

PROGRESS IN DEVELOPING A FLOTATION PHOSPHOROUS REDUCTION PROCESS AT
THE TILDEN IRON ORE MINE

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ABSTRACT

The Tilden mine employs selective flocculation-desliming, cationic silica flotation for beneficiating crude ore that averages 35% Fe. A grind of 82% minus 25 microns is required to achieve sufficient liberation. The final concentrate assays approximately 65% Fe and 4.85% SiO₂. Martite and hematite are the principle iron minerals present in the ore. Difficulties have been encountered with relatively minor phosphorous mineralization which reduces pellet quality.

This paper reviews the phosphorous reduction efforts that have decreased the concentrate phosphorous level from 0.052% P to approximately 0.030-0.035% P. The process changes that have been made include enhanced desliming of fine-grained apatite in the selective flocculation-desliming stage using a new dispersant and use of a specially developed apatite collector to remove additional amounts of apatite in silica flotation.

INTRODUCTION

The Tilden Mine Complex, managed by Cleveland-Cliffs Iron Company, is located 6 km south of Ishpeming, Michigan in the USA. The complex consists of an open pit, concentrator and pellet plant to beneficiate martite/hematite ore at an annual design pellet capacity of 8 million tons. The ore is ground in two stages to 82% -25 microns. Silicious gangue is removed using selective flocculation-desliming followed by flotation.

The phosphorous levels were acceptable in the late 1970's, when the pellet values ranged from 0.031 to 0.046% P. However, the pellet phosphorous levels increased until it reached 0.052% P in 1983. Increasing steel quality requirements necessitated a reduction in the phosphorous levels. Over time increasing phosphorous concentrations were encountered in the ore. At the same time, the pellet quality requirements became more stringent. To compound the difficulties, phosphorous was being concentrated in beneficiation by a factor of about 1.4. The net effect of these trends was that Tilden

pellets were becoming less competitive in the North American market.

A very extensive phosphorous reduction research program was initiated by Cleveland Cliffs in 1983. Various phosphorous reduction techniques were investigated which ranged from relatively minor reagent adjustments to full process conversions. Much of the research work was carried out at the Cleveland Cliffs Research Laboratory but important work was also conducted by outside organizations such as chemical suppliers, universities, and government organizations. Cleveland-Cliffs contacted Berol Kemi AB to work on the project because of their experience in the field of apatite flotation. After Berol Kemi conducted initial evaluations and before the final flotation collector development work was completed, Cleveland Cliffs and Berol Kemi entered into a non-exclusive development agreement.

ORE MINERALOGY

Mineralogically, Tilden ores are essentially highly disseminated, fine grained martite and quartz with and without some ultrafine-grained hematite. Goethite, earthy hematite, and magnetite are frequently present in the ores. Layered silicate minerals such as kaolin, chlorite, sericite, talc and montmorillonite are present in minor quantities. A plant grind of about 82% -25 microns with 50% of the iron oxides finer than 15 microns provides adequate liberation.

Study of the phosphorous mineralogy and mode of occurrence was conducted with optical microscope, electron microprobe, cathodoluminescence microscope and scanning transmission electron microscope methods. The findings showed that the phosphorous in the Tilden ores occurs in two forms: (i) as apatite and (ii) as highly disseminated phosphorous in the iron oxides (designated as phase 2). Very generally, half of the phosphorous occurs as apatite and the rest as phase 2, but the mode of occurrence is quite variable in the ore body.

Metallurgical aspects

In ground samples the apatite is fairly well liberated, although some iron oxide rimming on the grain surfaces and apatite inclusions in iron oxides and quartz occur. Apatite grain sizes range from 50 microns to less than 1 micron with approximately 50% of the particles less than 10 microns. Phase 2 was not mineralogically identified, however it is intimately associated and dispersed in the iron oxides. Therefore, from a metallurgical standpoint it is not possible to remove phase 2 from the ore. This partly accounts for the upgrading response observed in the plant. The mineralogical studies showed that only about half of the phosphorous, in the form of apatite, is rejectable; but, because some of the apatite is not sufficiently liberated, not all of it can be rejected. Based on mineralogical estimates, a concentrate phosphorous level in the 0.030% -0.035% P range could be achieved.

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2 in the ore body which makes prediction of pellet phosphorous levels on a day to day basis difficult. The considerable variability in the amount of phosphorous that can be rejected on day to day and period to period based had an impact on plant testing of phosphorous reduction schemes.

PROCESS DESCRIPTION

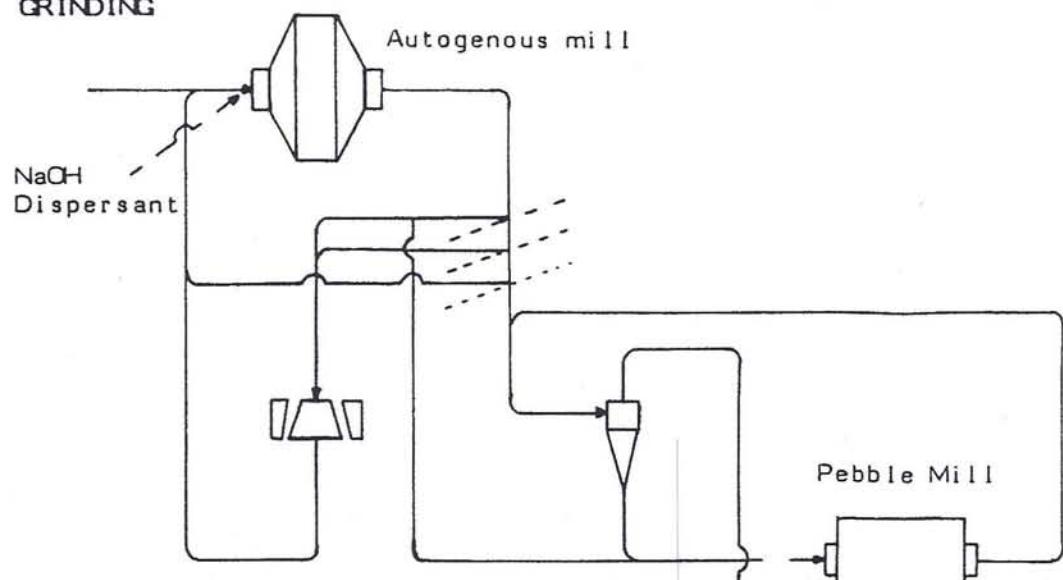
Ore is crushed by a 1.5 x 2.8 m gyratory crusher and conveyed to a covered storage building. Two-stage grinding is employed to achieve the target grind. Primary grinding is done in twelve 8.2 m diameter by 4.4 m autogenous mills at a feed rate of approximately 235 tph. The ground ore is discharged onto two and a half deck vibrating screens where pebbles, primary mill recirculating load and pebble mill feed are produced. A -30 to +75 mm pebble product is used as grinding media in pebble milling. Minus 2 mm material constitutes feed to the pebble mill circuit. The pebble mill section includes twenty four 4.7 m diameter by 9 m mills. The mills operate in closed circuit with cyclones where cyclone overflow of 82% -25 microns is produced for desliming (refs. 1-2).

Dispersing chemicals (pH-regulator and dispersant) required for selective flocculation-desliming and flotation are added in the grinding circuit.

Sodium hydroxide is added to the primary mill feed and the dispersant is added either to primary mill feed, the pebble mill distributor or cyclone overflow. The cyclone overflow pulp pH is 10.5-11.0 and highly dispersed for selective flocculation-desliming. Starch is added (115-230 g/ton) to the cyclone overflow which causes iron oxides to flocculate (ref. 3). Desliming is conducted in thickeners at 10-12% solids where 30-35% of crude by weight is rejected in slimes containing about 10-15% Fe. Deslime thickener underflow is conditioned at 52% solids with starch (450 g/ton) for iron oxide depression prior to silica flotation. Silica flotation is conducted in twelve flotation lines. An ether amine collector is added to the rougher flotation feed box and the sixth cell. There are a total of 10 rougher cells. The final concentrate is the rougher flotation cell underflow. The silica froth product from rougher flotation is successively scavenged (cleaned) in four flotation stages. The silica product from the last scavenger (cleaner) is pumped to the tailings system. All middling products are combined and recycled to rougher flotation. The final concentrate grade target is 4.85% SiO₂ which results in an approximately 65% Fe concentrate. The silica grade is assayed on line which controls the amount of amine addition in a feedback control loop. More amine is added if the silica level is above target level and vice versa.

Rougher flotation concentrate is treated with a flocculant and thickened in two 46 m and two 55 m diameter thickeners. Thickener underflow is neutralized with carbon dioxide and a synthetic polymer and filtering aid are added prior to the disc filtering with steam. The combined effect of pH neutralization, addition of surfactant and polymer, and use of steam produces a filter cake having a 12-13% moisture level.

The plant deslime thickener overflow, flotation tailings and concentrate thickener

GRINDING**DESLIMING**

Starch - - -

Pebble Mill

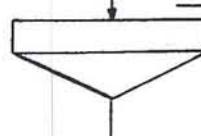
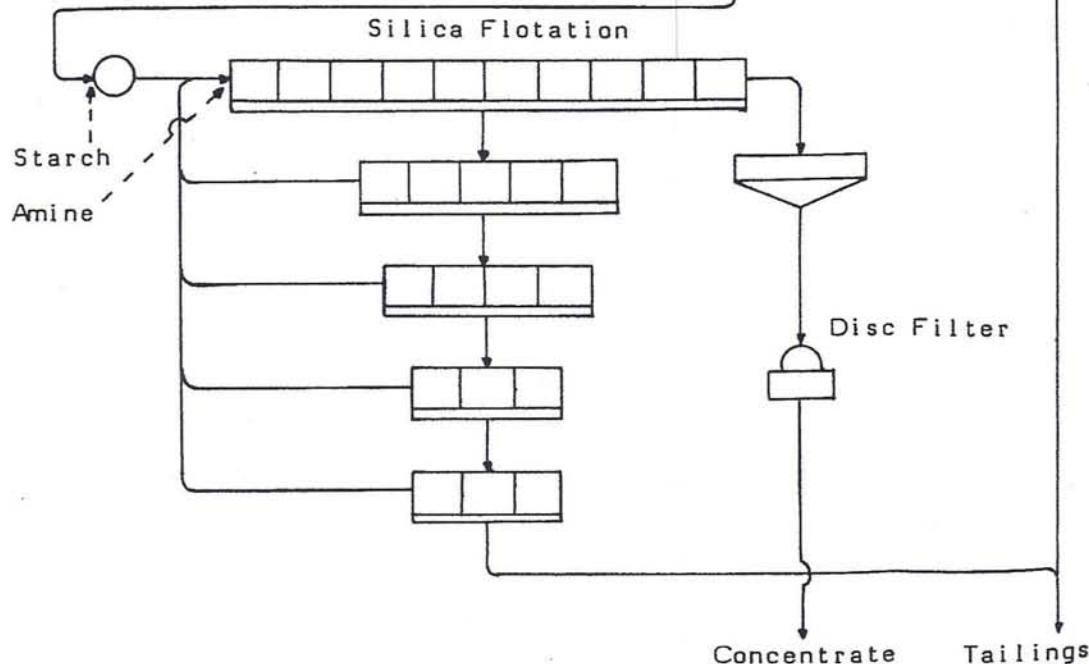
**FLOTATION**

Fig. 1. Concentrator flowsheet.

overflow are thickened in two 137 m diameter tailings thickeners. The tailings thickener overflow can be either directly recycled to the plant or recycled via a reuse water pond. About 95% of the total process water is recycled water. When maximum direct recycling is employed about 90-95% of the process water is obtained directly from the tailings thickeners overflow with the balance being make-up water from the pond.

Maximum direct recycle from the total tailings thickeners is used during winter months to conserve heat. The direct recycle level is roughly 50% during summer months because the combination of higher temperatures and organic breakdown products cause overdispersion in desliming (ref. 4).

PHOSPHOROUS REDUCTION RESEARCH AND DEVELOPMENT WORK

Cleveland Cliffs concentrated their phosphorous reduction studies in four major areas:selective flocculation-desliming, leaching, phosphorous flotation and alternative concentrating flowsheets.

Berol Kemi AB focused their efforts on development of apatite flotation systems.

Selective flocculation and desliming

In the selective flocculation-desliming area, numerous synthetic and natural organic and inorganic dispersant were evaluated for enhancing apatite rejection in desliming. Bench work showed that using polyphosphates as a replacement for sodium silicate increased the selective rejection of apatite in desliming. Rashid and Smith described the use of sodium tripolyphosphate, STPP, which resulted in significant apatite rejection in selective flocculation-desliming (ref. 5).

Plant tests were initiated and it was found that STPP increased the removal of fine apatite in the desliming stage which lead to a concentrate phosphorous reduction. Further testing with higher chain length polyphosphates (P6-, P13- and P21-chain lengths) showed that increasing deslime phosphorous rejection was obtained with increasing polyphosphate chain length. P21-chain length sodium polyphosphate was found to give the greatest phosphorous rejection with no metallurgical deterioration. Based on the positive plant test results, the P21-chain length polyphosphate replaced sodium silicate in 1984. Use of the polyphosphate dispersant reduced the concentrate phosphorous level from average of 0.052% P to approximately 0.040% P. Although a significant concentrate phosphorous reduction was achieved, other steps were researched to achieve the targeted 0.030 to 0.035% P.

Leaching

Acid leaching testwork showed technical promise for reducing the concentrate phosphorous level below 0.035% P. Although successful, the capital costs of installing the flowsheet are quite high and the negative effects of residual sulfuric acid in leached concentrate on filtering and pelletizing equipment was a highly negative factor. Although

a technical success, this alternative was abandoned for practical and economic reasons.

Flotation

Selective flotation of apatite concentrated on (i) apatite flotation prior to silica flotation and (ii) apatite flotation after silica flotation. Flotation of apatite in silica flotation was also investigated. A large number of collectors and conditioning/flotation schemes were tested. Only some of the anionic type collectors were found to be effective in pre- or post-rougher apatite flotation. The iron losses that occurred from the anionic-amine reagent interference made the pre- and post-rougher flotation stages technically feasible but economically impractical. Attention was then drawn to flotation of apatite in silica flotation. Investigations of cationic and anionic collectors led to no technically successful application.

Investigations into several alternative concentrating flowsheets were also conducted. The selective flocculation-desliming calcium activated, anionic silica flotation flowsheet worked particularly well when polyphosphate dispersant was used. However the costs to convert the process water would be very large and there were known grade control difficulties with the flowsheet.

Reagent development

Cleveland Cliffs approached chemical suppliers for the development of a collector that could be used for apatite removal without causing an iron unit recovery deterioration. One of the chemical companies approached was Berol Kemi AB.

The program begun by Berol Kemi AB in 1983 focused on the following key issues:

- 1. Since approximately 50% of the apatite is finer than 10 microns, the developed reagent system must be capable of producing high fine apatite recovery in the froth.
- 2. The flotation system developed must not increase iron losses but, since flotation of partially liberated apatite was desired, a slight increase in iron losses could result.
- 3. As demonstrated in the Cleveland Cliffs work, interaction between the apatite and silica (amine) collectors could have an adverse effect on the process. Flotation of apatite is generally accomplished with anionic or amphoteric typ collectors while cationic collectors are used in silica flotation. There is a high probability that the amphoteric or anionic compound will interact with amine to form complexes that would adversely affect the effectiveness of either collector.

The first phase of the reagent development work undertaken by Berol Kemi was carried out with the purpose of studying the collecting action of synthesized new products on apatite flotation in a separate flotation step, Fig. 2 a. A wide range of possible chemical structures were investigated . From this work a chemical structure was identified which gave a significant phosphorous reduction. The concentrate from a tap water bench test with a particular ore sample assayed 0.029% P, with an iron recovery of 83.2%, which compared quite favourable to 0.059% P in the reference test which had a

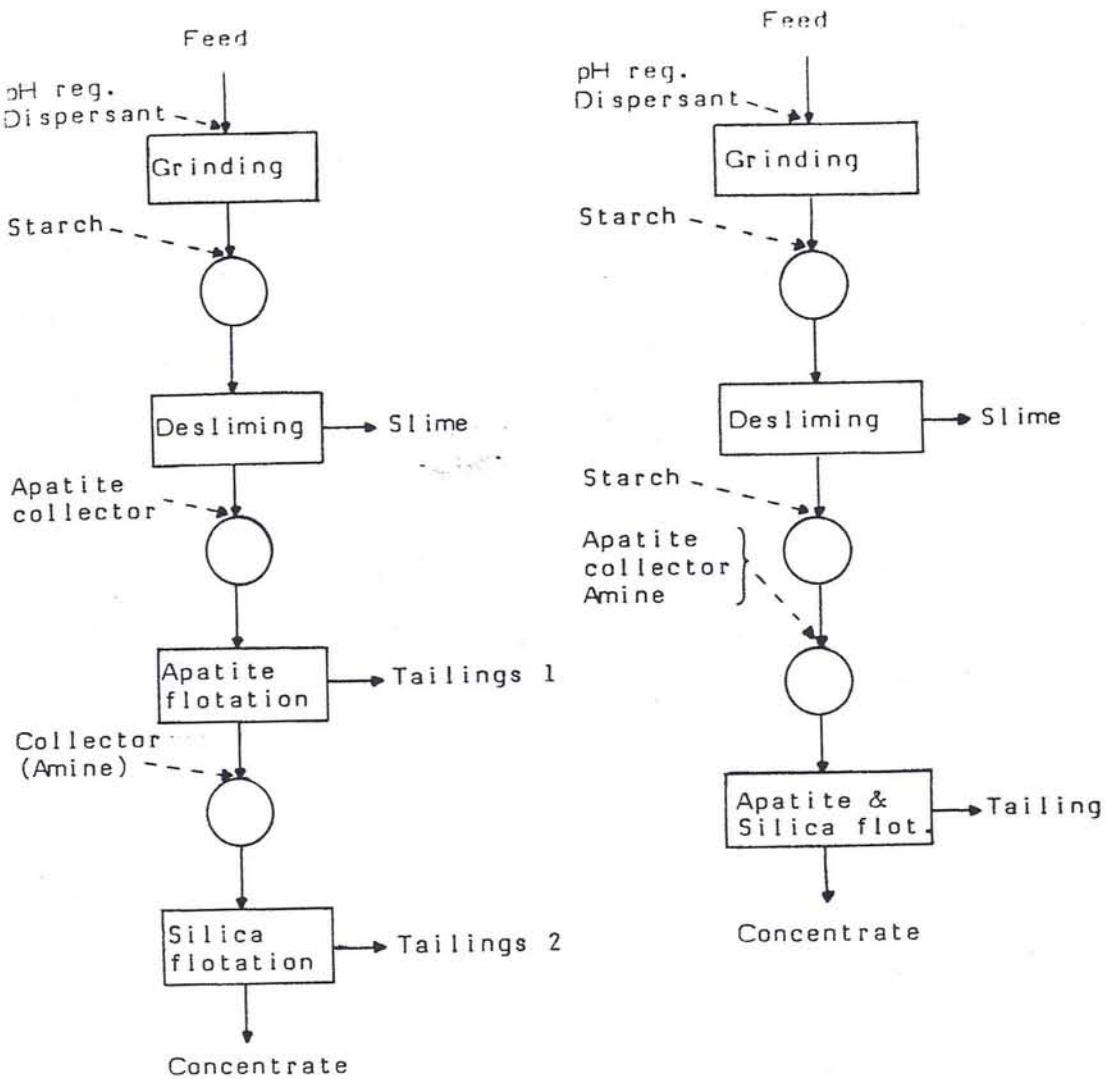


Fig. 2. a) Separate flotation. b) Bulk flotation.

79.2% iron recovery. These results showed that the reagent gave a significant phosphorous reduction without causing an iron recovery deterioration. The work showed that it was possible to develop collector structures with a good selectivity and a capacity to float fine apatite.

One way to make the phosphorous reduction flotation process more practical from an ease of installation standpoint would be to perform flotation of apatite and silica in the same circuit. A bench development phase was begun with the goal of developing a bulk flotation process as shown in Fig. 2 b. Testwork showed that the collector developed in the separate flotation process also removed apatite in the bulk flotation process but silica flotation selectivity deteriorated. A laboratory review of the different possible collector structure was conducted and a collector was found that had interesting characteristics

that met the requirements for bulk flotation removal of apatite. Final assessments of this collector, which was designated ATRAC 873, was performed at the Cleveland-Cliffs Research Laboratory which included evaluation of water quality, type of dispersant, dosage level, ore quality, and other variables. Table 3 summarized a fairly typical result from Berol laboratory tap water tests using this collector with the first amine addition.

TABLE 3

Test conditions and average metallurgical results obtained by bulk flotation in bench scale using ATRAC 873.

Reagents:

Polyphosphate (P-21)	90 g/ton	Added in mill
NaOH	450 g/ton	Added in mill
Starch	110 g/ton	Prior to desliming
Starch	680 g/ton	Prior to flotation
ATRAC 873 (in Atrac test)	140 g/ton	
Amine	145 g/ton	
Water	Reuse water	

	Weight-%	Assay-%		Distr-%	
		Fe	P	Fe	P
Head	100.0	34.6	0.040	100.0	100.0
Slime	20.8	12.0	0.060	7.2	31.8
<u>Concentrate</u>	<u>33.9</u>	<u>65.0</u>	<u>0.029</u>	<u>63.7</u>	<u>24.8</u>
Middlings	13.0	45.4	0.038	17.0	12.4
Tailings	32.9	12.9	0.038	12.1	31.1

When only performing silica flotation the concentrate analyzed 64.5% Fe, 0.041% P with an iron recovery of 62.7%.

A significant phosphorous reduction was obtained when adding the collector with the first amine addition. Importantly, the tests indicate that the new collector did not adversely affect metallurgy since comparable iron recoveries were obtained between the two tests.

ATRAC 873 is an amphoteric reagent. Amphoteric reagents are characterized by multipolar properties, that is, they possess both anionic and cationic groups. With decreasing pH, the ionic charge will change from being anionic to zwitterionic to cationic.

The degree of freedom of designing new collectors is greater with amphoteric because the reagents, unlike true anionic or cationic reagents, contain both anionic and cationic groups. There is an advantage of adapting an amphoteric structure to an application since two (or more) polar groups can be used to control adsorption. The collectors can thus be given a structure that utilizes subtle differences between minerals to obtain preferential collector adsorption to a specific mineral, for example with amphoteric reagents it has been possible to separate apatite from calcite and dolomite without the use of depressant (ref. 6).

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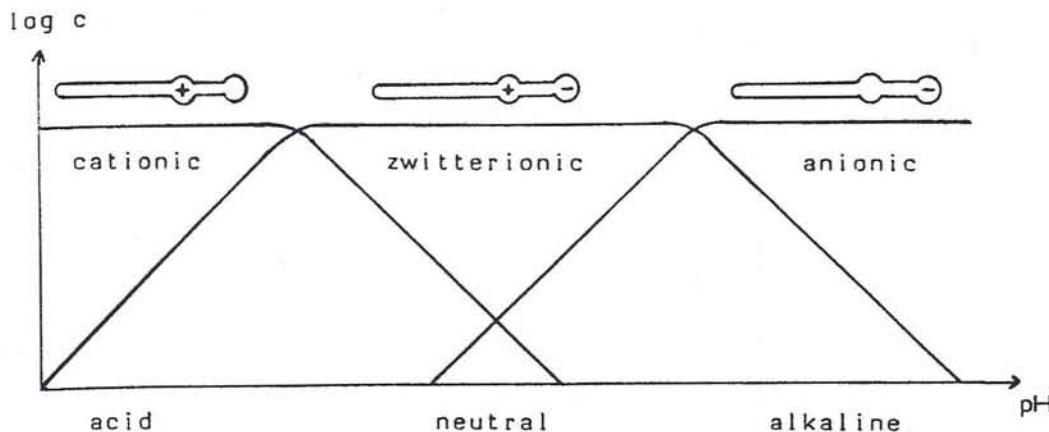


Fig. 3. Dissociation of amphoteric.

Plant testing of ATRAC 873

The first plant test conducted in April-May, 1986 confirmed that the apatite collector could reduce the concentrate phosphorous level. Test line phosphorous levels were reduced from about 0.042% P on the control line to the 0.032-0.035% P range on the test line with use of about 45 g/ton of the new collector.

Metallurgically, there was no deterioration in silica flotation. Weight recoveries were comparable between the test and control lines. Apatite collector addition to the rougher flotation feed box did not cause increased amine consumption. Interestingly, additions of the collector upstream caused increasingly higher amine consumptions levels. Based on the positive results from this testing a second plant test was conducted in July-August, 1986.

The main goals of the second plant test were 1) confirm the capability of the new collector to reduce concentrate phosphorous levels, 2) more fully assess the effect of the apatite collector on concentrate weight recovery and amine consumption, 3) evaluate the influence that a residual apatite collector build up in the process return water would have on the phosphorous reduction and metallurgical responses, and 4) compare different apatite collector addition points. ATRAC 873 was added to 5 of 6 operating flotation lines.

The concentrate phosphorous levels in the second plant test were 0.032% P and 0.036% P on the test and control lines, respectively. Although the magnitude of the phosphorous reduction was much less than in the first plant test, there was strong evidence that a residual apatite collector build up was causing a phosphorous reduction on the control line. Not only was residual apatite collector measured in the process water, the ATRAC 873 dosage level also decreased to about 18 g/ton in this second test compared to 45 g/ton in the first plant test. The discouraging finding was that a

significant metallurgical deterioration occurred in silica flotation. It was estimated that about 1.2-2.9% concentrate weight recovery decrease and 12-21% higher amine consumption was experienced on the test lines compared to the control. Bench time-recovery tests showed that, depending on test conditions, the collector could cause as much as a 60% decrease in silica flotation kinetics. A hypothesis was developed that the flotation circuit was capacity limited and caused a higher amine dosage which in turn increased silica flotation kinetics sufficiently to achieve the target concentrate grade. Higher amine levels generally result in increased iron losses. Analysis of the data supported the hypothesis. The amine consumption increase, decrease in iron unit recovery, and increase in rougher returns weight (which indicate decreased silica flotation selectivity) correlated to increased grinding through put rates. The crude grinding rates during the second plant trial were about 254 tph equivalent per flotation line compared to 189 tph in the first plant test. A third plant test was conducted in January-April, 1987 to again evaluate the apatite collector on a larger scale basis but with sufficient flotation capacity to prevent the flotation circuit from becoming capacity limited.

The ore grinding throughput rates averaged 199 tph equivalent per flotation line in the third plant test. ATRAC 873 was added to 4 of 8 flotation lines at dosage rates ranging from 14 to 18 g/ton. No metallurgical deterioration was observed in the test averages. Comparable weight recoveries and amine consumption levels were obtained between the test and control lines. The flotation feed phosphorous levels were lower than in the previous plant test (new flotation feed had a concentration of 0.025% P versus 0.034% P and 0.030% P in the first and second test, respectively) which probably accounted for the lower phosphorous reduction from 0.034% P on the control line to about 0.031% P on the test line. A residual ATRAC 873 build up in process water quite possibly also caused the lower control line concentrate phosphorous level since nearly twice the amount of directly returned process water was used in this test compared to the second test.

The following conclusions and observations summarize the findings from plant testing with the new apatite collector:

- a) Reduction of phosphorous is highly dependent on ore characteristics; however, use of bulk flotation apatite removal decreased phosphorous in the concentrate by 0.004% to 0.010% P.
- b) The effective apatite collector dosage level is influenced by the amount of process water direct recirculation. During the winter period, when maximum amount of recirculation is used, the consumption of the apatite collector is as low as 15 g/ton, but increases to 45 g/ton during summer months.
- c) Flotation capacity is a critical factor. The apatite-silica bulk flotation scheme using the new collector requires a longer retention time compared to the amine circuit. Insufficient flotation capacity leads to increased amine consumption and decreased iron recovery.

SUMMARY

Metallurgical development is an ongoing process. At the present stage of the Tilden phosphorous reduction project (May 1987), the following conclusions can be made:

-Mineralogical investigations indicate that roughly half of the phosphorous content in the Tilden ores occur as very fine apatite. The other half is intimately associated with the iron oxides and removal is not possible by conventional beneficiation methods. If all liberated apatite is removed, the concentrate phosphorous level would on average be in the 0.030 to 0.035% P range.

-Use of a long chain polyphosphate dispersant improved the rejection of phosphorous in the selective flocculation-desliming stage. Use of this dispersant resulted in a phosphorous level decrease by approximately 25%.

-Tests with a bulk flotation process of apatite and silica using an amine collector for silica and a new collector for apatite provided a further 15-25% concentrate phosphorous level decrease.

-The improved flocculation-desliming and apatite-silica flotation schema would, based on present experience, give the following typical metallurgical result in the plant:

	Weight-%	Assay-%		Distr-%	
		Fe	P	Fe	P
Crude ore	100	35	0.035	100	100
Slime	33	12	0.041	11	38.5
Feed to flotation	67	46.5	0.032	89	61.5
Silica tailings	28	19.5	0.032	16	26
Concentrate	39	65	0.032	73	35.5

Results at this stage of the investigations indicate that the target in developing a process for the production of iron ore concentrates analyzing 0.030-0.035% P can be obtained when applying the process modifications outlined above.

ACKNOWLEDGEMENT

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