### 1 Introduction

#### 1.1. Overview of iron ore reserves and production

Iron, the chemical element present in most of the naturally formed ores, has been used since the Neolithic period as raw material for the Iron steel market and with time, it is has become into the backbone of Mankind industrial development (Chemale and Takehara, 2013).

Worldwide production of iron ore has been increased in the last years and it is naturally and well distributed, in the five continents, from China to Australia, Brazil, Russia and India, as the major countries with vast iron ore reserves (Figure 1). According to the National Department of Mineral Production of Brazil (or DNPM in Portuguese, 2011), just in 2011, the global production of iron ore was of 2.8 billion tons, with significant contribution of the Chinese production, which became the world's largest producer, followed by Australia with 480 million tons and third is Brazil with 390 million tons.



Figure 1 - Global production of iron ore by countries (Chemale and Takehara, 2013)



Figure 2 – Evolution of the Brazilian and Worldwide production of iron ore between the years 2000-2011 (Chemale and Takehara, 2013)

According to Chemale and Takehara (2013), Brazilian production of iron ore increased since 2006 to 2011 (Figure 2). Brazilian reserves represent 6.4% (21 billion tons) of world reserves, ranking fifth among the largest in the world. Such reserves are distributed as follows: Minas Gerais (67%), Pará (29, 3%), and other states (3, 7%) (Chemale and Takehara, 2013).

Brazilian iron ores occurs in nature as oxides, carbonates, sulphides and silicates, being the iron oxides the most important between them, especially Magnetite (Fe<sub>3</sub>O<sub>4</sub>) with 72,4% of iron, hematite (Fe<sub>2</sub>O<sub>3</sub>) with 69,9% of iron, goethite (FeO<sub>3</sub>.H<sub>2</sub>O) with 62,9% of iron, siderite or iron carbonate (FeCO<sub>3</sub>) with 48,2% of iron, pyrite (Fe<sub>2</sub>S) with 46,5% of iron. Brazilian reserves are of high quality and known worldwide. Regarding the iron contained, Brazil occupies a prominent position, considering the high content of hematite (60-68% Fe) and itabaritos (50-60% Fe) (Mesquita, 2001).

#### 1.2. Mineral beneficiation of iron ores

Naturally, iron oxides often occur with titanium, phosphorous, sulfur, and the alkaline earth mineral constituents, and mostly limited by siliceous ores. Therefore, the flotation method employed depends on whether recover iron minerals in the froth (direct flotation), or alternatively, recover the siliceous gangue (reverse flotation) (Ma, 2012).

The evolution of Iron ore beneficiation should be considered of great interest due to fasten rise and establishment. Iron ore flotation has short history, starting in America, back in 1930s, when the commercial practice of iron ore flotation was limited. In 1947, Clemmer reviewed the scenario from that time, as the practice, problems and prospects of iron ore flotation. Since then, it was of great concern the isolation of the iron oxide minerals from those containing silica.

The history of iron ore flotation started with direct flotation of iron oxides using anionic collectors such as petroleum sulphonate, fatty acids and hydroxamates. In 1950s, the direct flotation route was integrated in plants, including Humboldt Mine (USA, 1954), Republic Mines, (USA, 1956), and Anshan Iron & Steel Corporation, (China, 1958). Theoretically, iron oxides should be easy to be separated from quartz in direct flotation. However, the presence of hydrolysable cations in flotation pulp significantly reduces the selectivity of the direct flotation route. The hydrolysable cations in iron ore flotation pulp are normally calcium, magnesium and iron. According to Krishnan and Iwasaki (1984), these cations are either released into the flotation pulp from mineral particles or occur from hard water.

The flotation routes of iron ore can be classified into five major groups: cationic flotation of iron oxide, cationic flotation of quartz, anionic flotation of iron oxide, anionic flotation of quartz, and combination. Despite the variety of flotation routes developed for iron ores, currently, the reverse cationic flotation route developed by the USBM branch in Minnesota is by far the most widely used flotation route in the iron ore industry. The two anionic flotation routes developed by Hanna Mining and Cyanamid, i.e. direct anionic flotation and reverse anionic flotation routes, are also being used in the iron ore industry (Ma, 2012).

Every flotation of iron ore in Brazil employs reverse flotation, in other words, the froth contains the gangue, which is mainly composed of quartz. The first Brazilian company operating a flotation plant to treat the itabaritic ore was Samarco in 1977. Since then, other circuits came into operation, but only few companies remained as the top in the industry. The largest producers in Brazil are: Vale (84, 52%), CSN (5, 45%), Samarco (6, 29%), MMX (2, 03%) and Usiminas (1, 71%) (DNPM, 2011).

#### 1.3. Mineral biotechnology

There are two uses of microorganisms in mineral processing: (1) bioleaching, a long-established technique, in which microorganisms assist in the dissolution of metallic ions for metal recovery from ores; and (2) biobeneficiation, in which microorganisms act as surface modifiers, depressants, collectors or dispersing agents to enhance the separation of minerals by either flotation or flocculation (Faharat *et al.*, 2008; Khoshdast and Sam, 2011).

The increasing demand of minerals as well as the decrease of the availability of high-grade ore made necessary the developing of technology to exploit lowergrade ores. Rigorous specification of concentrates, hard environmental legislation and a necessity to achieve lower operating costs, has led to numerous investigations aimed to finding better processing techniques and more effective flotation reagents.

Is in this context where an interesting research area came into development: a biotechnological route for mineral processing became attractive due to its selectivity (microorganisms exhibit specific interactions with minerals) and harmless environmental effect.

Such biotechnological route received the name of "Bioflotation", being described as the mineral processing in which microorganisms act as flotation reagents, whether collectors or modifiers, allowing the selective separation of minerals (Smith and Misra, 1993).

## Leaching

Bioleaching

# Mineral biotechnology

*Bioflotation* Flotation

Flocculation

**Bioflocculation** 

Figure 3 – Diagram of Mineral biotechnology in relation with Flotation, Flocculation and Leaching processes

The presence of functional nonpolar groups (hydrocarbon chains) and polar groups (carboxyl, hydroxyl, phosphates) at the microbial cellular surface or metabolic products lend the microbial culture similar characteristics of surfactant molecules. Therefore, the microorganism can modify the mineral surfaces, either directly or indirectly. The direct mechanism involves adhesion of cells to mineral particles while the indirect mechanism reagents (Sharma and Rao, 1999) or as soluble fractions of the microorganisms derived from their rupture. (Schneider *et al.*, 1994; Raichur *et al.*, 1997).

It has been demonstrated that it is possible to use microbial species as flotation reagents in selective separation for several systems: pyrite-coal (Raichur *et al.*, 1996), hematite-quartz and corundum-quartz (Deo and Natarajan, 1998), apatite-dolomite (Zheng *et al.*, 1998) and chalcopyrite-pyrite (Sharma *et al.*, 2000), hematite-quartz (Mesquita *et al.*, 2003), calcite-magnesite-barite (Botero *et al.*, 2007) and apatite-quartz (Merma *et al.*, 2013), as a few examples. This microbial cells-mineral particle interaction has led to the conclusion that there is a

significant change in the chemistry of the surface of the minerals (Mesquita *et al.*, 2003).

Previous researches showed that the hematite bioflotation succeeded using other hydrophobic non-pathogenic bacteria such as *Mycobacterium phlei* (Smith and Mishra, 1991; Dubel and Smith, 1992; Yang *et al.*, 2007), *Bacillus polymyxa* (Deo and Natarajan, 1997), *Paenibacillus polymyxa* (Deo and Natarajan, 1998), *Rhodococcus opacus* (Mesquita *et al.*, 2003), *Rhodococcus erythropolis* (Yang *et al.*, 2013) and *Bacillus subtilis* (Sarvamangala and Natarajan, 2011).

In this work, entitled "Fundamental aspects of hematite flotation using the bacterial strain *Rhodococcus ruber*", was studied the system hematite-*R.ruber*, as hematite and *Rhodococcus ruber* separately, by zeta potential and adsorption measurements; characterization lectures such as FTIR and SEM, and most specifically, flotation studies.