49**, 75 (1986).
3. R. R. Klimpel and P. T. Luckie, eds., Industrial Practice of Fine Coal Processing, SME-AIME (1988); S. K. Mishra and R. R. Klimpel, eds., Fine Coal Processing, Noyes (1987).
4. S. Chander, P. E. Richardson, and H. El-Shall, eds., Emerging Process Technologies for a Cleaner Environment, . (Littleton, CO: SME, 1992), 131-139.
5. C. E. Capes and R. J. Germain, in Physical Methods of Cleaning Coal, Y. A. Liu, ed., Marcel Dekker, New York, 1982, pp. 293-351.
6. V. P. Mehrotra, K. V. S. Sastry, and B. W. Morey, *Int. J. Miner. Process.*, **11**, 175 (1989).
7. P. A. Albertsson, Partition of Cell Particles and Macromolecules, 3rd. ed., Wiley-Interscience, New York (1986).
8. G. Johansson and F. Tjerneld, in Highly Selective Separations in Biotechnology, G Street, ed., Chapman and Hall, New York, 1994, pp. 55-85.
9. M.-R. Kula, in Enzyme Technology, Applied Biochemistry and Bioengineering, Vol. 2, L. B. Wingard, Jr., E. Katchalski-Katzier, and L. Goldstein, Eds., Academic Press, New York, p. 74 (1979).

10. T. I. Nifant'eva et al., *Russ. J. Inorg. Chem.*, 34, 707 (1989).
11. D. J. Chaiko, R. Mensah-Biney, C. J. Mertz, and A. Rollins, *Separ. Sci. Technol.*, 28, 765 (1993).