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Coal Flotation and Flocculation in the Presence of Humic Acids

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FINAL REPORT
January 1, 1989–August 31, 1990

Southern Illinois University at Carbondale
Carbondale, Illinois 62901

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ABSTRACT

The principle of coal cleaning using humic acid is as follows. Humic acid is an anionic polyelectrolyte which possesses a high density of carboxyl groups. The mechanism of coal depression involves the selective adsorption of humic acid on the hydrophobic coal through hydrophobic bonding. Pyrite and ash are hydrophilic in nature and are separated from the carbonaceous part of the coal, thus resulting in a cleaner coal. The adsorption characteristics of humic acid on coal are discussed. Humic acid adsorption on coal is modeled in terms of Langmuir adsorption isotherms. Coal cleaning was carried out using humic acid and xanthic acid for coal depression and mineral matter flotation, respectively. Dramatic decrease in ash content was observed, while significant recovery of the original coal was accomplished in these flotation experiments. The heating recovery ratios as a function of the xanthic acid addition are also reported.

BACKGROUND

This research is an exploratory investigation of physical coal cleaning using humic acid as a depressant for coal flotation. The principle of the coal cleaning technique employed is as follows. Humic acid, a naturally occurring hydrophilic agent which is also a product of coal oxidation, can selectively depress the flotability of the hydrophobic carbonaceous part of a high-sulfur Illinois coal. Pyrite and ash are hydrophilic in nature and will be separated from the carbonaceous part of the coal, thus resulting in a cleaner coal. Another advantage of using humic acid lies in its ability to act as a flocculating agent. It is anticipated that the humic acid should be able to aggregate fine particles and desulfurize coal simultaneously.

Wen (1986) and Moore (1986) first investigated the role of surface functional groups in fine coal preparation using humic acids in order to define modifications of coal surface properties that lead to lower ash and sulfur levels in the beneficiation of coal. Laskowski et al. (1986) also employed humic acid as a depressant for coal flotation. Their research with a Canadian (Prince Mine) coal reveals that both coal particles and kerosene (or fuel droplets) acquire more negative zeta potential values in the presence of humic acid. The drop of the zeta potential value in a more negative direction is pronounced in the acidic range of pH. They concluded that in the presence of humic acid, two-stage addition of common flotation agents (kerosene and MIBC) may substantially improve flotation selectivity. However, problems associated with obtaining high yield at improved selectivity need to be addressed. These problems involve the time which elapses after the first and before the second addition of the collector and the frother. One of the objectives of this research is the investigation of the effect and application of the collector and frother on the yield and selectivity of the coal flotation process.

WORK ACCOMPLISHED

Adsorption Studies

The coal used in our studies is from the Herrin (No. 6) seam (southwestern Illinois) mine-run containing high ash (38.1%). The ratio of pyritic to organic sulfur is estimated to be about 1:3. Coal when contacted with NaOH results in humic acid production. In one set of experiments at pH 11, coal was contacted with NaOH. The coal was filtered and a dark-colored solution was obtained. The solution was found to contain humic acids, as evidenced by UV spectroscopy (humic acids produce a peak at 400 nm). The amount of humic acid produced was estimated to be equal to 0.00105 g humic acid/g of coal.

In another set of experiments, coal was slurried for 24 hr with a technical grade (supplied by Aldrich Co.) humic acid at pH 11. The amount of humic acid in the slurry at equilibrium was determined by analyzing (UV spectroscopy) the solution obtained by filtering the coal from the slurry. The amount of humic acid adsorbed was determined by mass balance, taking into account the amount of humic acid produced by the coal itself.

Figure 1 is an adsorption isotherm for humic acid adsorption on the coal. Initially, the amount of humic acid adsorbed increases rapidly with the equilibrium humic acid concentration; however, a further increase in the humic acid concentration results in diminishing rates of increase in the adsorption density. The adsorption density of technical grade humic acid reaches an asymptotic value of 0.006 g humic acid/g of coal at an equilibrium humic acid concentration of 600 ppm. We feel this adsorption density to be very high, since our previous work has shown that as little as 20 ppm of humic acid is sufficient to depress coal flotation. According to Moore (1986), the high adsorption and the strong affinity of humic substances for coal surfaces are presumably due to the combined interaction of high molecular weight

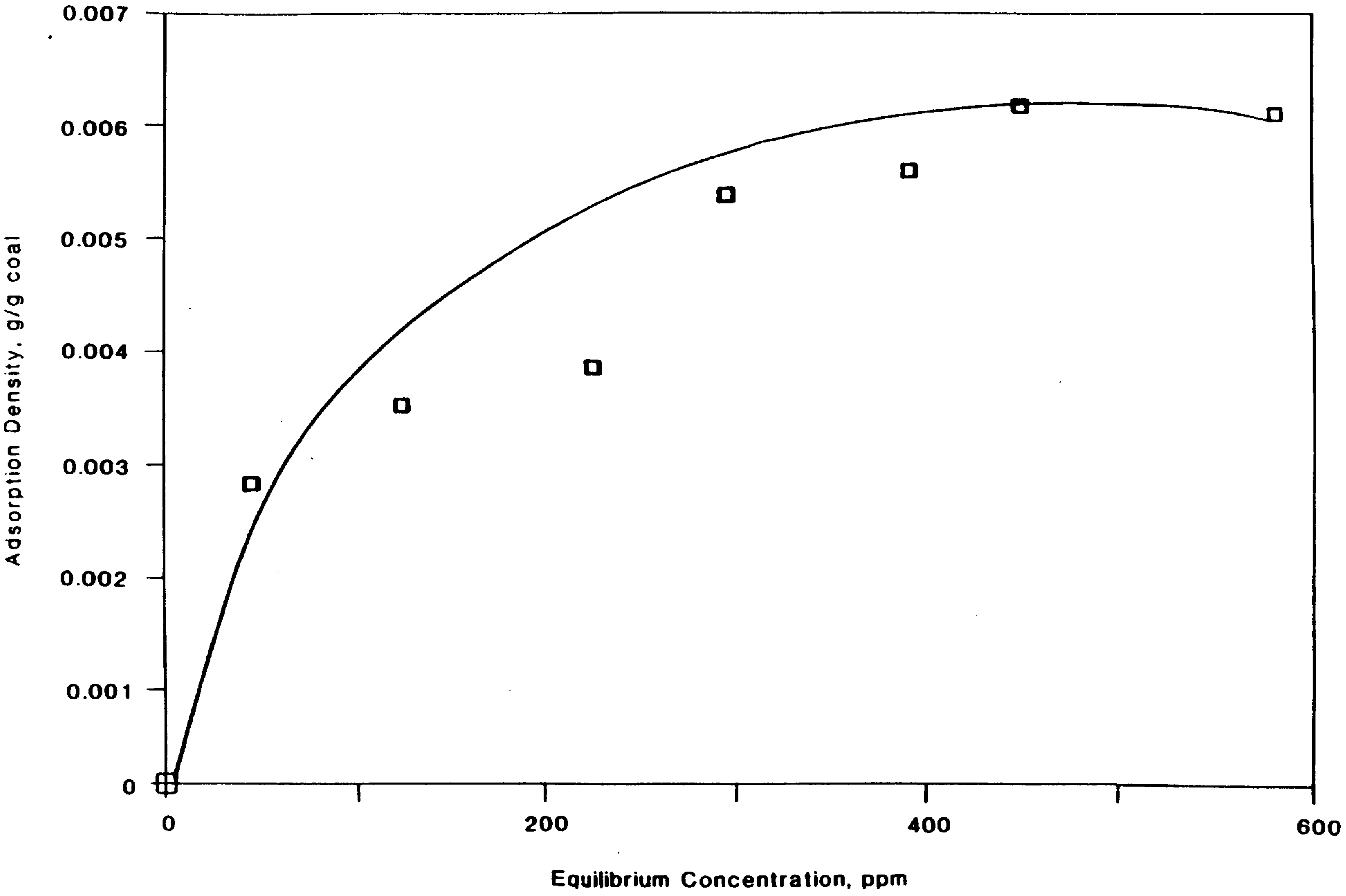

Figure 1. Adsorption isotherm for humic acid (reagent grade) adsorption on Illinois Coal at pH 11.

polymeric humic substances with polyfunctional groups on coal. Moore (1986) attributes several interaction forces responsible for humic acid adsorption. The functional groups from humic substances (such as hydroxyl, phenolic, carbonyl, or carboxylic) can interact with similar or dissimilar groups on coal surfaces through electrostatic attraction, hydrogen bonding, or hydrophobic bonding.

A Langmuir adsorption plot for the data obtained is shown in Figure 2. The reciprocal of the equilibrium uptake of humic acid by coal, Q_A (g adsorbed/g coal), is found to be a linear function of the reciprocal of the humic acid equilibrium concentration, C_A. From the slope and intercept of the straight line, the amount of adsorbate necessary for complete monolayer coverage (Q) and the constant for adsorption (K′) can be determined (Table 1).

The data obtained by Wen (1986) on the adsorption of technical grade as well as coal-derived humic acids on Bruceton mine coal was also evaluated according to the Langmuir adsorption plots (Figure 3). Again, a linear relationship between the reciprocals of Q_A and C_A is obtained. The constants Q and K′ are shown in Table 1. It is observed that as compared to the Illinois coal, the amount of adsorbate necessary for complete monolayer coverage of the Bruceton mine coal is much higher.

Table 1

Calculated values for adsorption constants

Coal	Q g humic acid/g coal	K′ cm^3/ g humic acid
Herrin No. 6 (reagent grade humic acid)	0.0059	1.78×10^4
Bruceton mine (coal-derived)	2913.8	0.204
Bruceton mine (technical grade)	109.8	8.10

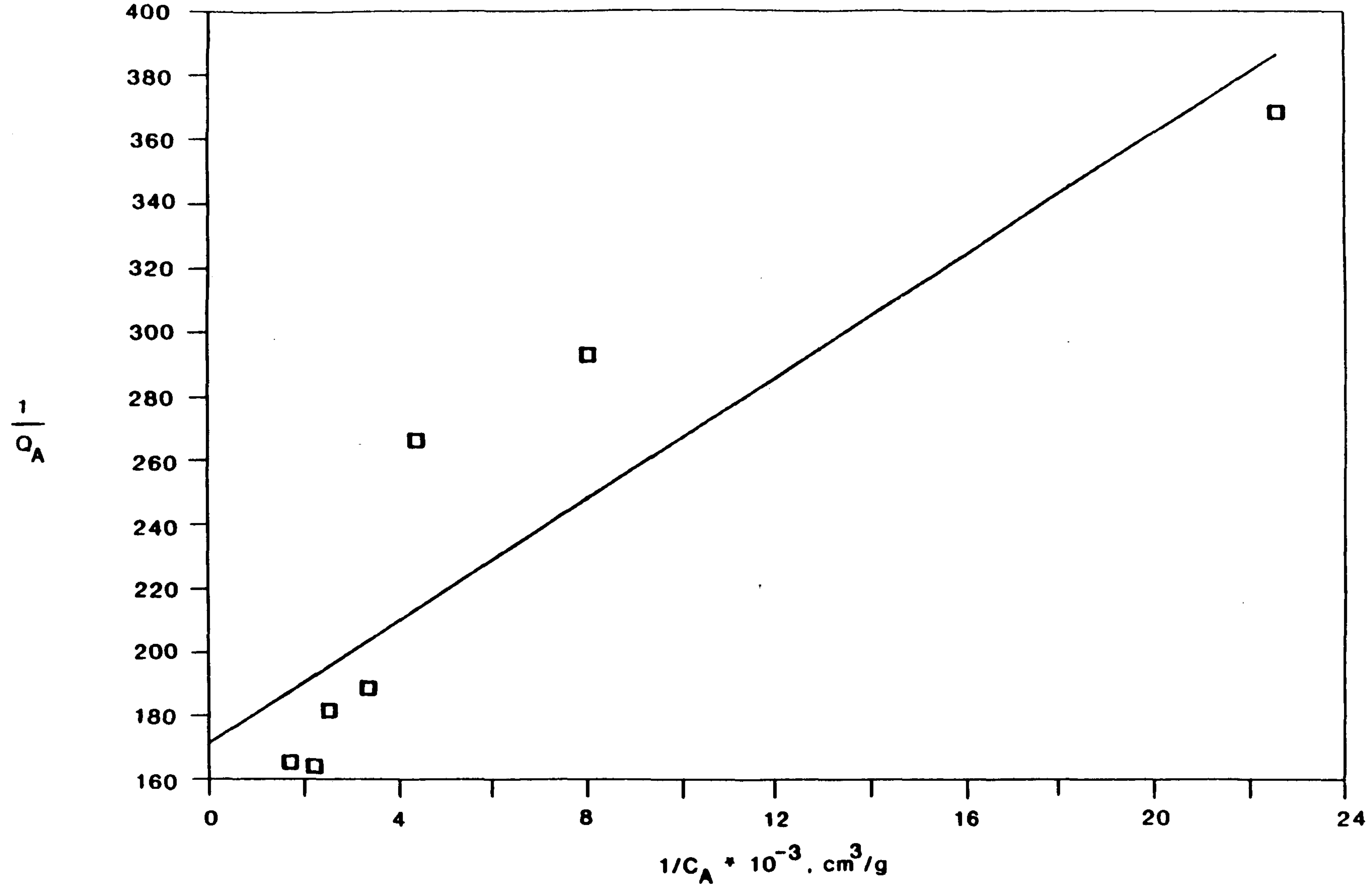

Figure 2. Langmuir adsorption isotherm for humic acid adsorption on Illinois coal at pH 11.

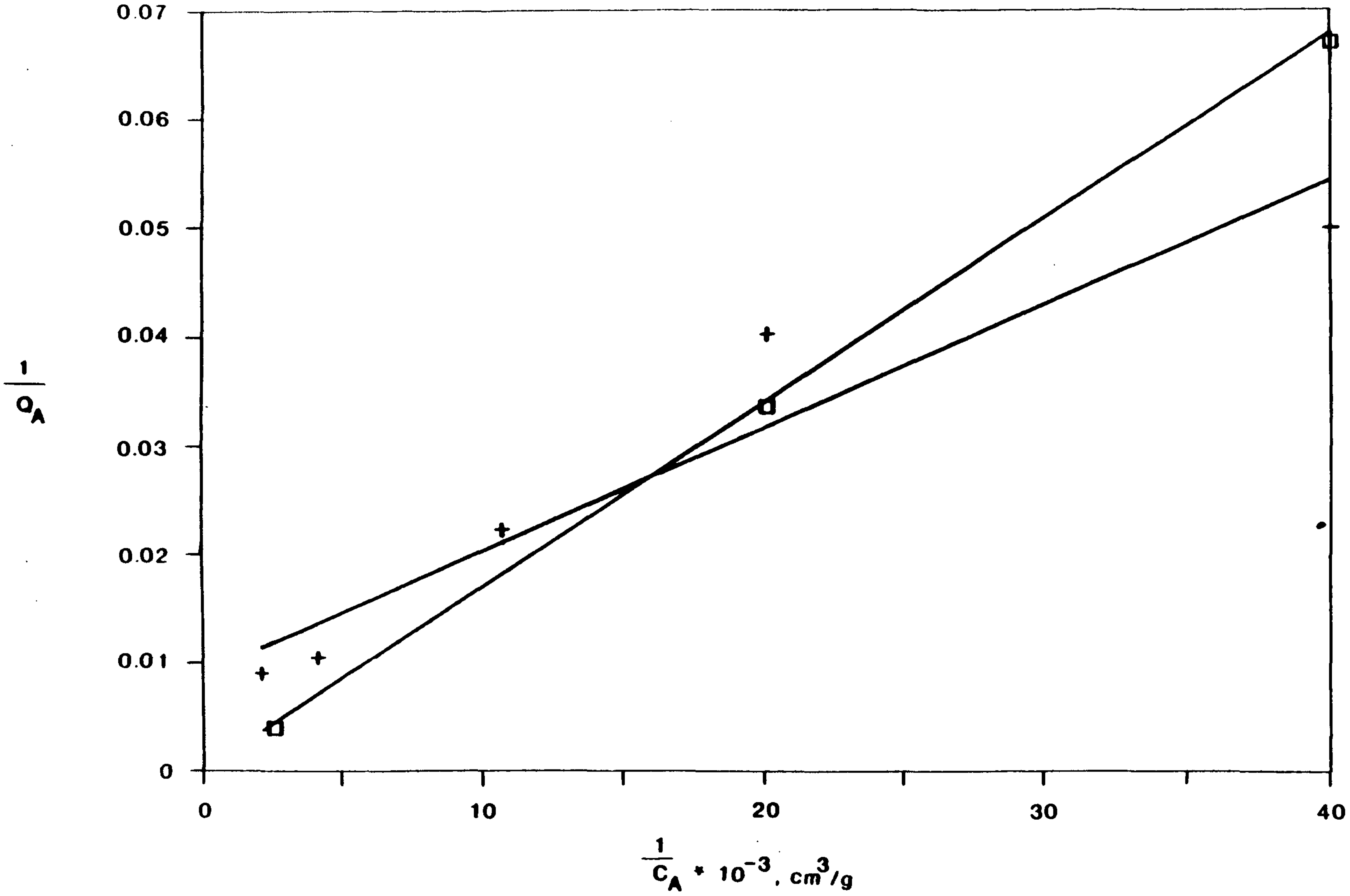

Figure 3. Langmuir adsorption curve for humic acid (+ = technical grade; □ = coal-derived) absorption on Bruceton mine coal. Data used was obtained from the work of Wen (1986).

- **Coal Cleaning**

Humic acid and xanthate were added to the coal slurries in experiments reported below. Coal flotation was carried out using an air flow rate of 600 mL/min in a glass reactor described elsewhere by Lalvani (1989). Initially, xanthate was added to the coal slurry prepared at natural pH (between 5 and 6), followed by a 20 mL addition of technical grade humic substances. The coal flotation experiment was carried out for a period of five minutes. The amount of the top and bottom product recovery as a function of the xanthate added is shown in Figure 4. The amount of ash in top and bottom products vs. xanthate concentration is shown in Figure 5. It is observed that both the amount of top product obtained and the top product ash content increase with the xanthate concentration. It is interesting to observe that the top product obtained is relatively free of ash content. It must be noted that the raw coal has an ash content of 38%, an amount which can be reduced to as low as 10.74% while accomplishing 24% top product coal recovery. For 40% recovery, the ash content of the clean coal can be expected to be about 17.8%, representing a decrease of 53% ash. The heating value recovery is observed to increase monotonically with the xanthic acid concentration. When a xanthic acid concentration of 1,000 ppm is maintained in the flotation cell, the heating value recovery can be expected to be about 79% (Figure 6).

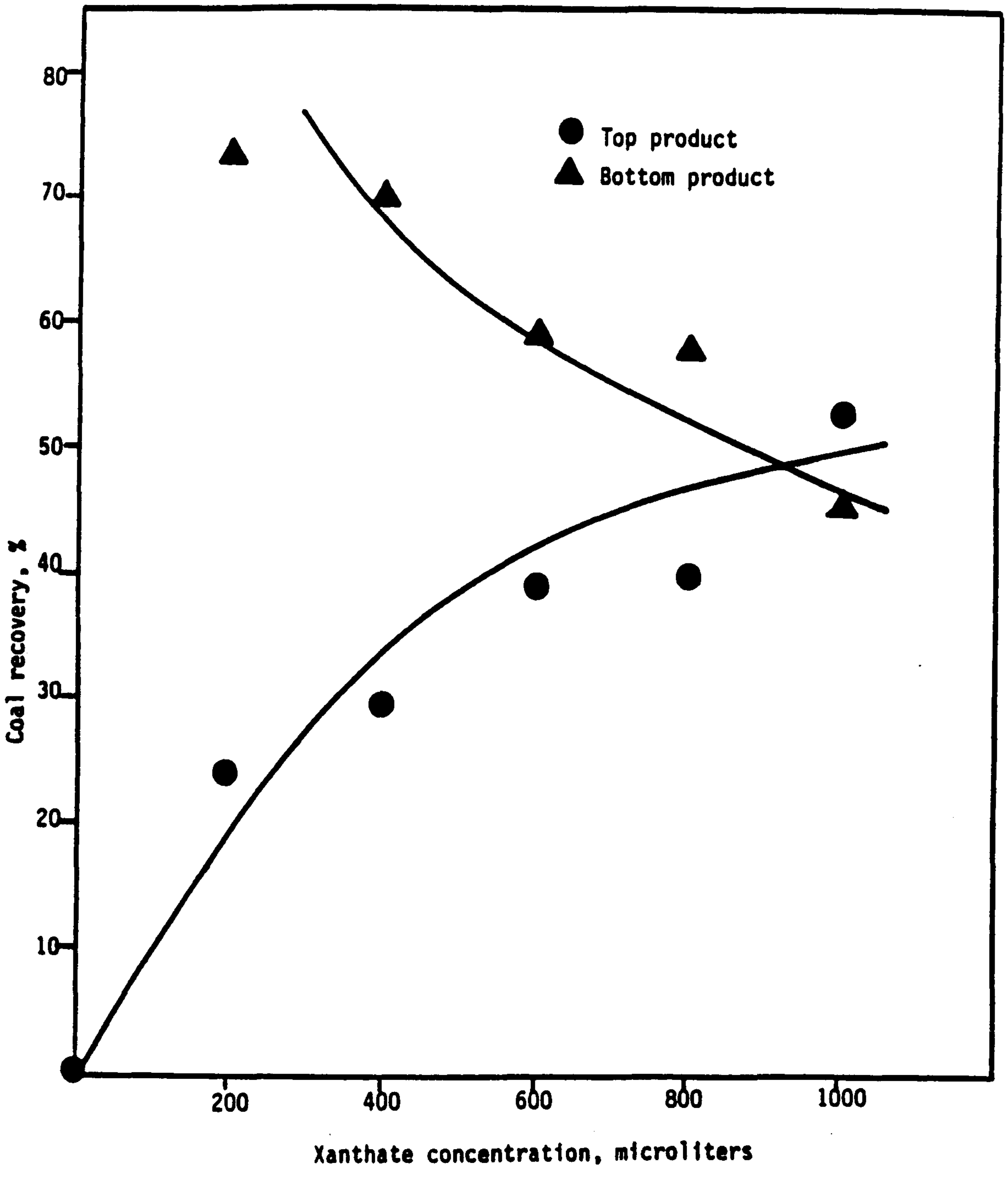

Figure 4. Coal recovery vs. xanthate added.

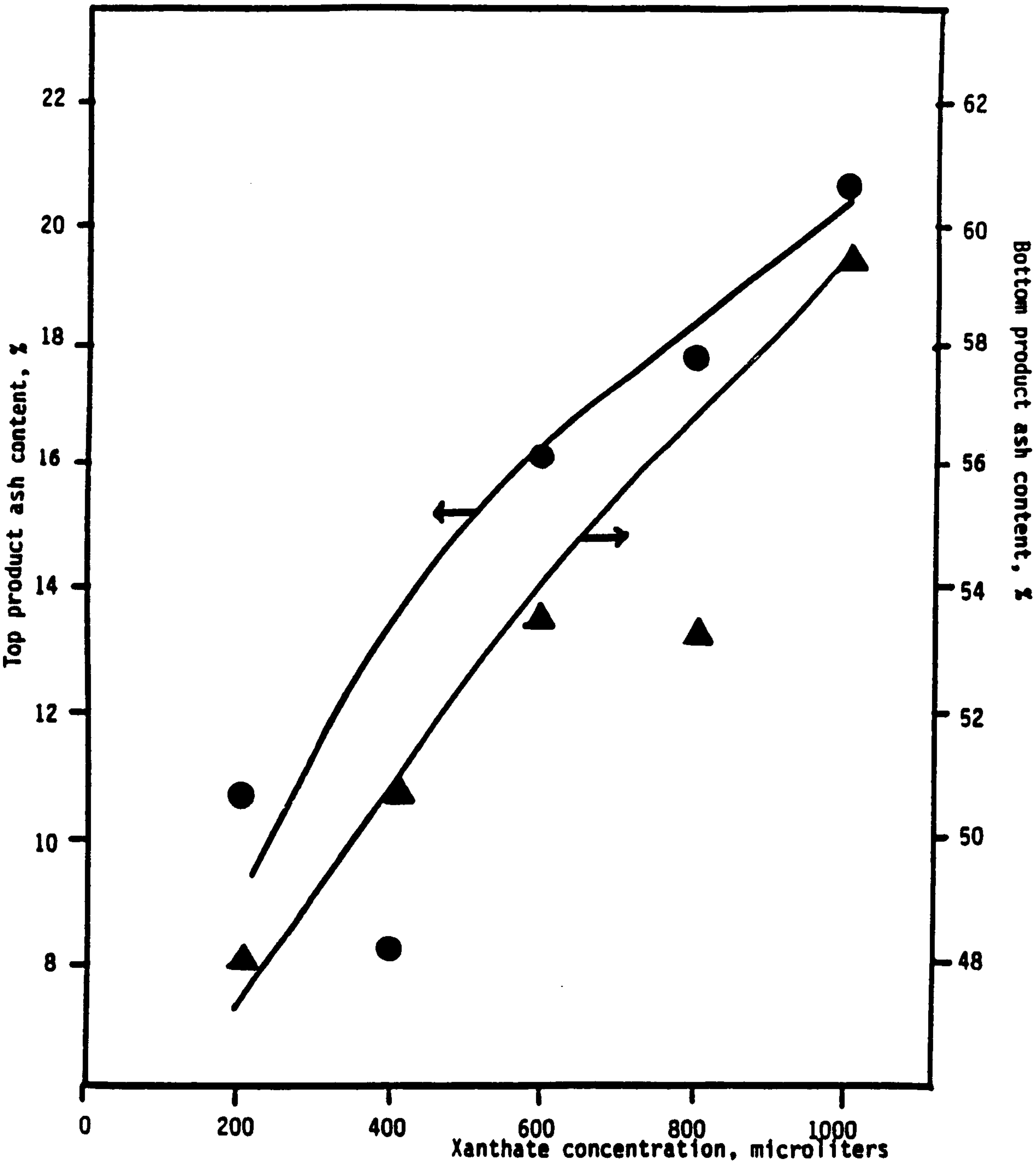

Figure 5. Ash content of coal cleaned via flotation.

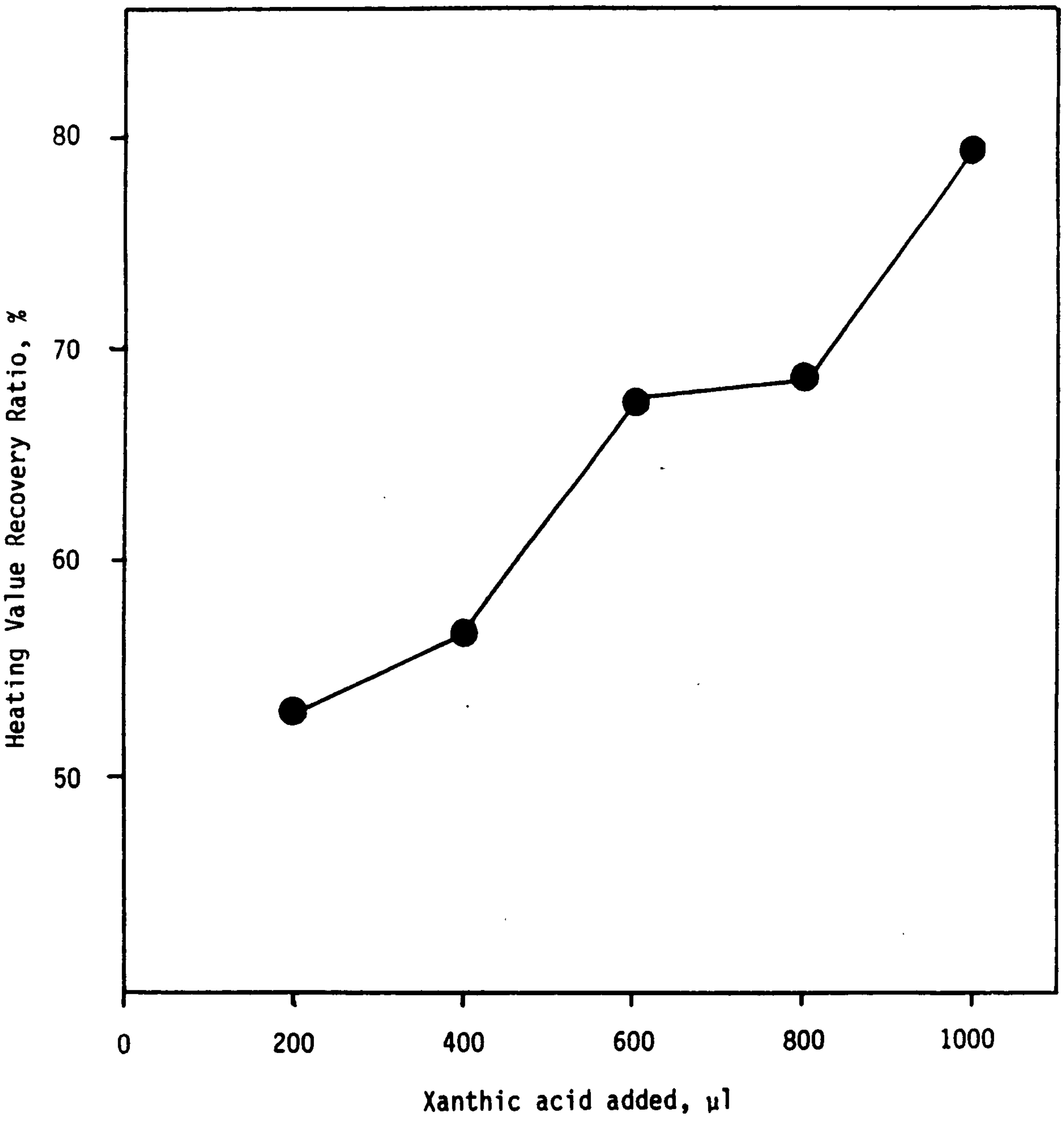

Figure 6. Heating value recovery ratio as a function of xanthic acid added.

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