

A Semi-continuous Autothermic Reduction Process for the Production of Ferroniobium

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A new autothermic reduction process for the production of ferroniobium has replaced the conventional batch thermite process at Companhia Brasileira de Metalurgia e Mineração (CBMM) in Araxá, Minas Gerais, Brazil. CBMM is the world's leading producer of niobium and has been responsible for supplying more than 60 per cent of the niobium consumed by the world during the past three decades.

The new plant consists of a single fixed reactor with a continuous, automated blending and feeding system, a tap-hole for the removal of slag and metal, and a complete exhaust and off-gas treatment system to solve the pollution problem, which was impossible to control in the former batch process. A decrease in the consumption of aluminium powder, the main single cost item in the production of ferroniobium, is expected owing to a better heat balance and less reduction of unwanted elements from the sand pit.

Pilot-plant runs revealed that the excellent recovery in the batch process can be matched by the continuous autothermic process, with an improvement in product quality. This kind of development is a key ingredient in CBMM's commitment to minimizing the impact of cost increases on the price of its products, while simultaneously protecting the environment.

Introduction

The pyrochlore deposit of Araxá is the world's largest known niobium (columbium) reserve¹. This mineral deposit, which represents more than 60 per cent of the world's known economically extractable reserves, has been mined since the early 1960's by CBMM (Companhia Brasileira de Metalurgia e Mineração). For the past 25 years, the mine has supplied more than 60 per cent of the niobium consumed in the Western World.

The Companhia Metropolitana de Comércio e Participação (Moreira Salles) owns 55 per cent of CBMM, while the other 45 per cent is held by Molycorp (UNOCAL).

History

The mine is located in the Araxá carbonatite complex, situated about 6 km south of the city of Araxá in the state of Minas Gerais (Figure 1). It is about 400 km north of the city of São Paulo. The presence of pyrochlore in the carbonatite was first confirmed in 1954 by Professor Djalma Guimarães² during investigations of the radioactive ore-body for uranium. Radioactivity is related mainly to the thorium contained in the pyrochlore.

Wah Chang (USA), with a Brazilian investment group (Melo Viana), first developed the property, and established a mine in the early 1960's capable of processing 500 t of ore per day. Production started in April 1961. In the early years of operation, difficulties were experienced with various impurities in the concentrate (Si, P, and S). The prob-

lems were overcome through modifications to the flotation process, which resulted in a reduction of the SiO₂ and S contents, and through the establishment of a caustic-soda leaching plant (built in 1964), which resulted in a lower P content. In 1965, the established aluminothermic process was introduced for the production of ferroniobium, which met all steel-making specifications. Also in that year, the company's shareholders changed on both the American and the Brazilian sides, and adopted the present name.

Later (in the 1970's), a new leaching plant using a calcium chloride process, which simultaneously removes S, P, and Pb, replaced the former plant, thus meeting the client's stricter requirements. The percentage of ferroniobium sales over concentrate steadily increased and, since 1980, concentrate has not been exported.

In 1979, a chemical plant designed to produce Nb₂O₅ was built so that, by January 1980, CBMM had the capability of producing high-grade niobium oxide in large quantities. The oxide plant's nominal capacity is 2,4 kt of Nb₂O₅ per year (5 million pounds), making this product readily available for the world market independent of tantalum production. During 1981, the company developed a process for the production of specially pure grades of Nb₂O₅ for optical, electronic, and chemical (catalyst) applications. In the mid 1980's, vacuum-grade ferroniobium and nickel-niobium alloys were made available.

Finally, in 1989 the company entered the pure niobium-metal market with an EB furnace capable of producing up to 40 t annually³.

Potential constraints on the availability of niobium in higher-purity forms have thus been overcome, and this, in turn, could stimulate interest in additional uses.

Mining

Ore reserves in all categories (measured, indicated, and inferred) total 461 Mt, with an average Nb_2O_5 content of 2,5 per cent. Since less than 1 Mt is being mined every year, this ore reserve provides more than 500 years of mine life at the present mining rate.

Because of the altered and decomposed nature of the overburden and ore, drilling and blasting are not necessary in the stripping and mining operations. The equipment used in the mine comprises D8L Caterpillar bulldozers, front-end loaders, and normal dump trucks. The bulldozers cut the ore in a downhill mode. The front-end loaders then load the trucks, which transport the ore about 500 m to the feed station of a 3 km long conveyor belt. This conveyor belt transports the ore to the mill, which has a daily capacity of 4 kt.

Concentration

The mine operates only during the day shift. The ore transported by the conveyor belt is crushed and stored in a 4 kt ore bin, which feeds the grinding mill continuously. After being ground, the ore is demagnetized and the magnetite discarded. The non-magnetic material is deslimed and then conditioned with reagents and, finally, concentrated by froth flotation.

The annual production capacity of the facility is 42 kt of

pyrochlore concentrate containing 60 per cent Nb_2O_5 (17 kt of contained metal).

Leaching

The flotation concentrate contains typically up to 1 per cent Pb, 0,5 per cent P and S, and 16 per cent BaO. Most of the Pb, P, and S remains in the alloy. It is thus mandatory to reduce these impurities to an acceptable level before the thermic reduction. This is achieved through high-temperature calcination of the concentrate with calcium chloride. Compounds of the above impurities that are soluble in hydrochloric acid are formed during the high-temperature treatment and can be eliminated by an acid leach. In the leached concentrate, P, S, and Pb are reduced by at least one order of magnitude. After the concentrate has been leached, it is dried in a rotary kiln and bagged in 3 t containers. All the leaching-plant effluents are treated with milk of lime, and the soluble barium ($BaCl_2$) is precipitated with sulphuric acid as the insoluble form $BaSO_4$.

Production of Ferroniobium

The major part of the niobium produced in Araxá is exported in the form of ferroniobium, since most of the niobium is used in the manufacture of high-strength, low-alloy steels. The refractory metals Nb, V, Ti, Mo, and W, when used in steelmaking, are produced via aluminothermic reduction in the form of a ferroalloy. This is done for two main reasons:

- the alloy has a lower melting point, being close to one of the eutectics of the binary system

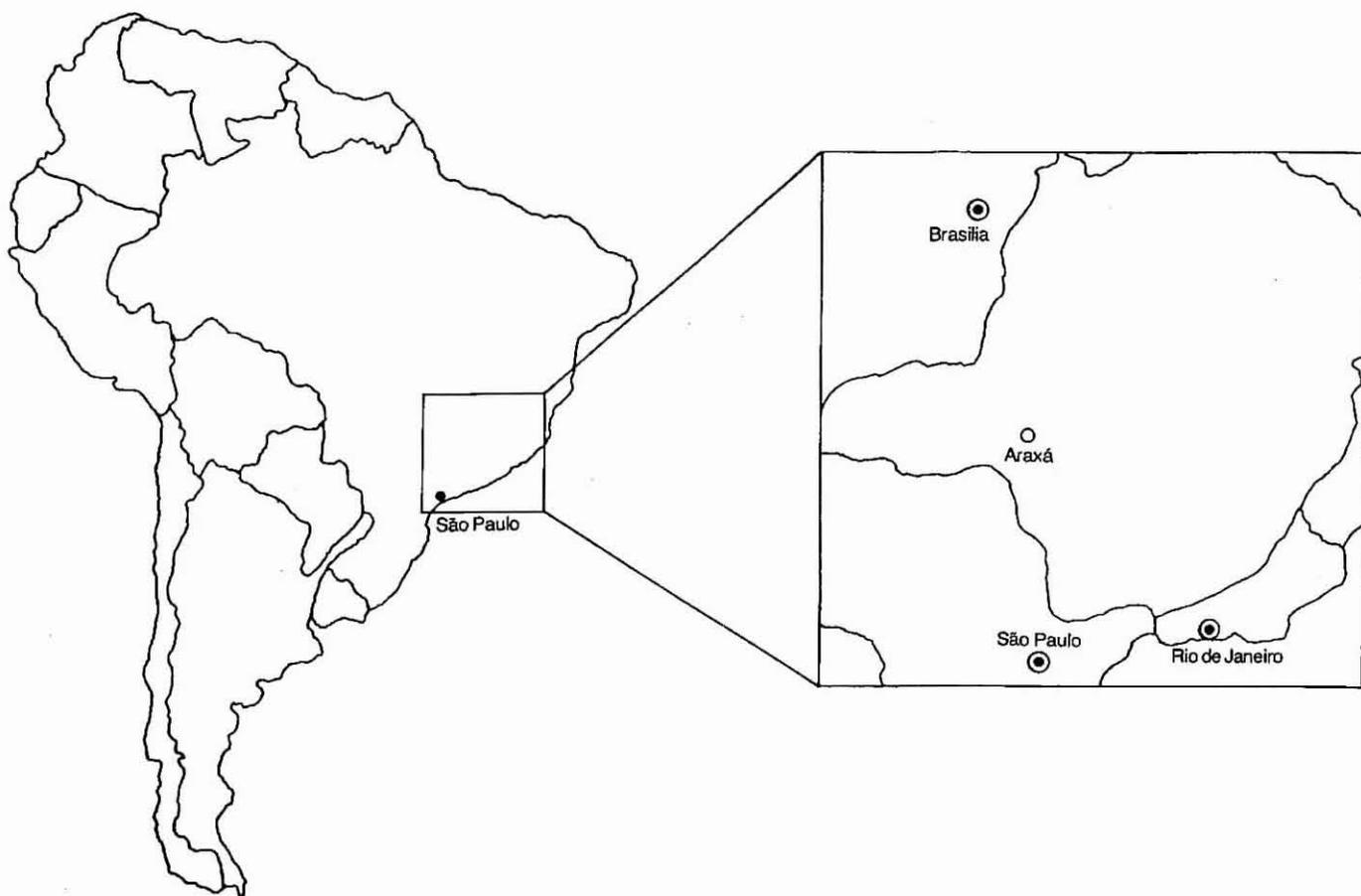


FIGURE 1. Location of Araxá

- the energy of the iron oxide (hematite) released during the reduction process is necessary to melt the bulk of the mixture autothermically and to permit good metal–slag separation.

Traditional Production of Ferroniobium

The traditional method of producing ferroniobium from pyrochlore concentrate was by batch aluminothermic reduction (Figure 2). The installations in Araxá probably represented the largest such facility in the world in terms of reactor size, quantity of aluminium powder used, and tonnage of alloy produced. A typical batch was composed of the following:

Pyrochlore concentrate	: 18 000 kg
Hematite	: 4 000 kg
Aluminium powder	: 6 000 kg
Fluorspar	: 750 kg
Lime	: 500 kg.

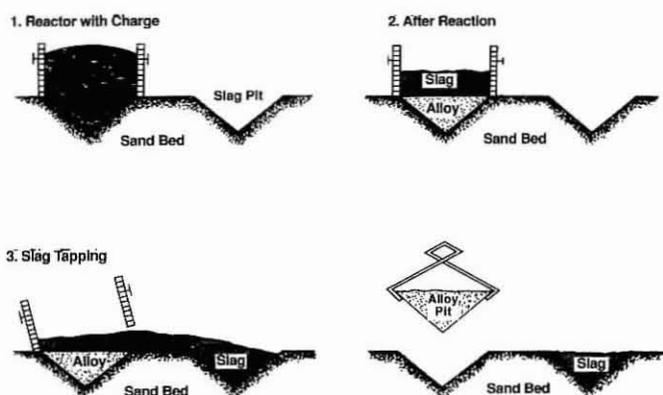


FIGURE 2. The traditional method of ferroniobium production

Each batch produced approximately 11 t of ferroniobium containing 66 per cent niobium. The plant was capable of firing six batches per day, giving an annual capacity of 22,8 kt per year operating 345 days. The yield was around 96 per cent.

The reactor charge was composed of several mixtures stored previously in steel containers. Each mixture, consisting of about one-third of a reactor charge, was mixed in a rotary mixer for 60 minutes.

The reactor consisted of a steel cylinder lined with one layer of magnesia bricks, 3,8 m in diameter and 1,8 m in height. Six of these cylinders were positioned over concave pits, lined with lime and fluorspar, prepared on a sand bed. Externally, the reactor base was sealed with sand, and the mixture that had been stored in the steel containers was charged to the reactors.

The reaction was initiated with magnesium turnings, and the total reaction time was about 20 minutes. During the reaction in open air, an enormous volume of fumes, mainly alumina, came from the reactor. The extraction of these fumes was never feasible owing to the short reaction time versus the large volume.

Metal and slag are readily separated by gravity. The metal settled in the concave pits in the sand bed, and the slag floated above the metal and was contained by the reactor. It was then tapped into a nearby pit when the reactor had been raised from the sand bed with an overhead crane. Most of the impurities, including Th and U, entered the slag.

Some 16 hours after the reaction had been completed, the slag was removed from the sand bed and transferred to a 35 t dump truck and hauled to a disposal area.

The ferroniobium ‘button’ was kept in the sand bed for about 6 hours until it solidified, and was then also removed from the sand bed. After 12 more hours of cooling in air, the ferroniobium was crushed in a jaw crusher, sampled, and stored.

Autothermic Semi-continuous Process⁴

The original ferroniobium plant in Araxá was designed in the early 1960’s and its capacity was gradually increased, basically by enlarging the reactor size. Despite offering a high yield and small investment costs, the operational and environmental conditions demanded a new engineering concept, incorporating modern materials handling, more safety, and fume control.

Studies carried out indicated that the ‘fed reaction process’ is the best alternative. In this process, the reaction occurs in a fixed vessel during mixture feeding. This enclosed controlled reaction, occurring in different cycles of a single reactor, makes it easier to treat the fumes generated. After the batch feeding has been completed, the slag is tapped through the upper hole, allowing water granulation, and afterwards the metal is tapped through the bottom hole, allowing casting.

In order to save on the aluminium powder, which is used to reduce the hematite, the use of an electric furnace as an external source of energy was considered, which would permit the replacement of the hematite by scrap iron. Studies, including some exploratory tests at Mintek, a South African research organization, and several meetings with manufacturers of electrical furnaces, led to the following conclusions.

- Investment in an electric pilot furnace would be of the same magnitude as that in an industrial furnace.
- Most of the pending questions such as metal–slag separation and tapping, slag granulation, and refractory life are common to both options.

As a consequence of these conclusions, it was decided to conduct a series of pilot tests on the autothermic ‘fed reaction process’. A pilot plant with a fixed reactor of 1,6 m in

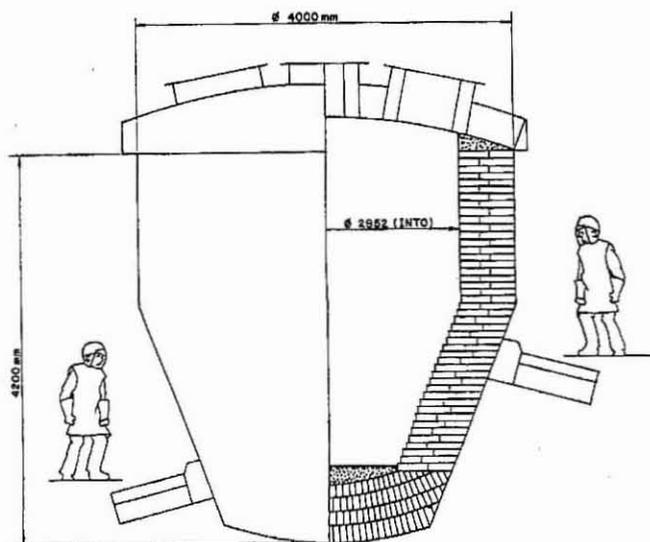


FIGURE 3. Furnace design

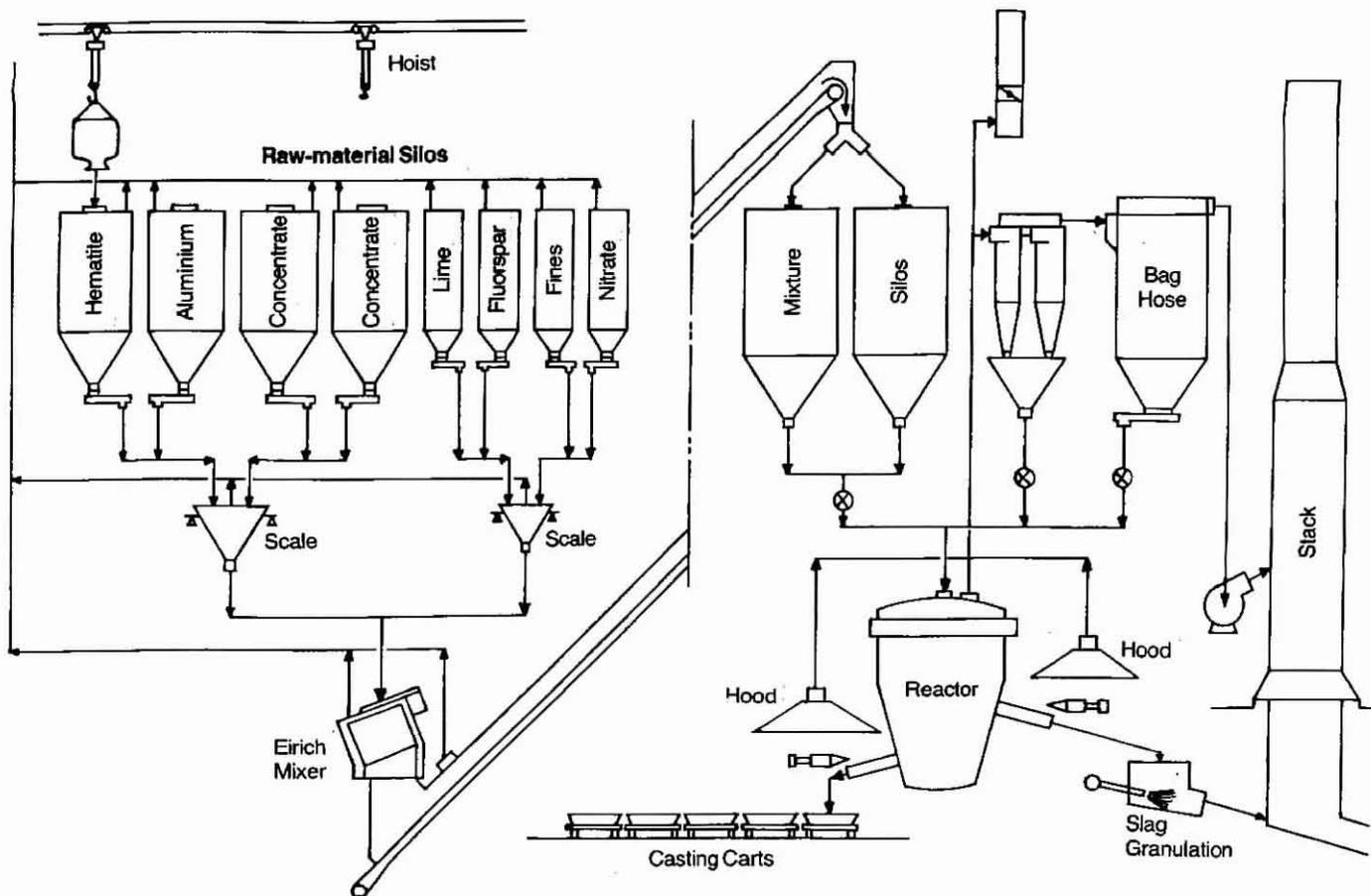


FIGURE 4. Process flow diagram of the autothermic semi-continuous process

internal diameter and 1,7 m in height was set up in May 1989, and a *modus operandi* was gradually developed during that year by use of the present autothermic mixture.

After the test had been completed, it was clear that the fixed reactor chosen could produce the same quality of alloy with the same yield. The refractory life was within expectations, and the slag granulation and metal casting did not restrict the continuous operation.

The improved heat balance due to the refractory roof, the pre-heated lining, and less reduction of unwanted elements (from the former sand bed) significantly reduced the consumption of aluminium powder, the main single cost item after the concentrate. Partial substitution of the hematite was possible, with a further reduction in the consumption of aluminium.

Based on the data generated during the pilot phase, it was decided to design an industrial facility with a reactor configuration that would, if necessary in the future, accept an external heat source to optimize the aluminium saving.

Production of Ferroniobium by the New Process⁵

Mixture

The raw materials for the production of ferroniobium, stored in 3 t plastic bags or 2 t metallic tote bins, are loaded into the silos in the mixing tower by a hoist-and-rail system, as illustrated in Figure 4. The two concentrate silos, along with the aluminium-powder and the hematite silos, each has

a 12 m³ capacity. The silos for lime, fluorspar, fines (ferro-niobium or scrap), and nitrate each has a capacity of 6 m³. All the silos are connected to an exhaust line through bag filters, which keep them at negative pressure, thus avoiding dust clouds during the transfer of materials. The aluminium-powder silo is purged with nitrogen for safety purposes.

Each mixture is composed of one-twelfth of a reactor charge, about 2500 kg, and the quantity of each component is pre-set. The mixing time in the Eirich mixer is about 4 minutes tap to tap. The mixed material is unloaded into a small silo and then extracted continuously by a screw feeder onto a conveyer belt that transports it to the two reactor silos (25 m³ each) in the metallurgy building. The total design capacity of the mixing tower is 37,5 t/h.

The overall plant design incorporates a reasonable degree of computer control. The Genesis Software⁶ provides a combination of flexible automatic operation according to a pre-established plan, in addition to automated data collection (analysis, including SPC, and data acquisition with filing for further use).

Reaction

The ferroniobium is produced by an autothermic process in a stationary covered reactor that resembles a normal electric-arc furnace for the production of ferroalloys.

The mixture, composed basically of pyrochlore concentrate, hematite, and aluminium, is fed to the reactor by a rotating valve. At the beginning of an operation campaign, the reactor is filled to one-third of its capacity (10 t) and ignited with magnesium turnings. After the completion of

the reaction of this first charge, the balance of the mixture (20 t) is fed at a rate of 1 to 3 t/min. After the reaction has been completed, the slag is tapped through the upper hole to a slag-granulation system, using high-pressure water.

The metal is tapped, after the slag, through the lower hole at the bottom of the reactor and cast into 4 t pieces. Each cycle takes 1 hour and produces 11 t of metal (FeNb 65) and 19 t of slag with a slag-to-metal volume ratio of 4,5. Owing to this high ratio, the cross-section of the reactor is conical in the bottom portion.

The slag and metal holes are opened with oxygen lances, and are closed immediately after each tapping with a 'mud' gun.

In subsequent cycles, the charge ignites spontaneously, and both the feeding and the reaction are almost continuous. A waiting time of a few minutes is necessary before slag tapping so that good slag-metal separation is obtained.

Treatment of Off-gas and Fume

During the aluminothermic reduction, a certain quantity of hydrogen is produced. This gas immediately recombines with the oxygen in the air that enters the reactor. This gas load, which carries some fines from the mixture and also volatilized alumina, needs to be treated.

The estimated volume to be treated is 10 000 Nm³/h at 400 °C. The temperature is reduced to a maximum of 150 °C by secondary air admitted through the hoods over the slag and metal tapholes. At this reduced temperature, all the gas can be filtered in a bag-house specified to reduce the particulate emission to 50 mg/m³. A cyclone precedes the bag-house to reduce the bulk of the fines, homogenize the gas, and avoid sparks. All the fines that are captured from the cyclone and the bag-house are returned to the reactor.

Granulation of Slag

After a few minutes of waiting time following the completion of the reaction cycle, the slag is tapped through the upper hole into a slag-granulation system. This kind of system is standard in most metallurgical processes involving large amounts of slag, such as steelmaking or the production of ferronickel.

The granulation process consists of tapping the liquid slag through continuous high-pressure water jets, which cool and simultaneously reduce the grain size to a sand-like consistency. The steam generated during the transfer of energy from the liquid slag to the water is captured by a natural-draught stack.

The slag-water slurry is separated by filtration in a specially designed concrete box. The water is returned to the process, and the slag is conveniently removed and disposed of under controlled conditions.

Metal Casting

After slag granulation, the metal (FeNb) is tapped from the bottom hole into a cast-iron mould. Tapping is continuous for each cycle and, after a cart has been filled, the next one is pulled into position. Once the metal tapping has been completed, the hole is plugged with the 'mud' gun and a new cycle can be initiated.

After 30 minutes, the partially cooled metal is dumped from the cast-iron mould. At this point, the hot metal is cooled with water, resulting in hand-sized pieces. Pieces selected manually are sent to the crushing section, which is composed of one Blake jaw crusher, one screen, and two gyratory crushers.

The Environment

The final stage of volcanic activity, which originally formed the Araxá carbonatite intrusion, is in the form of hot springs and sulphur-water springs, which have been known and explored since the last century. In Araxá, a resort town with a moderate tourist infrastructure near the mining areas, there is close scrutiny of the mining activities by both the authorities and the general public.

The company has traditionally maintained a highly responsible attitude with respect to environmental protection, always aiming to be ahead of the enforced regulations.

There is a reforestation programme of natural species, as well as eucalyptus (for energy), and there is a small game reserve for regional animals.

Personnel

CBMM's total work force in Araxá comprises 480 people: 100 staff members and 380 workers.

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