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Quarterly Report

A NEW APPROACH IN ULTRAPURIFICATION OF COAL BY SELECTIVE FLOCCULATION

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by

Brij M. Moudgil
Mineral Resources Research Center
Department of Materials Science and Engineering
University of Florida
Gainesville, Florida 32611

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SUMMARY

The experimental procedures and results on single and mixed mineral studies of coal/refuse system were outlined in the last quarterly report. In this quarter, single and mixed mineral studies of a coal/pyrite system that also contained a sizeable amount of coal refuse were conducted. Pyrite was observed to be well flocculated by Superfloc 362. Another flocculant, Superfloc 16, also showed excellent flocculating capabilities for pyrite as compared to coal. On the other hand, hydrophobic polymer, WCL-762, was observed to flocculate coal more than pyrite.

Mixed mineral studies of 90:10 mixtures of coal/pyrite showed loss of selectivity due to heteroflocculation with Superfloc 362. The increase in settling time at lower dosages of SF 362 did not significantly affect the supernatant coal grade. The effect of pH on the supernatant grade was also studied. No selectivity was achieved in the lower pH range whereas potential separation of coal from pyrite was indicated at higher pH values.

In the mathematical simulation of selective flocculation, no significant effect on the simulation results was observed when the number of particles was changed from 100 to 300 particles. It was determined that when the impurity component is flocculated, the selectivity decreases as the amount of impurity in the feed is reduced.

In the coming months, work on mixed mineral studies using Superfloc 362, hydrophobic polymer WCL-362 and non-ionic polymer Superfloc 16 will continue. The effects of pH, settling time and polymer dosage on the separation of pyrite from coal will be investigated.

EXPERIMENTAL

Materials and Procedures

Hand-picked coal pyrite procured from a southwestern Pennsylvania coal preparation plant was sampled and comminuted to -400 mesh size. Table 1 shows the ash and sulfur analyses of the coal pyrite sample performed by Commercial Testing and Engineering Company, Birmingham, Alabama.

The properties of the polymeric flocculants used in this study are given in Table 2. The experimental procedures were outlined in the last quarterly report. Deionized water of conductivity less than 1 μmho was used in all experiments.

Sulfur analysis of the feed, floc and supernatant: To evaluate the selectivity of a polymer towards pyrite separation, comparison of the pyritic sulfur content of both the floc and supernatant fractions with that in the feed is required.

In the ASTM procedure D2492 (1) used to analyze the pyritic sulfur, since sulfates are soluble in hydrochloric acid but pyrite and organic forms are not, sulfate sulfur is first extracted with hydrochloric acid. Pyrites (FeS_2) are extracted quantitatively by dilute nitric acid and the extracted iron is determined by Inductively Coupled Plasma (ICP) Spectrometer (Perkin Elmer, Plasma II). The pyritic sulfur is then calculated as a stoichiometric combination with the iron.

The pyritic sulfur content of the coal using the above ASTM procedure was analyzed to be 0.25%, whereas in the pyrite sample it was determined to be 18.0%. The pyritic sulfur content of the pyrite sample analyzed by a commercial testing company is 20.2% (Table 1) which is in reasonable agreement with that estimated by iron analysis.

TABLE 1

Analysis of the Pyrite Sample

Proximate Analysis

Content	As Received %	Dry Basis %
Moisture	16.12	--
Ash	60.11	71.66
Volatile	18.65	22.24
Fixed Carbon	5.12	6.10
TOTAL	100.00	100.00

Sulfur Analysis
(Eschka Method)

Pyritic sulfur, %	20.19
Sulfate sulfur, %	0.10
Organic sulfur, %	0.10
TOTAL SULFUR	26.39

TABLE 2

Properties of Polymers Used

Polymer	Source	M.W.	Charge
SF 362	American Cyanamid	High	Cationic
SF 16	American Cyanamid	4 million	Non-ionic
WCL-762	Calgon Corp.	10 million	N.A.

RESULTS

Settling Behavior of Coal and Pyrite

Dispersion characteristics of coal and mineral matter were reported in the last quarterly report. Pyrite dispersion studies were carried out by conducting settling tests under natural pH conditions and at 2 wt% solids. The use of 30 seconds of sonication was observed to be effective for the dispersion of pyrite. However, as discussed in the last quarterly report, 0.02 kg/t of Darvan C was used in the mixed mineral tests since it was observed to be effective in dispersing coal. The minimum settling of coal occurred at a 0.02 kg/t dosage of Darvan C (see Table 3).

Additionally, single mineral tests were carried out to study the effect of Darvan C addition on the flocculation of pyrite. As shown in Figure 1, there is no significant effect of Darvan C addition on the flocculation of pyrite. Since 0.02 kg/t of Darvan C is required to disperse the coal in a mixed mineral slurry, all mixed mineral experiments were carried out at this dosage unless otherwise mentioned.

Settling tests of pyrite without additional polymer were also conducted. Pyrite settling was examined by collecting sediments at various time intervals ranging between 1½ min. to 4 min. It is observed from Figure 2 that pyrite sedimentation increases from 9.8% to 24.2% as the settling time increases from 1½ min. to 4 min.

Single Mineral Flocculation

As discussed in the last quarterly report, several flocculants were tested and, based on single mineral studies, Superfloc 362 was observed to work best in flocculating mineral matter including refuse, quartz, and clay materials. Coal, on the other hand, was not flocculated by SF 362. Superfloc 362 was observed to efficiently flocculate pyrite suspensions also. The single mineral

TABLE 3

Effect of Darvan C on Coal Dispersion

Settling Time = 2 minutes

Darvan C Dosage kg/t	Amount Settled wt%
0	3.63, 4.32
0.01	3.73, 5.06
0.02	3.54, 3.29
0.03	4.1, 4.15
0.04	4.1, 4.74

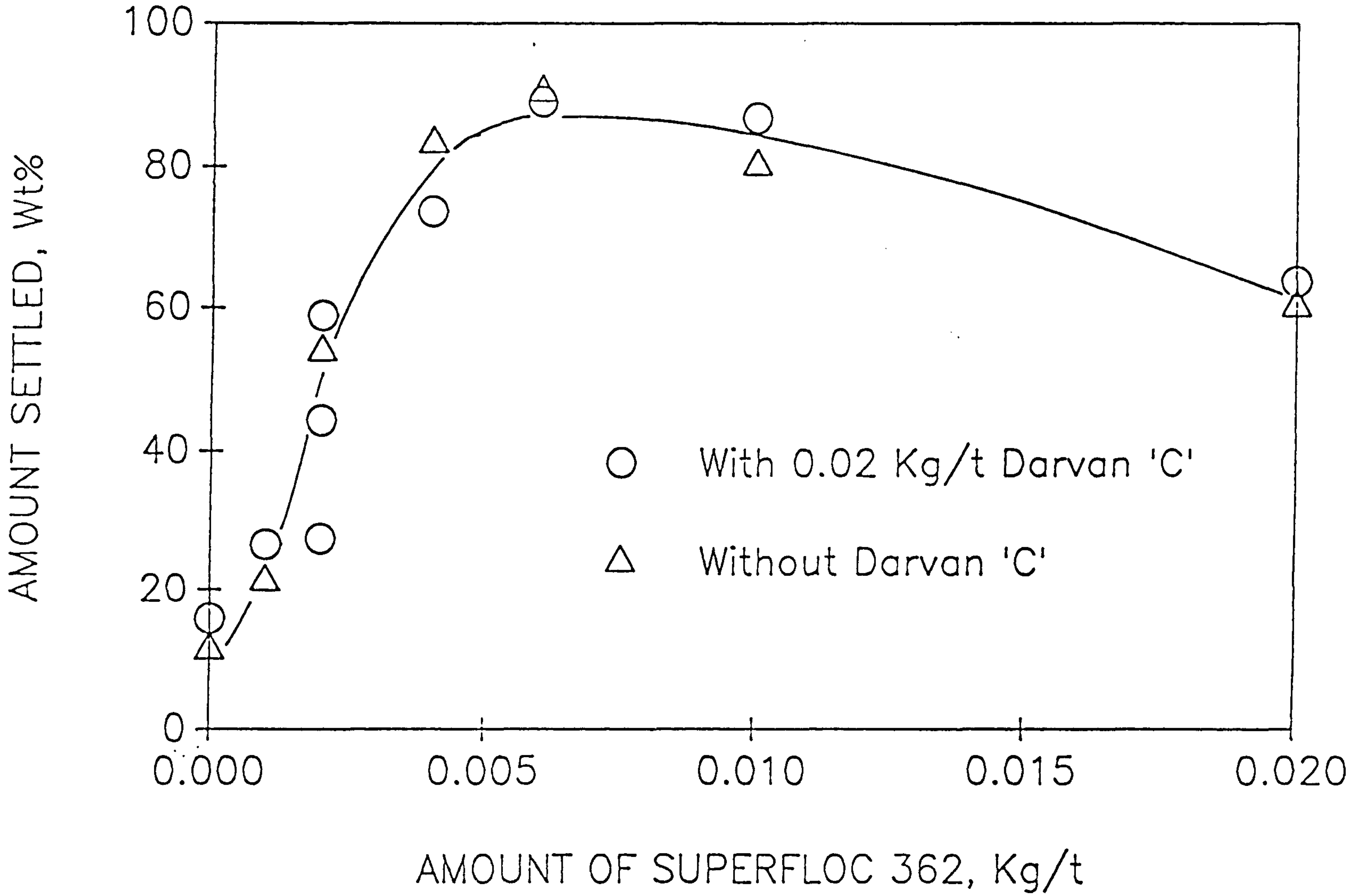

Figure 1. Effect of dispersant Darvan C on pyrite flocculation.

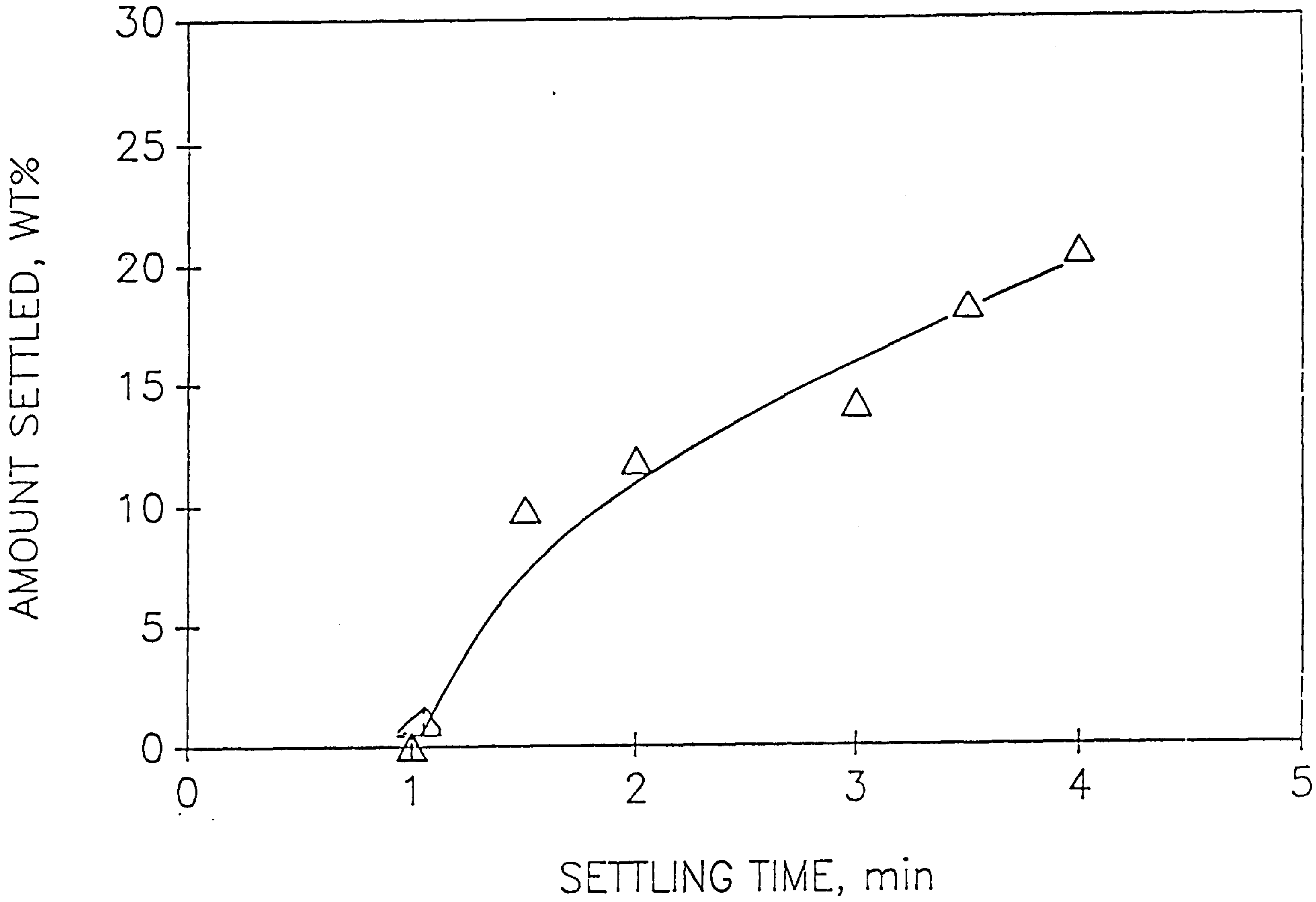

Figure 2. Effect of settling time on pyrite sedimentation (no polymer).

flocculation of pyrite and coal with SF 362 is compared in Figure 3. It is seen that at a dosage of 0.006 kg/t, more than 90% of the pyrite reported in the floc bed within 2 minutes of settling time.

In a continuing effort to screen more polymers, Superfloc 16 was examined. As seen in Figure 4, this polymer was observed to flocculate pyrite more than coal at a lower dosage level (0.001 kg/t) indicating that coal/pyrite separation may be achieved with this polymer.

Attia et al. (2) have used hydrophobic polymers to flocculate coal instead of pyrite and mineral matter. Coal, being hydrophobic in nature, flocculates better with polymers having similar characteristics. A hydrophobic polymer, WCL-762, was used with the pyrite and coal samples. As seen in Figure 5, coal is flocculated more than pyrite at a higher dosage level of WCL-762. There is some flocculation of pyrite, probably because the sample contains 6.1% coal.

Mixed Mineral Flocculation

The mixed mineral selective flocculation of pyrite from a coal/pyrite mixture was attempted as a next step. Synthetic mixtures of coal and pyrite in the ratio of coal:pyrite = 90:10 were prepared and the selective flocculation tests were carried out using the procedures outlined in the previous report. The flocculated material and the supernatant were collected separately and analyzed for ash and sulfur content.

Effect of polymer dosage: The effect of polymer dosage on the selective flocculation of pyrite from coal was studied at a constant settling time of 2 minutes. The settling time was selected on the basis of single mineral flocculation of pyrite.

The coal recovery and grade based on the solids amount and the ash analysis of the supernatant are compared in Table 4. It is observed that although the coal recovery is high, there is no significant change in the supernatant coal grade indicating heteroflocculation under the present experimental conditions.

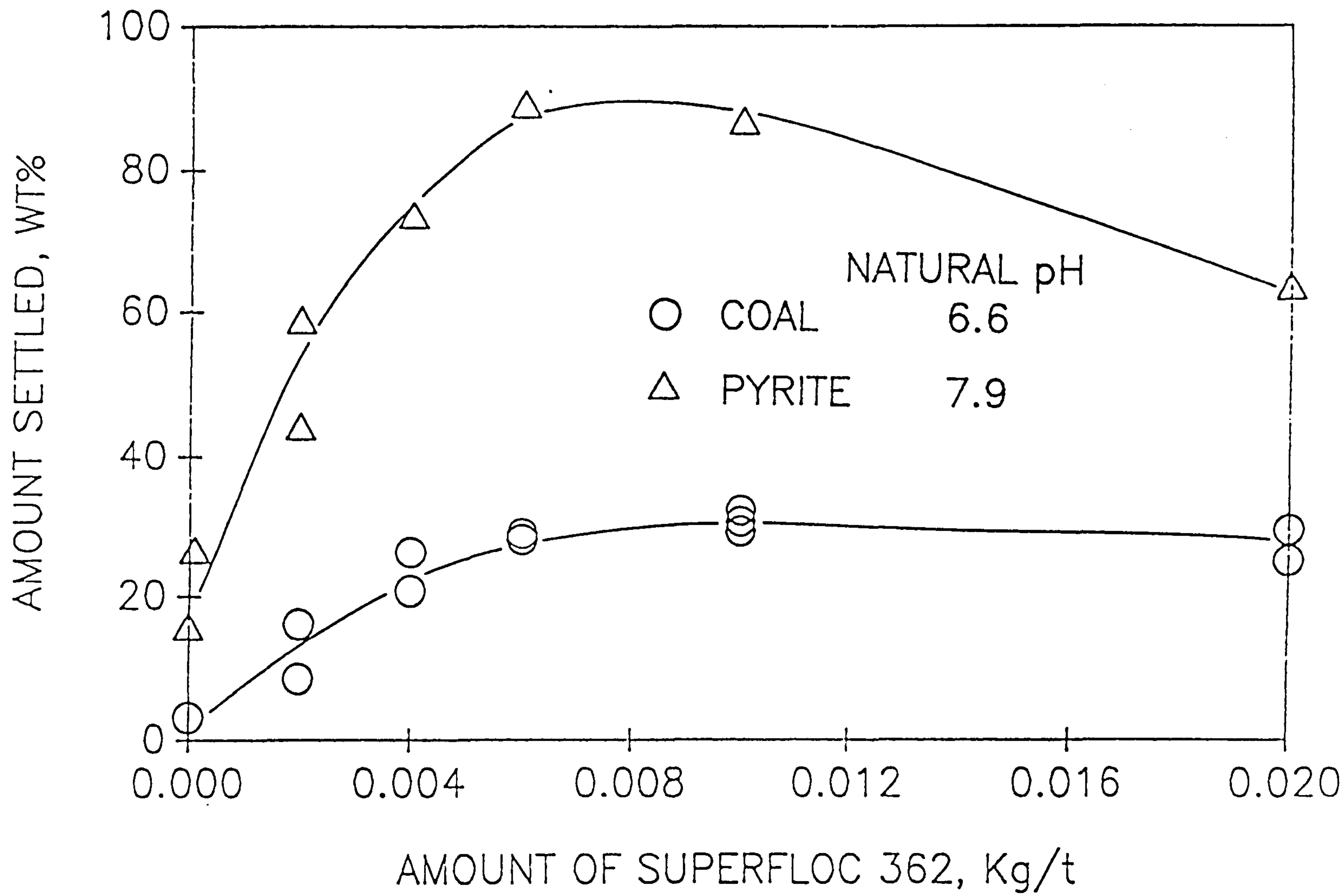

Figure 3. Effect of SF 362 dosage on single mineral flocculation of coal and pyrite.

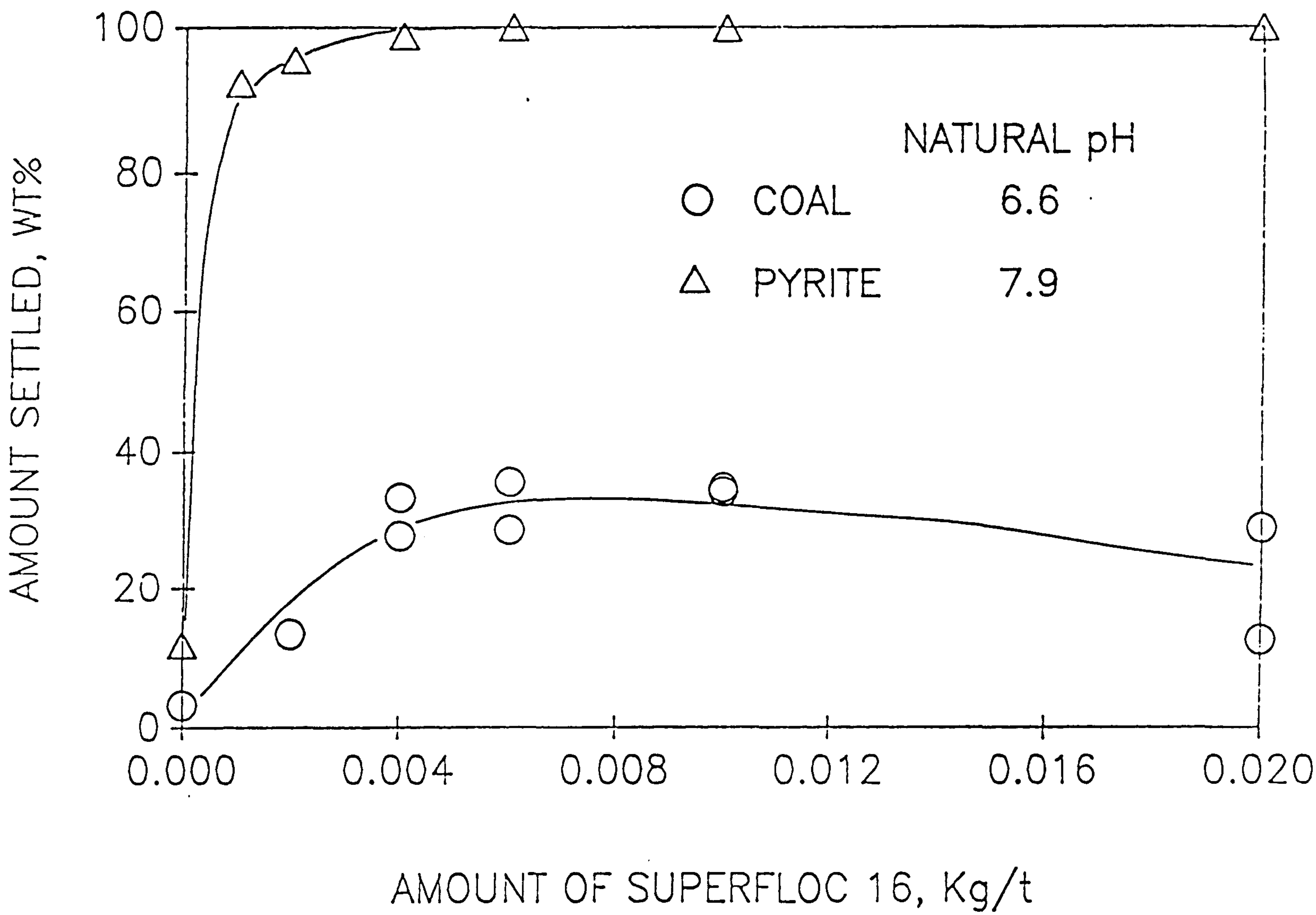

Figure 4. Effect of SF 16 dosage on single mineral flocculation of coal and pyrite.

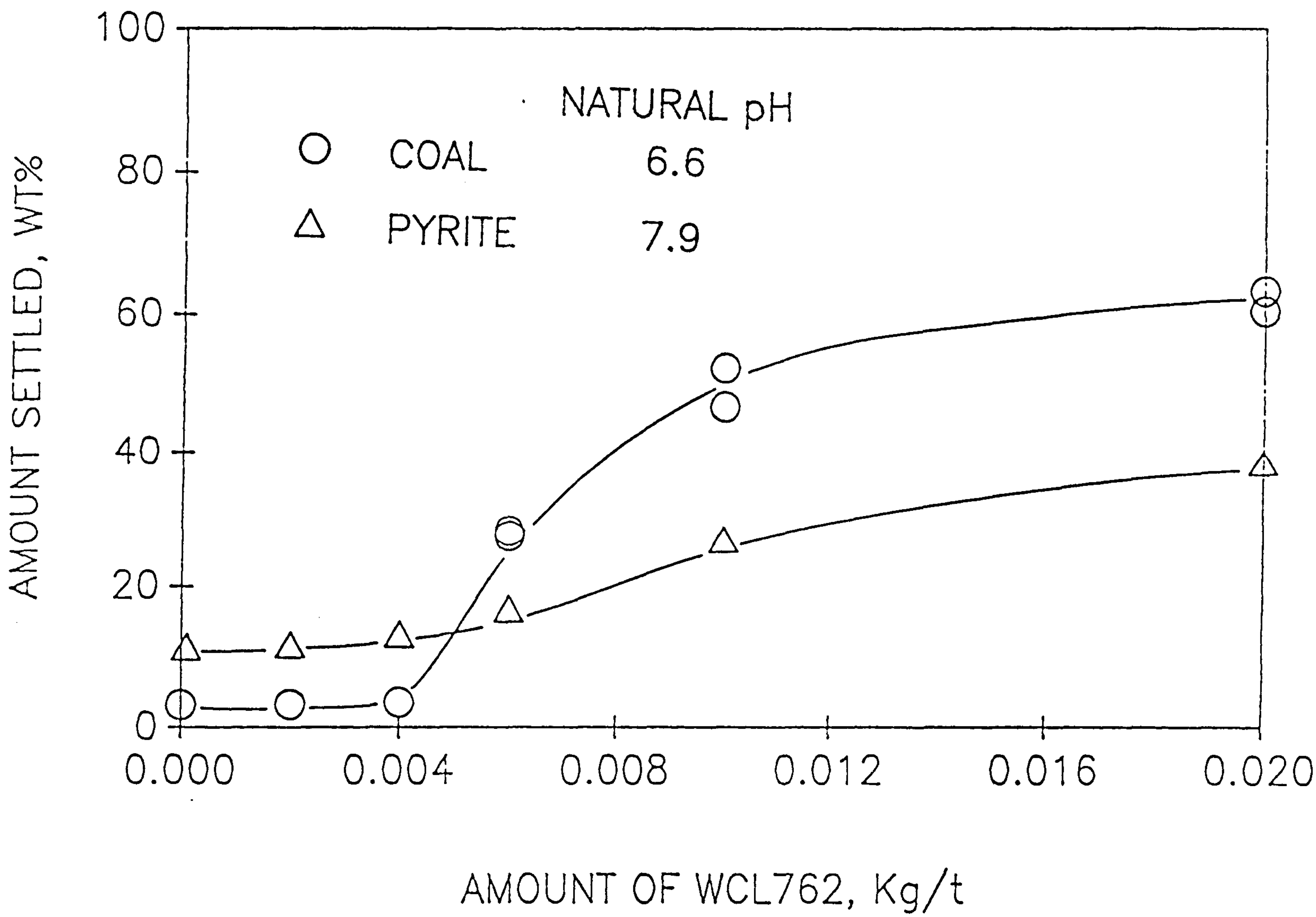

Figure 5. Effect of WCL-762 dosage on single mineral flocculation of coal and pyrite.

TABLE 4

Effect of SF 362 Dosage on Selective Flocculation of Pyrite

Coal:Pyrite = 90:10
Average Feed Coal Grade = 87.0%

SF 362 Dosage kg/t	Coal Recovery in Supernatant wt%	Ash Analysis in Supernatant wt%	Coal Grade in Supernatant wt%
0	96.4	11.4	88.6
0.001	96.3	11.0	89.0
0.002	95.8	11.1	88.9
0.004	95.9	10.7	89.3
0.006	96.8	10.6	89.4
0.01	87.3	11.5	88.5

The floc bed and supernatant from these studies were analyzed also for pyritic sulfur (see Table 5). The pyritic sulfur content of the material flocculated with 0.0, 0.001 and 0.006 kg/t of SF 362 was analyzed to be 6.6%, 4.4% and 4.9%, respectively. The supernatant for these experiments were observed to contain 1.8%, 1.5% and 1.9% sulfur, respectively, showing selectivity towards pyrite at these polymer dosages.

Some preliminary results of mixed mineral flocculation using hydrophobic polymer WCL-762 are shown in Table 6. As discussed earlier, this polymer flocculates coal rather than the mineral matter. At a polymer dosage of 0.01 kg/t, no significant flocculation of the suspension was observed. As seen from the results presented, maximum separation of the coal from pyrite/mineral matter was achieved at a polymer dosage level of 0.023 to 0.03 kg/t. It is probable that multistage processing would yield higher selectivity.

Effect of pH of the slurry: The experiments discussed in earlier sections were performed at the natural pH of the coal/pyrite mixture (pH 8.3). In order to identify the optimum pH, flocculation experiments were conducted as a function of pH.

The slurry pH was observed to significantly affect the selective flocculation by SF 362. As seen in Figure 6, maximum flocculation occurred at pH 7. The ash analysis of the supernatant fraction at pH 6 and 7, indicated coal grades of 88.1% and 88.5%, respectively, which were slightly higher than the feed grade of 87% coal. At higher pH values of 8 and 10, the recovery in the supernatant fraction was high and the coal grade was measured to be 89.1% and 88.9%, respectively, indicating marginally improved selectivity at higher pH. This was confirmed by the ash analysis of the floc bed which showed higher ash content (19.6% and 21.1% ash, respectively) than observed at lower pH. These experiments were repeated with a lower dosage (0.004 kg/t) of SF 362 to determine the effect of polymer dosage. Again, higher selectivity was obtained at higher pH values. These observations are in agreement with Attia et al. (2).

TABLE 5

Effect of Polymer Dosage on Pyrite Separation

Sedimentation Time = 2 min.
Polymer = SF 362
Average Feed Sulfur = 2.08%

SF 362 Dosage kg/t	Pyritic Sulfur in Floc Bed %	Pyritic Sulfur in Suspension %
0.0	6.6	1.82
0.001	4.44	1.50
0.006	4.89	1.89

TABLE 6

Mixed Mineral Flocculation of Coal/Pyrite

Coal:Pyrite = 90:10
Polymer: WCL-762
Average Feed Ash = 13.0%

WCL-762 Dosage kg/t	Ash Analysis, wt% Floc Bed	Supernatant
0.01	18.09	11.08
0.02	12.02, 11.4	31.2, 27.36
0.03	11.64, 10.58	29.02, 30.6
0.04	12.64	24.54

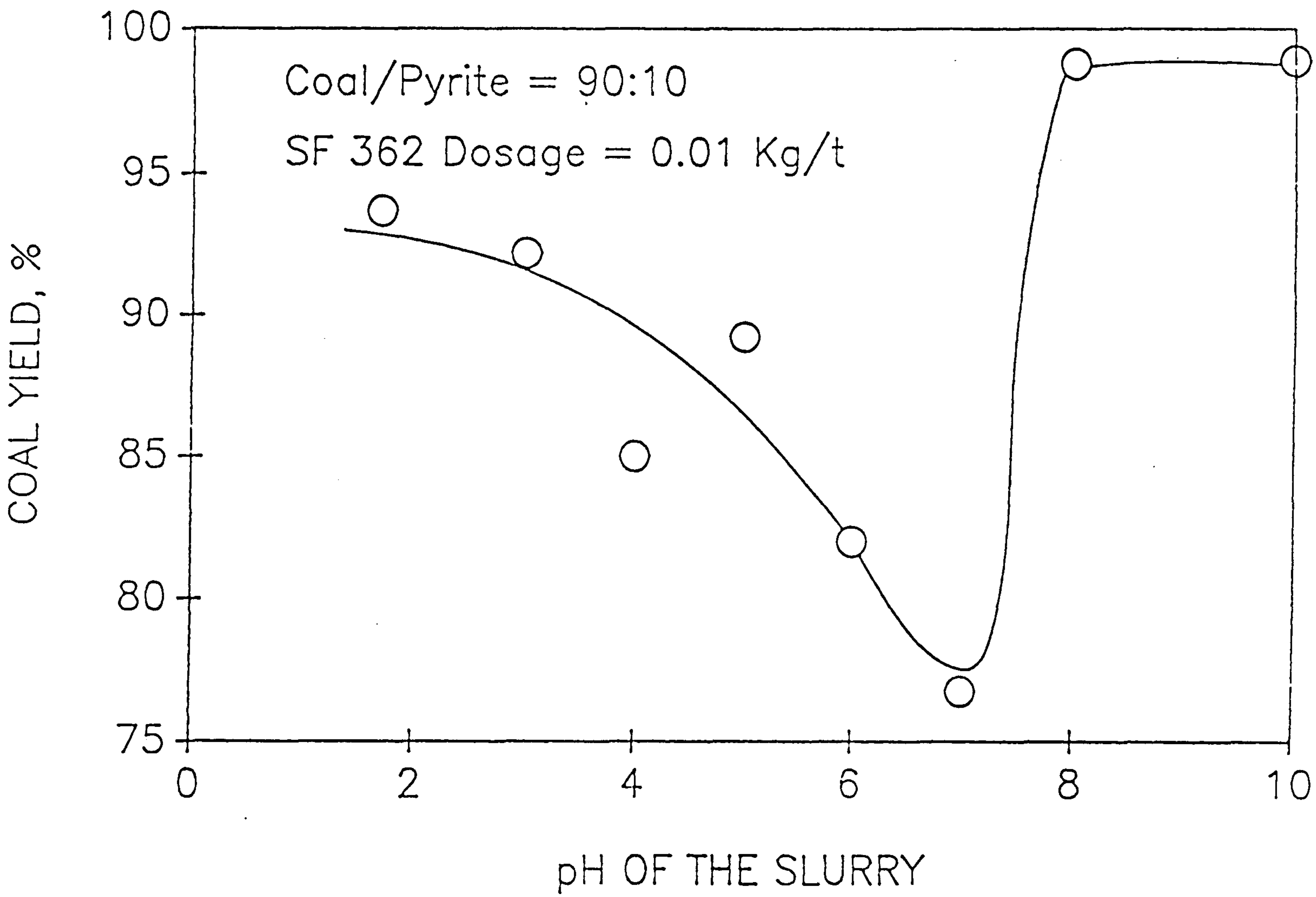

Figure 6. Flocculation of coal/pyrite mixture as a function of pH.

Effect of settling time: Since higher recovery was observed in the supernatant at lower dosage levels of SF 362, it was decided to increase the settling time to determine its effect on the supernatant grade. The settling experiments conducted with 0.001 kg/t dosage of SF 362 indicated a lower yield of coal at higher settling times (see Figure 7). The coal grade in the supernatant fraction, however, was not significantly affected (average value = 88.5%).

Mathematical Modeling of Selective Flocculation

In modeling of the selective flocculation process, ideally it is desired to use the largest number of particles to have a realistic representation. It should, however, be noted that the computational power and cost increases exponentially with the increase in the number of particles.

To examine the effect of the number of particles on the simulation results, 100, 200 and 300 particle simulations were carried out for the coal:clay = 90:10 system. As seen in Figure 8, the number of particles do not significantly affect the simulation results. However, to avoid any artifacts introduced due to the number of particles, 300 particles will be used in the future simulation work.

Effect of active sites ratio on selectivity: The effect of active sites ratio on the selectivity index of various ratios of coal and clay was studied with clay being flocculated instead of coal. The results plotted in Figure 9 indicate that the selectivity for a 40:60 ratio of coal to clay increases to as high as 90% at active sites ratios of 80 and above. At lower concentrations of clay material in coal, however, the selectivity does not exceed more than 80%, with poorer selectivities for a 70:30 ratio. The selectivity index values at a ϕ_R value of 10 in Figure 9 appear to be simulation artifacts that need to be corrected.

The above results are similar to the ones obtained by Moudgil et al. (3) for an apatite/dolomite system, in which they observed that when the component that represents the

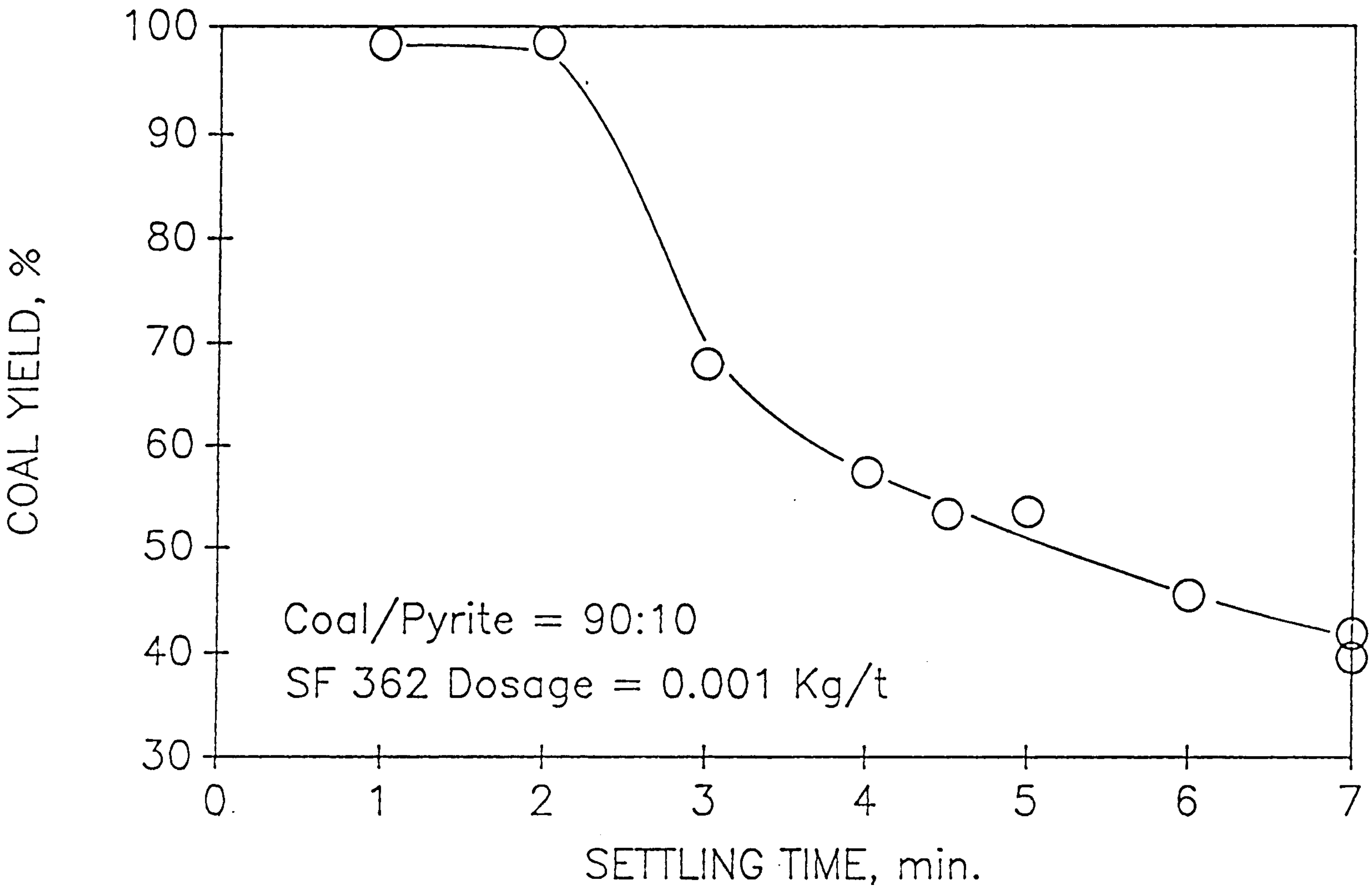

Figure 7. Effect of settling time on coal yield.

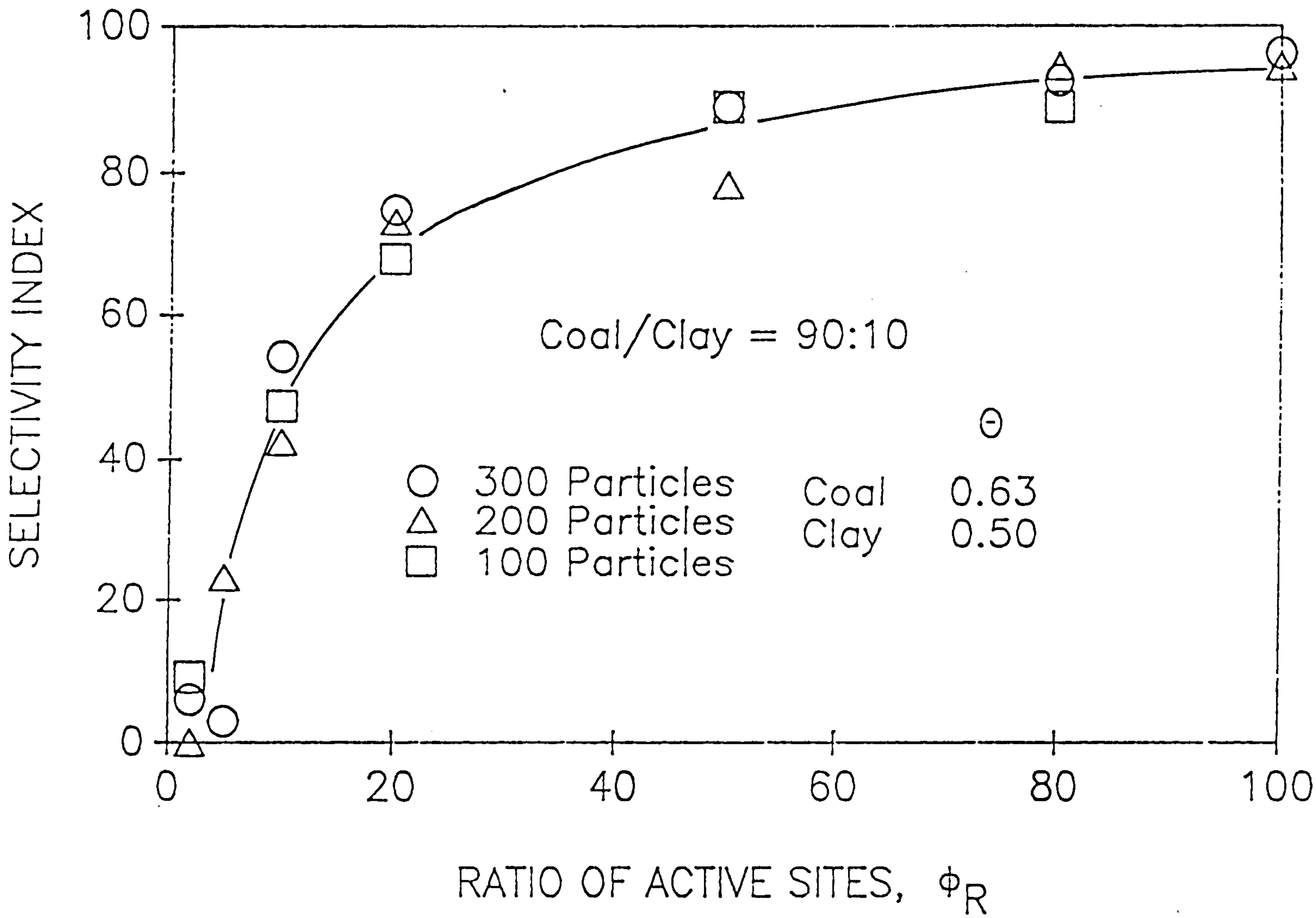

Figure 8. Effect of number of particles used in simulation on the selectivity index.

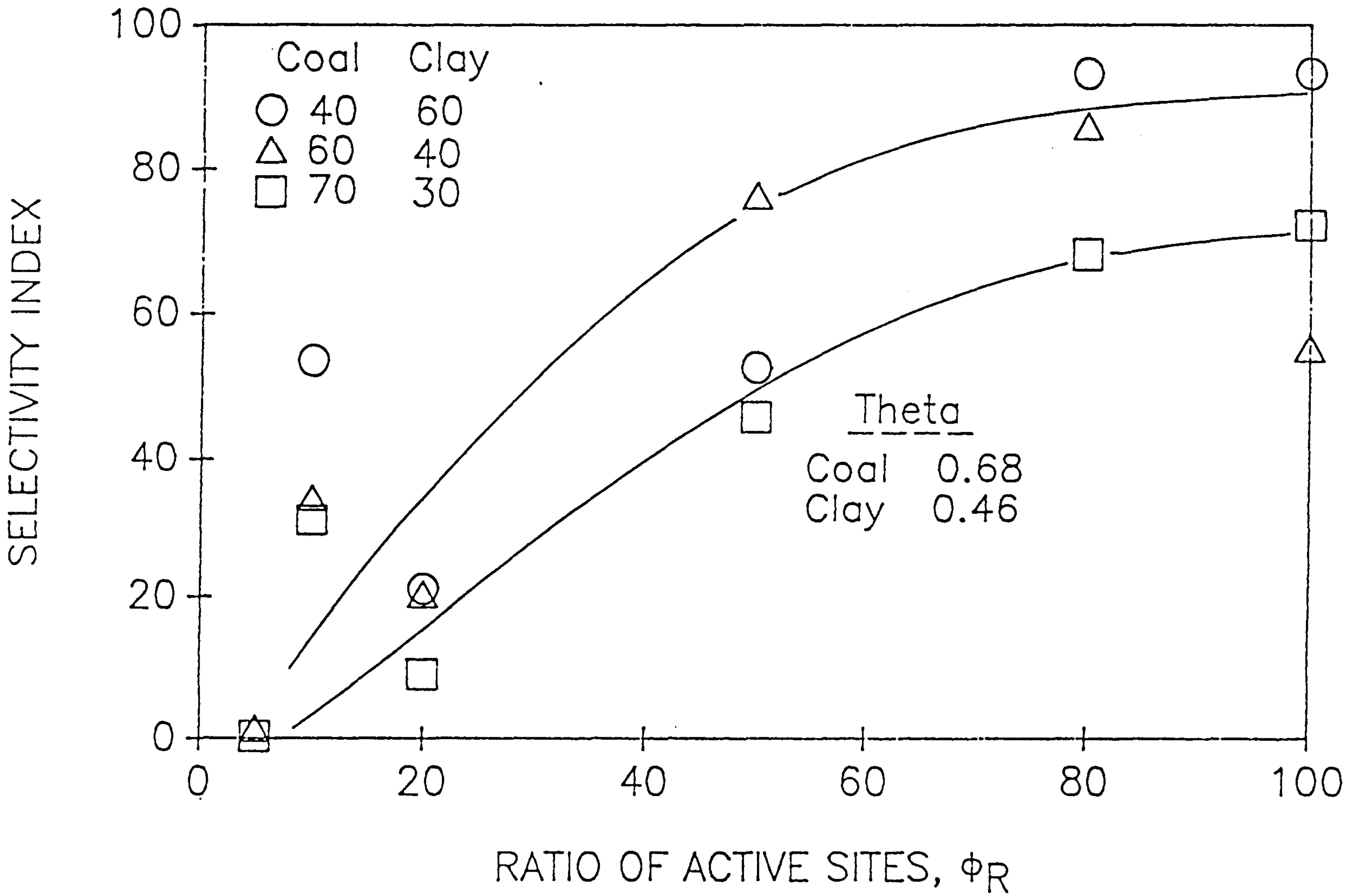

Figure 9. Effect of amount of impurity on the selectivity index.

impurity (dolomite) is flocculated, the selectivity decreases dramatically, as the percentage of impurity in the feed is reduced. In another system (ultrapurification of ceramic powders), however, they observed that this conclusion is not always true and they could achieve higher selectivity at very low impurity levels when floc flotation instead of gravity settling was employed for separating the settled mass from the suspension.

The current simulation program which was written using PASCAL has to be rewritten using either FORTRAN or "C" language. This has been necessitated because the Supercomputer Facility at the Florida State University has recently switched compilers and will no longer be supporting the PASCAL compiler.

FUTURE WORK

The selective flocculation of coal/pyrite mixed mineral systems will be continued using SF 362, SF 16 and WCL-762. The emphasis of the future efforts will be on reduction of pyritic sulfur in coal. Further screening of polymers will continue, and rewriting of the mathematical simulation program will be undertaken.

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3. Moudgil, B. M., Vasudevan, T. V., and McCombs, A., "Selective Flocculation Method for Purification of Ceramic Powders," ***Ceramic Transactions: Ceramic Powder Science II***, Vol. 1, G. L. Messing, Ed., The American Ceramic Society, Westerville, Ohio, 1988, p. 372.