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MINES BRANCH INVESTIGATION REPORT IR 61-90

RECOVERY OF GRAPHITE FROM CYANAMID OF CANADA LIMITED CARBONATE SLUDGE

by

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MINERAL PROCESSING DIVISION

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SUMMARY OF RESULTS

A series of ten pilot plant runs was made to obtain a quantity of graphite flotation concentrate. Maximum recovery produced was 76% at 55.4% free carbon; maximum grade was 68.2% free carbon at 25.1% recovery.

Good reproducibility of results was possible. The material was resistant to upgrading beyond 70% free carbon.

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INTRODUCTION

At Niagara Falls, Ontario, Cyanamid of Canada Limited, produce a by-product, referred to as "Waste Carbonate Sludge", consisting essentially of very fine calcite and graphite. Carbon content runs approximately 10%.

Bench scale flotation work, done by Cyanamid, indicated that a large part of the graphite in the sludge could be recovered by flotation in such a form that subsequent acid treatment produced a marketable graphite product.

The Mines Branch undertook to recover on a pilot plant scale, as quickly as possible, enough flotation concentrate to yield 200 pounds of carbon for market research and development. Although the production of the material was the main objective of this investigation, data [redacted] useful in designing a larger size operation was also desired.

Because of the urgency to supply the concentrate, pilot plant work was carried out largely along the lines shown to be most effective by Cyanamid's earlier tests. Only enough bench type flotation experiments were done to confirm the conditions to be used.

Description of Samples

One drum of sludge (Sample A), weighing approximately 150 pounds, was received for bench scale tests.

Before the pilot plant runs started, 71 drums of sludge (Sample B), having a total weight of 9423 pounds, arrived. For the last pilot plant test, 4 drums of material (Sample C), weighing together 472 pounds, were used.

All samples were shipped wet, in metal containers with polyethylene bags protecting the contents.

Samples A and B were from a similar source. Sample C was from current production, and differed somewhat in composition.

The material consisted mainly of very finely divided graphite mixed with precipitated calcite. This produced a black sludge, that tended to form a hard cake on standing. Optical microscopy and X-ray diffraction analysis provided little information on particle size or the textural relations of the contents. Electron microscopy is being applied to the problem and will be reported separately.

Analytical Procedures

On the pilot plant tests each product was analyzed for 1) acid soluble, 2) free carbon, and 3) ash.

For the bench flotation tests, the acid insoluble content only was determined.

The "free carbon" method, carried out on the sample remaining after the acid soluble compounds were removed, consisted of burning off the carbon in an electric furnace at 1000°C while drawing air slowly over the material. This procedure was worked out by G. A. Kent, Mineral Processing Division, who also supervised the analytical work done by one technician.

TEST WORK

Bench Flotation Tests

Six tests were run in a Denver 500 gram "Sub A" Fahrenwald flotation machine. These were to check reagent combinations, the effect of emulsification, and whether a dispersant would be beneficial.

Results are given in Table 1.

Pilot Plant Flotation Tests

A series of ten runs were made using a rougher bank of 6 Denver No. 5 "Sub A" Fahrenwald flotation cells, and three cleaning stages each consisting of two units of the same size. Feed to No. 1 rougher cell went first to a Denver 12" x 18" agitator, used as a mixer, and then to a Denver 24" x 36" conditioner, from which it overflowed to the flotation circuit. Concentrate was dewatered and removed on a leaf filter.

In Run No. 6 and Run No. 7 the concentrate was given a further three cleanings by feeding it back to the head of the cleaner bank after the main test was completed (Runs No. 6B and No. 7B).

In Run No. 9 carried out using No. 1 stove oil and only the residual pine oil from previous work, a special set of samples were cut at the end of the run to check the effect of having removed more of the pine oil.

Except in Runs No. 1 and No. 9, the cell levels in the cleaners were kept low to give a thick bed of froth. Run No. 1 was made with the levels fairly high - down approximately 1"; Run No. 9 was carried out with the levels as high as possible without having the paddles dipping into the pulp.

Various reagent combinations were tried in order to check recovery and grade. Additions were made to the conditioner only.

Results and conditions under which they were obtained are presented in Tables 2, 3, 4, 5 and Figure 1.

TABLE 1

Batch Flotation Tests

Test No. 1 - Sample A

A qualitative test, using pine oil only, to see how the graphite would float. Results are inconclusive.

Test No. 2 - Sample A

	Wt %	Acid Insoluble %	Dist. %
Conc.	10.7	58.4	54.2
Cl. 2 Tails	4.3	22.4	8.4
Cl. 1 Tails	12.2	6.1	6.5
Rougher Tails	72.8	4.9	30.9
	100.0	11.5	100.0

Reagents   Pine Oil - 0.33 lb/ton, Kerosene - 0.66 lb/ton - emulsified

Test No. 3 - Sample A

	Wt %	Acid Insoluble %	Dist. %
Conc.	10.4	57.6	51.5
Cl. 2 Tails	3.1	28.0	7.5
Cl. 1 Tails	11.8	6.4	6.5
Rougher Tails	74.7	5.4	34.5
	100.0	11.7	100.0

Reagents   Sodium Silicate - 0.5 lb/ton

Pine Oil - 0.33 lb/ton, Kerosene 0.66 lb/ton - emulsified

Test No. 4 - Sample A

	Wt %	Acid Insoluble %	Dist. %
Conc.	12.4	55.6	59.3
Cl. 2 Tails	2.8	12.2	2.9
Cl. 1 Tails	11.2	5.9	5.7
Rougher Tails	73.6	5.1	32.1
	100.0	11.7	100.0

Reagents Pine Oil - 1.2 lb/ton, Kerosene - 0.7 lb/ton,

Aerofroth 70 - 0.2 lb/ton - all emulsified

Test No. 5 - Sample A

	Wt %	Acid Insoluble %	Dist. %
Conc.	9.6	59.3	49.0
Cl. 2 Tails	3.5	30.8	9.3
Cl. 1 Tails	8.0	9.1	6.3
Rougher Tails	78.9	5.2	35.4
	100.0	11.6	100.0

Reagents Pine Oil - 0.33 lb/ton, Kerosene 0.66 lb/ton

Test No. 6 - Sample A

	Wt %	Acid Insoluble %	Dist %
Conc.	12.3	57.1	60.0
Cl. 2 Tails	2.0	22.9	3.9
Cl. 1 Tails	7.7	6.6	4.3
Rougher Tails	78.0	4.8	31.8
	100.0	11.8	100.0

Reagents Pine Oil - 0.7 lb/ton, Kerosene - 1.3 lb/ton

TABLE 2

Pilot Plant Runs

Run No. 1 - Sample B

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	12.8	42.4	4.6	53.0	74.1
Cl. 3 Tails	1.5	74.0	4.3	21.7	3.7
Cl. 2 Tails	1.4	83.4	3.5	13.1	2.0
Cl. 1 Tails	1.9	90.3	2.8	6.9	1.4
Rougher Tails	82.4	96.8	1.1	2.1	18.8
	100.0			9.17	100.0

Feed Rate: 1.05 per min
Reagents: Pine Oil - 1.0 lb/ton
Kerosene - 1.7 lb/ton

Run No. 2 - Sample B

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	10.4	36.1	4.6	59.3	58.7
Cl. 3 Tails	2.1	48.9	4.8	46.3	10.0
Cl. 2 Tails	1.5	65.9	3.9	30.2	4.6
Cl. 1 Tails	1.8	84.4	2.9	12.7	2.4
Rougher Tails	84.2	96.1	1.1	2.8	24.3
	100.0			9.72	100.0

Feed Rate: 0.9 lb per min
Reagents: Pine Oil - 1.0 lb/ton
Kerosene - 1.2 lb/ton

continued

Run No. 3 - Sample B -

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	13.7	40.6	4.0	55.4	76.0
Cl. 3 Tails	0.8	64.7	6.6	28.7	2.3
Cl. 2 Tails	1.0	76.8	6.2	17.0	1.7
Cl. 1 Tails	2.0	88.3	2.8	8.9	1.8
Rougher Tails	82.5	96.7	1.1	2.2	18.2
	100.0			9.99	100.0

Feed Rate: 0.97 per min
Reagents: Pine Oil - 1.0 lb/ton
No. 1 Stove Oil - 1.7 lb/ton

Run No. 4 - Sample B

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	12.5	40.5	3.9	55.6	72.0
Cl. 3 Tails	0.6	70.6	4.2	25.2	1.6
Cl. 2 Tails	1.3	80.4	3.4	16.2	2.2
Cl. 1 Tails	3.0	85.9	2.7	11.4	3.6
Rougher Tails	82.6	96.7	1.0	2.3	20.6
	100.0			9.63	100.0

Feed Rate: 0.85 lb per min
Reagents: Pine Oil - 2.0 lb/ton
No. 1 Stove Oil - 1.2 lb/ton

Run No. 5 - Sample B

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	7.8	33.9	4.5	61.6	52.0
Cl. 3 Tails	1.3	47.6	5.5	46.9	6.6
Cl. 2 Tails	1.2	59.5	4.3	36.2	4.7
Cl. 1 Tails	3.4	69.6	4.2	26.2	9.7
Rougher Tails	86.3	96.1	1.0	2.9	27.0
	100.0			9.24	100.0

Feed Rate: 1.03 lb per min
Reagents: Pine Oil - 2.0 lb/ton

continued

continued

Run No. 6 - Sample B - See also Run No. 6B -

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	13.2	38.3	5.1	56.6	73.3
Cl. 3 Tails	0.7	66.9	5.6	27.5	1.8
Cl. 2 Tails	0.9	77.8	4.9	17.3	1.6
Cl. 1 Tails	3.0	82.7	3.5	13.8	4.0
Rougher Tails	82.2	96.4	1.2	2.4	19.3
	100.0			10.21	100.0

Feed Rate: 0.97 lb per min
Reagents: Pine Oil - 2.0 lb/ton
No. 1 Stove Oil - 1.2 lb/ton

Run No. 7 - Sample B - See also Run No. 7B

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	14.0	39.4	5.3	55.3	75.8
Cl. 3 Tails	0.9	68.5	5.1	26.4	2.5
Cl. 2 Tails	1.1	80.5	4.6	14.9	1.7
Cl. 1 Tails	2.2	87.2	3.3	9.5	2.2
Rougher Tails	81.8	96.6	1.2	2.2	17.8
	100.0			9.63	100.0

Feed Rate: 0.99 lb per min
Reagents: Pine Oil - 1.0 lb/ton
No. 1 Stove Oil - 1.7 lb/ton

Run No. 8 - Sample B

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	13.3	40.0	4.7	55.3	75.1
Cl. 3 Tails	1.0	67.6	4.6	27.8	2.9
Cl. 2 Tails	0.9	81.6	3.8	14.6	1.3
Cl. 1 Tails	2.2	87.6	3.0	9.4	2.1
Rougher Tails	82.6	96.7	1.1	2.2	18.6
	100.0			9.80	100.0

Feed Rate: 0.89 lb per min
Reagents: Pine Oil - 1.0 lb/ton
No. 1 Stove Oil - 1.7 lb/ton

continued

continued

Run No. 9 - Sample B

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	4.6	30.5	4.0	65.5	30.4
Cl. 3 Tails	1.0	41.0	4.8	54.2	5.5
Cl. 2 Tails	1.4	47.4	5.0	47.6	6.9
Cl. 1 Tails	4.0	56.4	4.4	39.2	15.9
Rougher Tails	89.0	94.0	1.4	4.6	41.3
	100.0			9.89	100.0

Feed Rate: 0.98 lb per min
Reagents: Pine Oil - 0.1 lb/ton
No. 1 Stove Oil - 1.7 lb/ton

Run No. 9 (Special) - Sample B

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	3.1	29.7	3.1	67.2	20.4
Cl. 3 Tails	0.7	40.9	3.7	55.4	3.8
Cl. 2 Tails	1.1	44.1	4.3	51.6	5.6
Cl. 1 Tails	3.5	53.5	4.0	42.5	14.5
Rougher Tails	91.6	92.4	1.4	6.2	55.7
	100.0			10.19	100.0

Feed Rate: 1.04 lb per min
Reagents: No. 1 Stove Oil - 1.7 lb/ton

Run No. 10 - Sample C

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	11.8	40.2	4.4	55.4	71.3
Cl. 3 Tails	1.3	64.5	4.9	30.6	4.4
Cl. 2 Tails	1.2	79.2	3.8	17.0	2.2
Cl. 1 Tails	2.5	89.4	2.7	7.9	2.2
Rougher Tails	83.2	96.7	1.1	2.2	19.9
	100.0			9.17	100.0

Feed Rate: 0.94 lb per min
Reagents: Pine Oil - 1.0 lb/ton
No. 1 Stove Oil - 1.7 lb/ton

continued

concluded

Run No. 6B (Conc. from Run 6 Recleaned)

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	3.7	27.7	4.2	68.2	25.1
Cl. 6 Tails	1.3	37.7	5.2	57.1	7.3
Cl. 5 Tails	3.4	40.8	5.3	53.9	18.2
Cl. 4 Tails	4.8	46.8	5.6	47.6	22.7
	13.2			56.0	73.3

Feed Rates: 0.11 lb per min
Reagents: none

Run No. 7B (Conc. from Run 7 Recleaned)

	Wt %	Acid Soluble %	Ash %	Free C %	Dist. Free C %
Conc.	12.8	36.8	4.5	58.8	72.8
Cl. 6 Tails	0.3	60.3	5.6	34.1	1.0
Cl. 5 Tails	0.3	67.0	5.4	27.7	0.8
Cl. 4 Tails	0.6	71.0	5.2	23.8	1.2
	14.0			56.0	75.8

Feed Rate: 0.14 lb per min
Reagents: Pine Oil - 3.0 lb/ton

TABLE 3

Effect of Cleaning - Per cent Carbon

Run No.	Rougher Froth	Cleaner 1 Froth	Cleaner 2 Froth	Cleaner 3 Froth
1	42.2	46.6	50.0	53.1
2	46.6	50.9	53.4	59.3
3	46.7	51.5	53.9	55.4
4	44.0	50.7	54.1	55.6
5	49.4	56.7	59.4	61.6
6	46.3	52.8	55.1	56.6
7	43.2	48.1	50.6	55.2
8	45.8	51.1	53.4	55.3
9	52.8	60.6	63.6	65.5
9 (Special)	53.8	62.0	63.5	67.2
10	43.6	50.0	53.0	55.4

Reruns	Cleaner 4 Froth	Cleaner 5 Froth	Cleaner 6 Froth
6B	61.4	66.0	68.2
7B	53.6	54.2	58.8

TABLE 4

Dilution in Cells - Per cent Solids

Run No.	Rougher	Cleaner 1	Cleaner 2	Cleaner 3
1	7.3	7.8	5.4	3.2
2	6.2	2.5	3.1	4.4
3	6.7	4.9	4.2	6.2
4	5.9	4.1	3.6	4.1
5	7.1	3.0	2.1	2.7
6	6.7	3.6	3.0	3.1
7	6.8	4.4	3.6	4.9
8	6.2	4.0	2.9	3.7
9	6.8	1.7	1.7	1.8
10	7.6	3.6	3.1	3.3
Average	6.7	4.0	3.3	3.7

Rerun	Cleaner 4	Cleaner 5	Cleaner 6
6B	3.7	1.6	1.5
7B	3.0	3.5	4.8

TABLE 5

Retention Time

Conditioner	23 minutes
Roughing	7 minutes
Cleaner 1	4.0 minutes (approx.)
Cleaner 2	4.5 minutes (approx.)
Cleaner 3	5.0 minutes (approx.)

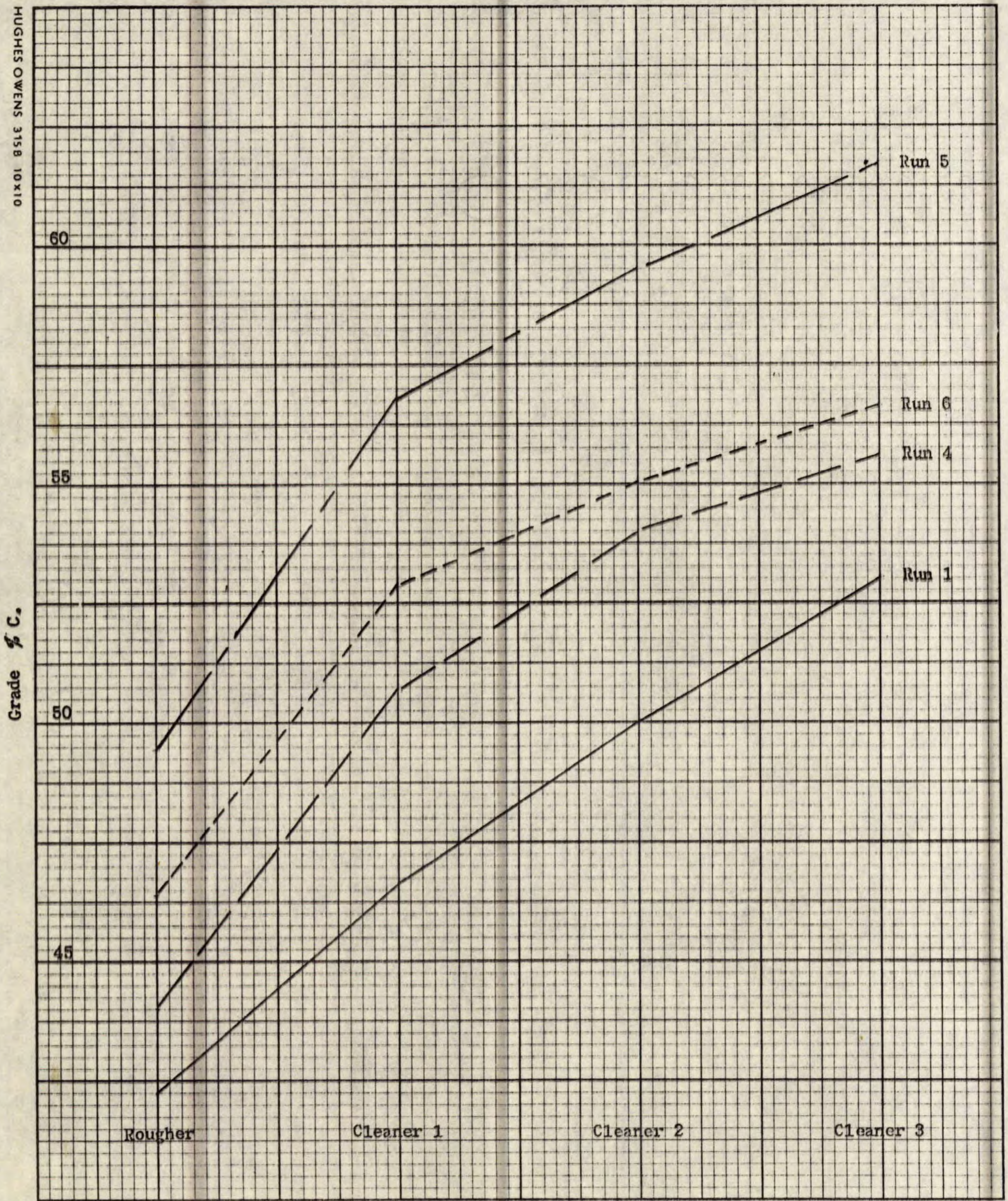

Figure 1. Effect of cleaning on grade of concentrate

DISCUSSION

The few batch flotation tests made showed that emulsifying the pine oil and kerosene did not appreciably improve grade or recovery; the use of sodium silicate as a dispersant seemed unnecessary.

In the pilot plant runs, the graphite floated well with a good recovery using pine oil and kerosene or No. 1 stove oil. However, a high grade concentrate with a good recovery was not obtained. The limited test work done to date by Cyanamid has not shown that it is possible to increase the grade of concentrate much above 70-80%. Electron microscope study may explain this problem.

The combination of pine oil and kerosene or No. 1 stove oil works well. If the pine oil is left out, as in Run No. 9 and Run No. 9 (Special), the froth becomes too soft and the recovery drops off with the grade of concentrate improving. It is probable, however, that the input of pine oil could be reduced to well below the 1.0 lb/ton used in most tests with less cleaning required. This would also be likely to entail some loss of recovery, but a circuit balance could be worked out.

The reproduction of results is good. The calculated heads check well.

A dilute pulp and long conditioning were used since the material is very fine. These conditions should be evaluated in design of a large scale process.

The effect of cleaning, see Figure 1, shows the grade levelling off. Extra cleanings as carried out in Run No. 6B and Run No. 7B gave improved grade only with a much lowered recovery. It is interesting to note that the ash constituents seem to float with the graphite. There is some indication that these drop off in the fourth, fifth and sixth recleanings, but do not in the first three.

Sample C, used in Run No. 10, seems to float in a similar manner to Sample B.

Highest grade material was obtained in Run No. 6B, when the concentrate from Run No. 6 was given an additional three cleanings without the addition of any further reagents. Recovery was low.

Highest recovery was made with Sample B in Run No. 3, using 1 lb/ton pine oil and 1.7 lb/ton No. 1 stove oil.

No middling products were recirculated in any of the test runs. Carbon losses to middlings were nominal and it is problematical whether recirculation in practice would be profitable.

CONCLUSIONS

1. A product analyzing 53 - 57% free carbon, with a recovery of 73-76%, can be obtained by flotation.

2. If an improved grade of concentrate is required, further bench tests should be done, preferably after it is determined whether some calcite is attached to, or combined with, the carbon.

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