

Aqueous Biphasic Extraction for Processing of Fine Coal

**Grant No. DE-FG22-96 PC96211
Semi-Annual Report**

Reporting Period Start Date: 10/01/99

Reporting Period End Date: 04/01/00

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

Date Report was issued: 06/02/2000

DOE Award Number: DE-FG22-96 PC96211--07

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

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 fly ash in the PEG-2000 Na₂SO₄/H₂O system was studied and the solid in each fraction was characterized by CHN analysis (carbon content), X-ray diffraction (XRD; crystal component), and inductively coupled plasma spectrophotometry (ICP; elemental composition in the ash). In the pH range from 2 to 5, the particles separated into two different layers, i.e., the polymer-rich (top) and salt-rich (bottom) layers. However, above pH 5, the particles in the polymer-rich phase split into two zones. The percent carbon content of the solids in the upper zone (~80 wt%) was higher than that in the parent sample (63.2 wt%), while the lower zone in the polymer-rich phase had the same percent ash content as the original sample. The particles in the salt-rich phase were mainly composed of ash (with < 4 wt% carbon content). However, when the solid concentration in the whole system increased from 1 wt% to 2 wt%, this 3-fraction phenomenon only occurred above pH 10. XRD results showed that the main crystal components in the ash included quartz, hematite, and mullite. The ICP results showed that Si, Al, and Fe were the major elements in the fly ash, with minor elements of Na, K, Ca, Mg, and Ba. The composition of the ash in the lower zone of the polymer-rich phase remained almost the same as that in the parent fly ash. The largest amount of product (~60% yield) with the highest carbon content (~80 wt% C) was obtained in the range pH 6 - 9. Based on the experimental results obtained, a flowsheet is proposed for the beneficiation of high-carbon fly ash with the aqueous biphasic extraction process.

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
Publications Published/Submitted.	12

LIST OF FIGURES

Fig. 1	Effect of pH on the partition of fly ash in the PEG-2000/ $\text{Na}_2\text{SO}_4/\text{H}_2\text{O}$ system (solids content: 1 wt%).	13
Fig. 2	The carbon contents in each fraction (solids content: 1 wt%).	13
Fig. 3	XRD result of the parent sample (-400 mesh)	14
Fig. 4	XRD result of the sample in the upper zone of the polymer-rich phase at pH 12 (solids content: 1 wt%).	14
Fig. 5	XRD result of the sample in the lower zone of the polymer-rich phase at pH 12 (solids content: 1 wt%)	15
Fig. 6	XRD result of the sample in the salt-rich phase at pH 12 (solids content: 1wt%)	15
Fig. 7	Proposed flowsheet for aqueous biphasic extraction of high-carbon fly ash.. . . .	16

LIST OF TABLES

Table 1	Effect of pH on the partition of fly ash in the PEG-2000/Na ₂ SO ₄ /H ₂ O system (solids content: 2 wt%).	17
Table 2	Elemental composition of ash in the parent fly ash and several beneficiated samples.	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 the 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 fly ash in the PEG-2000/Na₂SO₄/H₂O system was studied and the solid in each fraction was characterized by a CHN analyzer (carbon content), XRD (crystal component), and ICP (elemental composition in the ash). In the pH range from 2 to 5, the particles separated into two different layers, i.e., the polymer-rich (top) and salt-rich (bottom) phases. However, above pH 5, the particles in the polymer-rich phase divided into two zones. The percent carbon content of the solids in the upper zone (~80 wt%) was higher than that in the parent sample (63.2 wt%), while the lower zone in the polymer-rich phase had the same percent ash content as the original sample. The particles in the salt-rich phase were mainly composed of ash (with < 4 wt% carbon content). However, when the solids concentration in the whole system increased from 1 wt% to 2 wt%, this 3-fraction phenomenon only occurred above pH 10. XRD results showed that the main crystal components in the ash included quartz, hematite, and mullite. The ICP-AES results showed that Si, Al, and Fe were the major elements in the fly ash, with minor elements of Na, K, Ca, Mg, and Ba. The composition of the ash in the lower zone of the polymer-rich phase remained almost the same as that in the parent fly ash. The largest amount of product (~60% yield) with the highest carbon content (~80 wt% C) was obtained in the range pH 6 - 9. Based on the experimental results in the report, a flowsheet is proposed for the beneficiation of high-carbon fly ash with the aqueous biphasic extraction process.

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.

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 50s that their potential use as separation media was recognized. Albertsson, who pioneered the separation of microbial cells, cell organelles, and virus performed the initial work (3). 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). 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).

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.

Fly ash, as a major coal combustion byproduct (CCB), is produced in the amount of 50 million tons/year in the USA (10). The utilization of fly ash is about 20%, most of this is used in the cement industry, as a road base, and as structural fills (11). In response to the Clean Air Act Amendment of 1990, low temperature combustion of coal is being carried out in order to reduce the emission levels of NO_x and SO_x . However, as a side effect of this new technology, the carbon content in fly ash is increased significantly. This limits the utility of fly ash as a construction material in the cement industry (12, 13). High amounts of carbon in fly ash that is used in concrete promote the undesirable adsorption of air-entraining admixtures in concrete (these admixtures are added in order to prevent cracking). It is necessary to separate the high carbon component from ash in fly ash. Also, beneficiated fly ash has potential applications as a raw material for the synthesis of mullite (10, 14), as fillers in the plastic industry (15), and as adsorbents (12, 16). Several beneficiation methods have been developed, such as froth flotation (17-22), density gradient centrifugation (23), and triboelectrostatic (24) processes. In this report, aqueous biphasic systems were employed as new separation media for the beneficiation of fly ash. The partitioning behavior of fly ash in polyethylene glycol (PEG)/salt/water aqueous biphasic systems was studied, and characterization of the solid fraction in each phase was carried out.

RESULTS AND DISCUSSION

Effect of pH on the Partitioning Behavior of Fly Ash

Fly ash was obtained from the Coal Utilization Laboratory, Penn State University. It was classified with ASTM certified screens, and the -400 mesh fraction was used in all the experiments. Figure 1 shows the effect of pH on the partitioning behavior of fly ash in the PEG-2000/Na₂SO₄/H₂O system (solids concentration: 1 wt%). In the pH range from 2 to 5, two solid fractions were obtained. The particles in the salt-rich phase were brown, while the particles in the polymer-rich phase were black. However, above pH 5, the particles in the polymer-rich phase separated into two zones. The upper zone was still black, while the newly formed lower zone was grayish. At pH 12, most of the fly ash was concentrated in the lower zone of the polymer-rich phase. With decrease in pH, the yield in the lower zone of the polymer-rich phase decreased; while the solid content in the upper zone increased simultaneously. However, the fraction of the solids that partitioned into the salt-rich phase was very low for the entire pH range investigated, from almost 0 wt% at pH 2 to ~6 wt% at pH 12.

When the amount of the added fly ash increased to 2 wt%, this 3-fraction phenomenon only happened above pH 10 (Table 1). Comparing the data in Figure 1 and Table 1, it can be seen that, the yields obtained at pH 12 with 2 wt% solids (i.e., 9.4 wt% for the upper zone of the polymer-rich phase, 81.4 wt% for the lower zone of the polymer-rich phase, and 9.3 wt% for the salt-rich phase) are similar to those obtained for the experiments conducted with 1 wt% solids. At pH 11, the yield in the upper zone of the polymer-rich phase increased to 39.6 wt%, while the yield in the lower zone of the polymer-rich phase decreased to 52.1 wt%. These two values were similar to the results at pH 7 when the amount of added fly ash was only 1 wt%. At pH 10, only two fractions of solids were obtained after phase separation. The yields in the salt-rich phase (6.2 - 9.3 wt%) was comparable to those obtained in the same pH range (pH 10 - 12) for the experiments with 1 wt% solids.

Characterization of the Solids in Each Fraction

Carbon Content. Figure 2 shows the carbon content in each of the fractions obtained in the above partitioning experiments. The particles in the salt-rich phase had a low carbon content, which satisfies the requirement for application in cement manufacture. Because the amounts of the samples in the salt-rich phase at pH 2 and 3 were too small for the carbon content measurement, data for these two pH values could not be included in Figure 2. However, from the trend shown in this plot, these samples are also expected to have low-carbon contents. In all the cases of 3-fraction partitioning, the solids in the upper zone of the polymer-rich phase had a carbon content of 80 wt%. This value was much higher than the C-content in the parent fly ash (63.2 wt%). In the case of the 2-fraction partition systems (pH < 5, Figure 2), the carbon content of the solids in the upper zone of the polymer-rich phase was almost the same as that in the parent fly ash. In terms of the mass balance, this was easy to understand because almost all the solid materials stayed in the polymer-rich phase, while the yield in the salt-rich phase was very small. For the 3-fraction partition systems (pH > 5), the carbon content of the solids in the lower

zone of the polymer-rich phase was intermediate between that of the upper zone and the salt-rich phase. With decrease in pH, the carbon content decreased from 66 wt% at pH 12 (almost the same as that in the parent fly ash) to 41 wt% at pH 6. Comparing Figure 2 with the yield results in Figure 1, it can be seen that the largest amount of product (~60% yield) with the highest carbon content (~80 wt% C) was obtained in the range pH 6 - 9.

XRD Results. The XRD results are shown in Figures 3-6. The diffractograms show that in the parent fly ash, quartz, mullite, and hematite are the main crystalline components (Figure 3). The intensities of the peaks coming from quartz and mullite are much stronger than those associated with hematite. The strong, broad peak may come from amorphous carbon. The several small peaks indicate that there are other crystalline components present, but at low amounts. After beneficiation with aqueous biphasic extraction, the solid in the upper zone of the polymer-rich phase only showed several weak peaks (identified as quartz and mullite) with a strong broad peak (amorphous carbon), as shown in Figure 4. This result indicates that there is only a small amount of crystalline components in this solid fraction, which is consistent with the carbon content results (Figure 2). The diffractogram of the solids in the lower zone of the polymer-rich phase (Figure 5) is very similar to that of the parent fly ash (Figure 3). Quartz, mullite, and hematite are identified as the main crystalline components. The strong, broad peak of amorphous carbon is also apparent. However, for the solids in the salt-rich phase (Figure 6), the peak of amorphous carbon is relatively weak when compared to the results for the other beneficiated solid samples and the parent fly ash. Similar to the result of the parent sample, quartz, hematite, and mullite are the main crystalline phases in this solid fraction. But the relative intensity of these peaks (i.e., compared to amorphous carbon) is stronger than that of other samples.

Elemental Analysis. Table 2 lists the elemental composition of the parent fly ash, as well as the corresponding results for the beneficiated samples at pH 10, 11, and 12 (solids content: 2 wt%). The data show that in both the parent and beneficiated samples, Si, Al, and Fe are the major elements in the ash (in agreement with the XRD results). The concentrations of K, Ca, and Mg were in the range of 1 - 2 wt%, with Na, Ba, Sr, and Mn content less than 1 wt%. After the aqueous biphasic extraction, the fly ash in the salt-rich phase had more Si, with less Ca, Fe, and Mg at the same time; other elements remained almost the same as in the parent samples. In contrast, the Si content of the fraction in the upper zone of the polymer-rich phase was reduced, and the concentration of Ca increased. There was no apparent change for the other elements. The solids in the lower zone of the polymer-rich phase had the same composition as the original samples. The reason for this trend is not very clear, and it needs further investigation, especially for the texture and morphology of the individual particles in each fraction.

Preliminary Flowsheet

Based on the above results, a preliminary flowsheet is proposed for the aqueous biphasic extraction of high carbon fly ash (Figure 7). After contacting the fly ash and aqueous biphasic solutions, the mixture is allowed to phase separate. For the condition of 3-fraction partition (e.g., pH 11 and 2 wt% fly ash), a carbon product will be obtained from the upper zone of the polymer-rich phase, and an ash product can be produced from

the salt-rich phase. The solid in the lower zone of the polymer-rich phase will be recycled to the mixing tank.

CONCLUSIONS

In order to improve the utility of fly ash, it is necessary to separate the carbon fraction from the fly ash to give a product with low carbon content. This report studied the partitioning behavior of fly ash in the PEG-2000/Na₂SO₄/H₂O system, then characterized the samples for carbon content, elemental composition, and mineralogy. In the pH range from 2 to 5, the particles partitioned to give two aqueous fractions when the solid content was 1 wt%. Above pH 5, the particles in the polymer-rich phase divided into two zones. The weight percent carbon content in the upper zone was higher than that in the parent sample, and the lower zone had almost the same ash content as the original sample. The particles in the salt-rich phase were mainly composed of ash. XRD results showed that the main crystal components in the ash included quartz, hematite, and mullite. The ICP results showed that Si, Al, and Fe were the major elements in the fly ash, with minor elements of Na, K, Ca, Mg, and Ba. The composition of the ash in the lower zone of the polymer-rich phase remained almost the same as that in the parent fly ash. Comparing Figure 2 with the yield results in Figure 1, it can be seen that the largest amount of product (~60% yield) with the highest carbon content (~80 wt% C) was obtained in the range pH 6 - 9. Based on the experimental results obtained, a flowsheet is proposed for the beneficiation of high-carbon fly ash with the aqueous biphasic extraction process.

REFERENCES

1. Asst. Sec. of State for Fossil Energy, *Clean Coal Technology.- The New Coal Era*, U. S. Department of Energy, June, **1990**.
2. M. J. Mankosa, G. F. 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: 1091.
7. K. P. Ananthapadmanabhan and E. D. Goddard, *Process for the Separation of Solid Particulate Matters*, U. S. Patent 4,725,358, **1987**.
8. D. J. Chaiko et al., in *Proceeding 14th Annual Army Environmental R & D Symposium*, 1989, p. 305.
9. D. J. Chaiko, Y. Vojta, and M. Takeuchi, *Sep. Sci. Technol.*, **1995**, 30: 1123.
10. X. Huang, J. Y. Hwang, and B. C. Mutsuddy, *Interceram*, **1995**, 44: 65.
11. S. Tyson and T. Blackstock, *Preprint of ACS Div. Of Fuel Chem.*, **1998**, 41: 587.
12. I. Kulaots, Y.-M. Gao, R. H. Hurt, and E. M. Suuberg, *Preprint of ACS Div. Of Fuel Chem.*, **1998**, 41: 980.

13. X. M. Song, J.-Y. Hwang, and X.-P. Liu, *Proc. 12th Intern. Symp. on Coal Combustion By-Product (CCB) Management and Use*, **1997**, VI: 30-1.
14. J.-Y. Hwang, X. Huang, and A. Hein, *JOM*, **1994**, May: 36.
15. X. Huang, J.-Y. Hwang, and J. M. Gillis, *Proc. 12th Intern. Symp. on Coal Combustion By-Product (CCB) Management and Use*, 1997, VI: 22-1.
16. U. M. Graham, J. G. Groppo, and T. L. Robl, *Preprint of ACS Div. Of Fuel Chem.*, **1998**, 41: 985.
17. J. G. Groppo, T. L. Robl, W. M. Lewis, and C. J. McCormick, *Miner. Metall. Proc.*, **1999**, 16(3): 34.
18. J. G. Groppo, T. L. Robl, U. M. Graham, and C. J. McCormick, *Mining. Eng.*, **1996**, 48(6): 51.
19. S. K. Kawatra, T. C. Eisele, and D. D. Banerjee, *Preprint 96-87, SME Annual Meeting and Exhibit*, Phoenix, AZ, **1999**, p. 1.
20. J. Groppo, U. Graham, T. Rohl, C. J. McCormick, S. Medina, and T. Edens, *Proc. 12th Intern. Symp. on Coal Combustion By-Product (CCB) Management and Use*, **1997**, V3: 82-1.
21. V. J. Hurst, and R. W. Styron, "Fly Ash Beneficiation Process", US Patent 4,121,945, **1978**.
22. J. Y. Hwang, "Fly Ash Beneficiation Process", US Patent 5,047,145, **1991**.
23. M. M. Maroto-Valer, D. N. Taulbee, and J. C. Hower, *Energy Fuels*, **1999**, 13: 947.
24. H. Ban, T. X. Li, J. C. Hower, J. L. Schaefer, and J. M. Stencel, *Fuel*, **1997**, 76: 801.

PUBLICATIONS PUBLISHED/SUBMITTED

1. K. Osseo-Asare and X. Zeng, **Aqueous Biphasic Extraction of Particulates: Controlling the Hydrophilic-Hydrophobic Balance for Separation**, in: K. C. Liddell and D. J. Chaiko (Eds.), *Metal Separation Technologies Beyond 2000*, The Minerals, Metals, and Materials Soc., Warrendale, PA, **1999**, pp. 347-356.
2. K. Osseo-Asare and X. Zeng, **Partition of Pyrite in Aqueous Biphasic Systems**, *Intern. J. Miner. Proc.*, **2000**, 58: 319-330.
3. X. Zeng and K. Osseo-Asare, **Partition of Pyrite and Hematite in Aqueous Biphasic Systems: Effects of pH and Surfactants**, *Colloids Surf.*, in press.

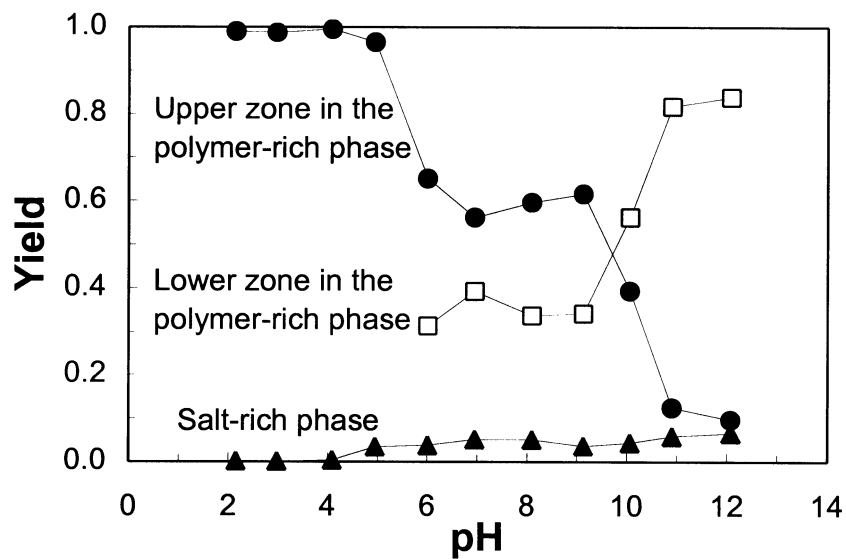


Fig. 1 Effect of pH on the partition of fly ash in the PEG-2000/Na₂SO₄/H₂O system (solids content: 1 wt%).

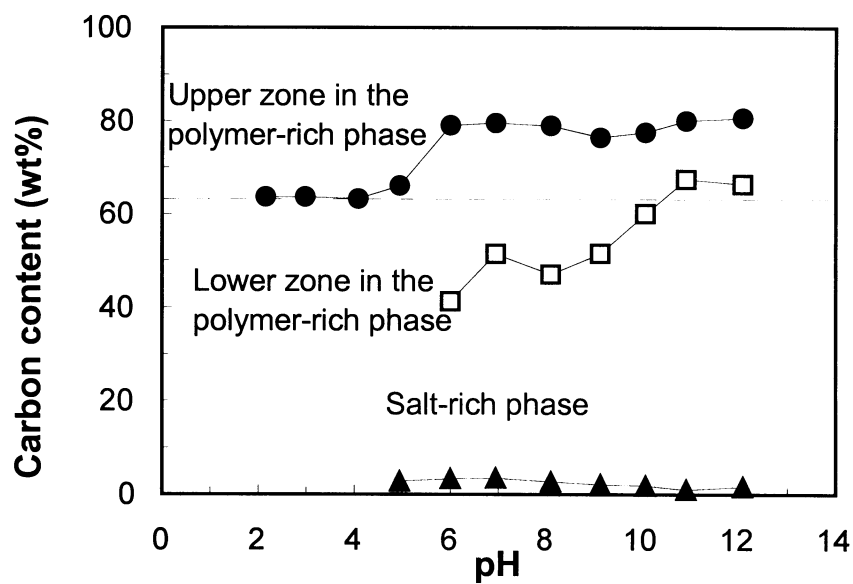


Fig. 2 The carbon contents in each fraction (solids content: 1 wt%). The dashed line indicates the carbon content in the original fly ash.

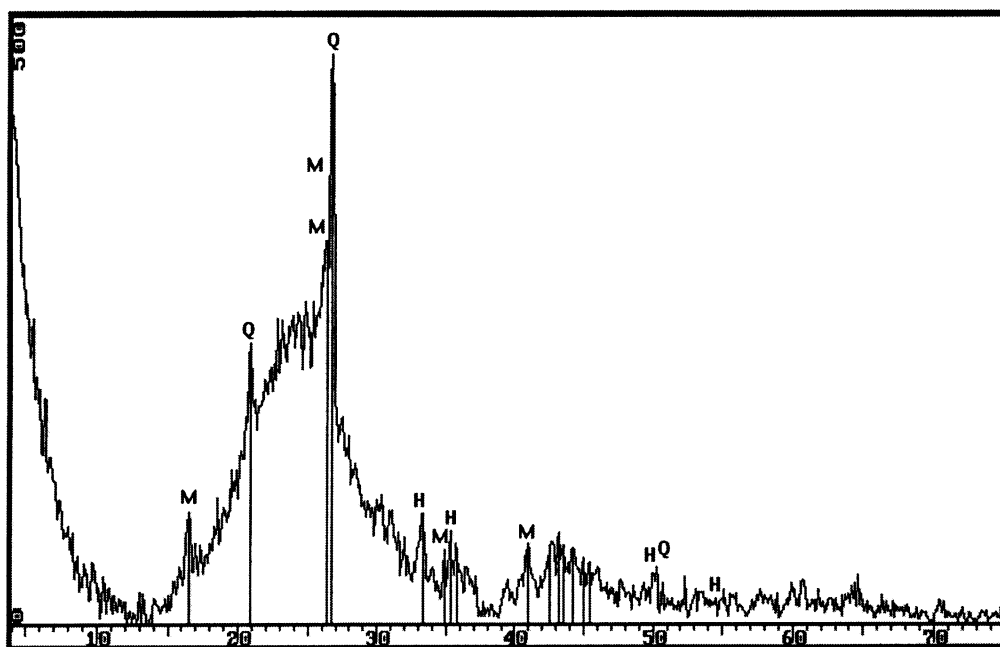


Fig. 5 XRD result of the sample in the lower zone of the polymer-rich phase at pH 12 (solids content: 1 wt%). Q = quartz, M = mullite, and H = hematite.

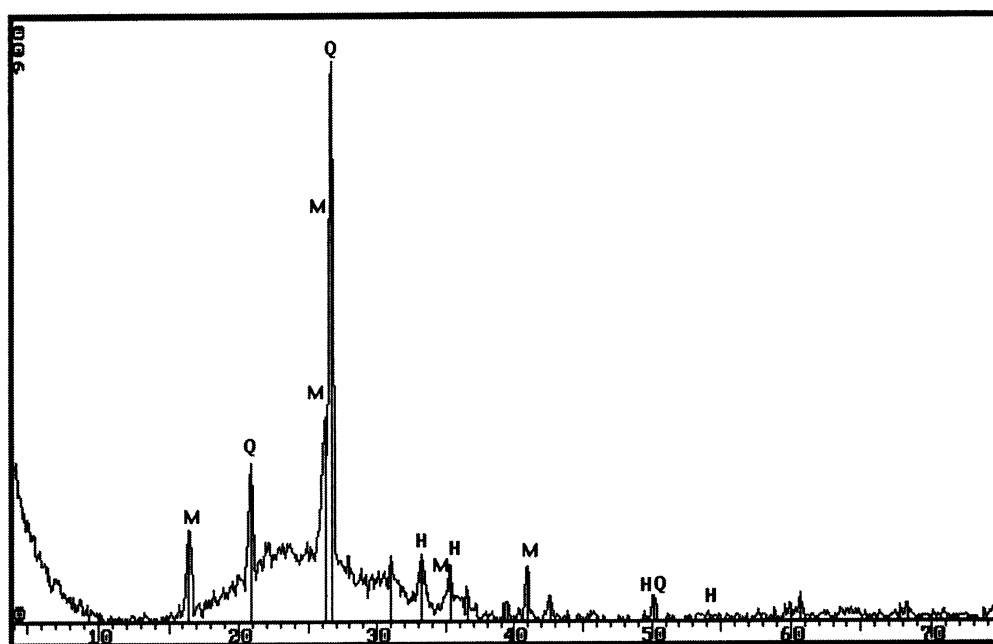


Fig. 6 XRD result of the sample in the salt-rich phase at pH 12 (solids content: 1 wt%). Q = quartz, M = mullite, and H = hematite.

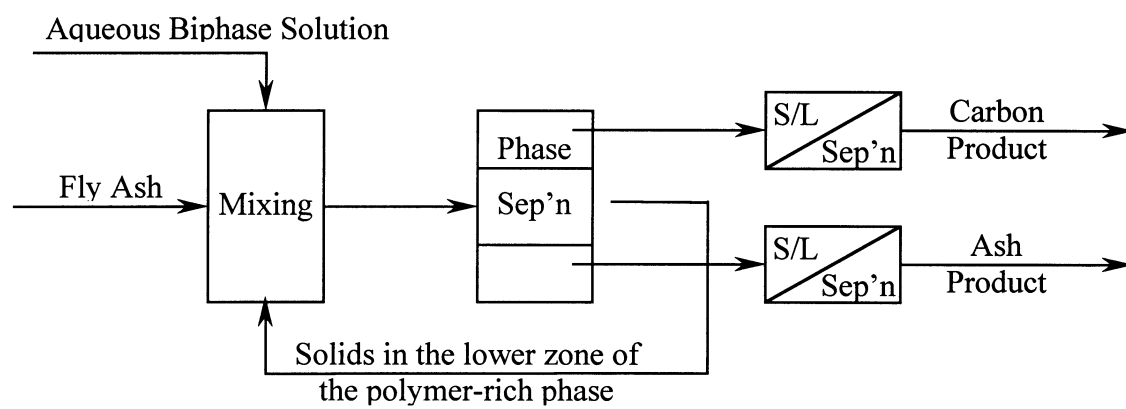


Fig. 7 Proposed flowsheet for aqueous biphasic extraction of high-carbon fly ash.

Table 1 Effect of pH on the partition of fly ash in the PEG-2000/Na₂SO₄/H₂O system (solids content: 2 wt%).

pH	Yield (wt%)			Ash Content (wt%)		
	Upper zone*	Lower zone*	Salt-rich phase	Upper zone*	Lower zone*	Salt-rich phase
12.0	9.4	81.4	9.3	11.8	27.7	91.5
11.1	39.6	52.1	8.3	14.3	35.4	97.5
9.9	96.6	-	6.2	29.1	-	92.7

*: In the polymer-rich phase.

Table 2 Elemental composition of ash in the parent fly ash and several beneficiated samples (solid content of 2 wt%).

Sample*	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO ₂	CaO	MgO	Na ₂ O	K ₂ O	BaO	SrO
Parent	52.2	31.3	1.34	9.17	0.0355	1.82	1.04	0.385	2.13	0.366	0.0990
12-T	46.2	30.6	1.52	9.48	0.0372	2.35	0.682	2.01	1.89	0.283	0.128
11-T	48.0	31.6	1.63	10.8	0.0457	2.38	1.29	1.50	2.12	0.322	0.127
10-T	51.3	31.6	1.38	9.41	0.0377	1.68	1.04	0.823	2.05	0.369	0.106
12-M	51.0	31.7	1.40	9.28	0.0386	1.78	1.11	0.876	2.03	0.388	0.109
11-M	52.2	32.1	1.37	9.28	0.0372	1.71	1.05	0.691	2.08	0.414	0.107
12-B	56.9	30.9	1.08	7.93	0.0283	0.841	0.801	0.347	2.01	0.225	0.0616
11-B	58.1	30.9	1.05	7.46	0.0259	0.726	0.733	0.277	2.02	0.219	0.0557
10-B	56.4	30.5	1.01	6.63	0.0247	0.689	0.710	0.295	1.95	0.210	0.0548

*: Parent: the parent fly ash;
the number means the pH value;
T: the upper zone in the polymer-rich phase,
M: the lower zone in the polymer-rich phase,
B: the salt-rich phase.