

THE PRODUCTION OF FERRONIBIUM AT THE NIOBEC MINE

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Abstract

This paper describes the process used at Niobec in the production of ferroniobium once the ore is brought from the underground mine. It also briefly presents the Niobec operation, which is celebrating its 25th anniversary as a niobium producer. The metallurgical process is not a straightforward operation and requires many steps before delivering ferroniobium to our customer. The concentration of pyrochlore ores is known to be a very complex process. In the case of Niobec, the process requires some 15 different types of reagents, a sophisticated control system, and the process is very sensitive to pH control. Finally, the article is written to enable most readers to understand the various steps in the production of ferroniobium.

Introduction

In 1974, Copperfields Mining Corporation and Soquem formed a new company, Niobec Inc., to bring the niobium deposit of the St-Honoré carbonatite into production.

St-Honoré is located in the Saguenay area, near the cities of Chicoutimi and Jonquiere, and about 140 miles north of Quebec city, Quebec, Canada. The discovery of the carbonatite complex was made by Soquem in the fall of 1967 as a result of an airborne radiometric survey in search of uranium. The detailed exploration of the carbonatite indicated two niobium-bearing formations besides the original discovery of a rare earth zone. During the following years, the niobium formations were defined by diamond drilling and a shaft was driven down to obtain adequate samples for metallurgical evaluation. In 1974, after 700 bench scale tests, 11 months of pilot plant operation and a worldwide market research, a joint decision was taken to initiate the development of 1500 st/day, mine and mill, under the management of Teck Corporation. The construction was completed in early 1976 both on time and within budget. In 1986, Cambior acquired the SOQUEM share in the mine and earlier this year, Teck Corporation sold their interest to Mazarin of Quebec City. Niobec is the only North American and one of the three major world producers of ferroniobium.

The process used at Niobec was developed from the pilot plant programs and later modified by the mill personnel. A simplified flowsheet of this process is shown on Figure 1. Briefly, run of mine ore is crushed to minus 5/8" and fed to a rod mill, ball mill, and classification circuit where the ore is ground to 65#. The ore is deslimed in two stages of cycloning, and underflow is conditioned prior to flotation of a carbonate-apatite concentrate. This concentrate is cleaned twice and then pumped to tails. The carbonate flotation rougher and cleaner tails are cycloned in two stages to change the process water and then sent to the pyrochlore rougher flotation. The rougher concentrate is cleaned five times. This is followed by pyrite flotation to remove sulfur, leaching with hydrochloric acid to remove phosphorus and dried to less than 0.1% moisture before being sent to packaging prior to being converted into ferroniobium.

Ferroniobium production in 2001 should end up in the neighborhood of 4,250 mt or a 30% increase from a year ago. The expansion was necessary to enable Niobec to maintain its worldwide market share. Furthermore, we are at present designing a second expansion whose goal is, apart from the maintenance of our present market share, the reduction of the ore cut-off ratio by maintaining a higher throughput. By doing so, we will delay the development of a fourth block of ore which requires a significant investment and increase the ore reserves as unit operation costs decrease. This expansion will take place only when market prevail. The Table I below summarizes Niobec's production data since 1998.

Table I Niobec's production data since 1998

Year	1998	1999	2000	2001
Tonnage (mt)	817.500	818.000	900.000	1.060.000
Head Grade (%Nb ₂ O ₅)	0.69	0.71	0.66	0.69
Recovery (%)	58	58	54	58
Production (000 Kg FeNb)	3.306	3.476	3.288	4.250

Comminution

Primary crushing is done underground with a Nordberg C-125B crusher 4" blake type jaw crusher set at 4". The run of mine ore is accumulated in a 700 ton capacity shaft bin and two 1350 ton insulated mill bins. Four vibrating feeders (30"X 84") regulated by a belt-scale

provide the feed to the secondary crushing ahead of the rod mill. From there it is conveyed to a four by (4'X 8') rod deck screen with a $\frac{3}{4}$ " aperture. The oversize goes to a cone crusher (1051 hydrocone A.C.) set at $\frac{5}{8}$ ". The sized product and crusher discharges which are equivalent to 131 tph are then conveyed directly to the rod mill.

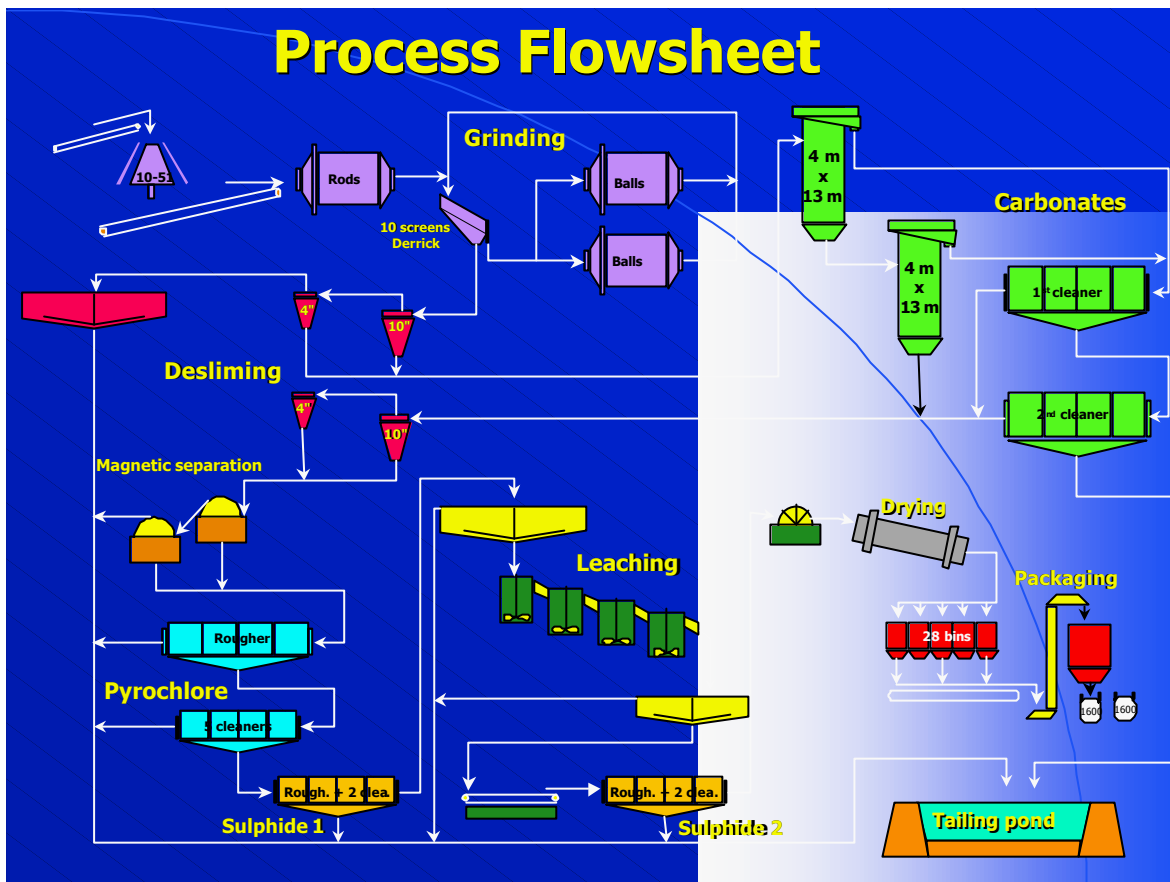


Figure 1: Simplified flowsheet of Niobec process.

With this arrangement, the crusher is operating continuously with the mill and at the same throughput. The capital cost and operating cost of this arrangement are lower than with a conventional crusher house. The underground jaw crusher and the rock breaker are operated by the hoistman located at the surface using video monitoring and joystick control.

The rod mill is a 10.5' X 14' Allis-Chalmer operated in open circuit driver by a 700 Hp motor. The discharge is pumped to a distributor box feeding 12 Derrick multifeed vibrating screens installed with 0.23 mm urethane panel. The oversize from the Hardinge grate discharge ball mill operated in closed circuit with the Derrick screens. The undersize is pumped to the desliming circuit.

The softness of the ore, the relatively high specific gravity of the pyrochlore and the chemistry of the flotation process necessitated this grinding and close sizing arrangement to avoid large amounts of slimes and overgrinding of the pyrochlore crystals.

Desliming

The desliming circuit was designed to remove the $-10 \mu\text{m}$ material before flotation. The slurry is first diluted to 18% solids and then pumped to a bank of seven 10" cyclones operated at 15 psi. The vortexes are 4" and apexes 1.75". The overflow at 4 to 6 % solids is fed to a second

stage of fifty 4" cyclones operated at 25 psi. The vortexes are 1" and apexes at 5/8". Underflows from both stages 1% solids is sent to an 85' thickener for water recovery prior to pumping to the tailing area at 50% solids. The cyclones achieve a very close sizing by removing nearly all of the -7 μm and nearly none of the plus 20 μm particles. The separation size is 9 μm . About 18% of the mill feed by weight and 15% of the pyrochlore are removed as slime.

Carbonate Flotation

After desliming, the slurry is conditioned at 55% solids with an emulsified fatty acid collector and sodium silicate. The pH stays close to its natural level at about 8.0. The silicate is added to partially soften the water and prevent the formation of an insoluble soap of fatty acid. Conditioning is done in an 8X 8' tanks in series with an average residence time of 15 minutes. A rougher carbonate concentrate is floated in two flotation columns followed by a bank of 2 DR-300 cells. Feed to the cells is maintained at 43% solids. About 30% by weight of the mill feed is floated off. The flotation concentrate consists of very fine calcite particles (-50 μm) and medium size apatite.

During the pilot plant test it was shown that the removal of these particles was necessary to achieve a good pyrochlore flotation. Without removal, the fine calcite particles would be partially collected with the pyrochlore and would need 4 additional stages of cleaning to achieve the same grade of concentrate as obtained with preflotation. Also the consumption of acids used to control the pH during cleaning was twice as large without preflotation. Hence it was decided to use this preflotation stage to facilitate the control of the process.

The rougher concentrate is cleaned twice in DR-300 cells prior to pumping to the tailings box. These two cleaning stages do not reduce significantly the total weight of material discarded but they do reduce the Nb_2O_5 content from 0.20% in the rougher to less than 0.10% in the final concentrate. No reagents are added to these cells and the cleaning action is simply the liberation of pyrochlore that has been mechanically trapped in the froth. The pyrochlore loss in this discarded product is less than 5% of the mill feed.

Water Change

Mine water was used for make-up in the comminution circuit. It has a very high salts content of up to 6 grams per liter and had a deleterious effect on the collection of pyrochlore by amine. Therefore only reclaimed water is now used in the grinding circuit.

After carbonate flotation, the slurry is cycloned in an arrangement similar to the desliming circuit. The slurry is first diluted with fresh potable water from 30% to 20% solid. It is then pumped to three 10" cyclones operating at 10 psi and equipped with 2 1/2" vortexes and 1 3/8" apexes. The overflow, at about 4% solids is pumped to nine 4" cyclones operating at 25 psi and equipped with 1" vortexes and 1/2" apexes. The two stage underflows are combined and diluted with potable water from 64% solids to 40% solids. The second stage overflow at <1% solids is sent to the slimes thickener for water recovery. The total salt content is reduced about 3.5 fold by this process.

Pyrochlore Flotation

The slurry is pumped to a bank of flotation cells where the pyrochlore collector, emulsified tallow diamine acetate, is stage added. The pH is maintained at 6.8 to 7.5 with a combination of oxalic acid and fluorosilicic acid. The rougher concentrate is then sent through five

countercurrent stages of cleaning where the pH is gradually reduced to 2.7 with the same combination of acid. Each stage, including the rougher, achieves a concentration ratio of about 1.9.

Pyrochlore is a sodium calcium fluoroniobate ($\text{Na Ca Nb}_2\text{O}_5 \text{ F}$). Its surface chemistry is thus similar to many other minerals since some of its potential determining ions are calcium, and oxygen. Hence selectivity cannot be achieved solely by choosing a given collector, especially when the ore contains mostly calcite, dolomite and silicates.

During the development period it became evident that mild cationic collectors were preferable to either strong cationic collectors or anionic collectors because of their ability to collect less calcite and dolomite.

Hence tallow diamine acetate was chosen. Nevertheless this collector floats all of the silicates present, iron oxides, apatite, sulfides and part of the dolomite. But by gradually reducing the pH, and by introducing silicate surfactants all of these except pyrite are depressed. A 50/50 mixture of oxalic and fluorosilicic acids is used both for pH control and for silicate and oxide depression.

Pyrite Flotation

The cleaned pyrochlore concentrate contains about 20 wt% of pyrite, which after addition of sodium hydroxide is conditioned with starch to depress the pyrochlore. Potassium amyl xanthate (PAX) is then added and a rougher pyrite concentrate floated. This is cleaned twice and then pumped to the final tailing box. About 95% of the pyrite is removed at this stage.

Phosphate Leaching

The pyrite flotation tailing is sent to a 20' thickener prior to leaching. The thickened slurry at 55% solids is then pumped to four 5'X 8' leaching tanks where concentrated hydrochloric acid is added at the rate of 2.6 kg/tonne. The small amount of apatite present is rapidly dissolved. The leached slurry is discharged in a second 20' thickener and diluted with a small amount of fresh water.

Second Pyrite Flotation

The underflow at a pH of about 0.5 is then filtered, repulped and conditioned with copper sulfate to activate the trace amounts of sulfides left. The pH is adjusted to 10.5 with NaOH and PAX is added to float off the sulfides. This concentrate is sent to the first pyrite flotation circuit for cleaning. The overflow from both thickeners are sent to tailings.

Drying

The final pyrochlore concentrate is pumped, at about 40% solids to a 4' disk filter and sent to a 30"X 20' countercurrent dryer where the moisture level is reduced to less than 0.1%. The dryer is equipped with a cyclone and a bag house for dust collection. About 25% of the concentrate is collected through the dust system, the other portion being collected at the normal dryer discharge.

Packaging

The dried product is stored in twenty-eight 6500 kg bins before being mixed in a four compartment loading bin equipped with a recirculating bucket elevator. The concentrate is packed into 1650 kg Big bags where it is transferred to the converter.

Converter

After the pyrochlore concentrate is dry, it is transferred to the converter where the material is transformed into ferroniobium (standard grade).

The niobium oxide is converted into FeNb by using an aluminothermic reaction on a batch basis.

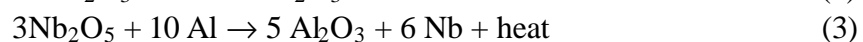
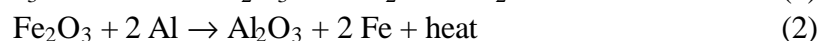
The raw materials used in the reaction, apart from the pyrochlore concentrate, include aluminum flakes and chops, a source of iron oxide hematite or mill scale, quick lime (to lower the fusion point of the slag) and sodium nitrate (chemical agent to increase the available energy).

Each element in the reaction is calculated to obtain the desired quantity of Nb contained in the FeNb. The total batch size contained a total of 5,500 kg of raw materials to produce 2,000 kg of ferroniobium.

After the raw material is well mixed and added to the reaction vessel (a vertical cylinder), the reactor is placed under a hood and the reaction is started after the fuse, made of barium peroxide and aluminum powder, is ignited.

The conversion process serves two basic functions: the reduction of niobium oxide (pyrochlore) and iron oxide to ferroniobium metal, and the separation of impurity elements from the ferroniobium.

The reaction is between the aluminum and the oxide materials. The reaction is strongly exothermic and once it is ignited, it cannot be stopped. The aluminothermic reaction is summarized as follow:



The iron will combine with the niobium in the ferroniobium metal and the alumina will be collected as slag.

It only takes 5 minutes to liquefy all material at a temperature of 2,200°C. During the next 7 to 8 minutes separation of the alloy and slag occurs. After cooling the slag is brought back underground while the ferroniobium ingot is sampled and store.

The metal ingots are selected and withdrawn from storage according to their chemical analysis and customer's requirements. They are then crushed and fed to a classification section where the ferroniobium is packed to suit the customer's product size specifications.

In 2001, total ferroniobium production is estimated at 4,250 mt.

Conclusion

The production of ferroniobium is a very challenging venture from all aspects of the production flowsheet. We are continuously striving to improve the efficiency of our operation to enhance the quality of the ferroniobium produced, and also to maintain our competitiveness on the market place.

This year, we are proud to celebrate our 25th anniversary. Our goals have always been to maintain our world class reputation, our market share (15% - 16%) and in an environment climate of reducing margins, we must always increase customer's engagement.