Optimization of Flotation for the Reduction of Heavy Minerals and Iron Content on Silica Sand

Alonso, Liliana M.

Instituto Superior Técnico
Universidade Técnica de Lisboa
Dezembro 2014

Resumo

Este estudo teve como objetivo a otimização de um processo industrial de flutuação de areias siliciosas para minimização dos teores de Fe_2O_3 e minerais densos. Foram efetuados diversos testes laboratoriais seguindo a técnica de "Design Experimental" para definir as condições ótimas de trabalho que possibilitam a minimização dos teores de Fe_2O_3 e minerais densos no afundado. A flutuação é um processo tecnológico complexo fortemente influenciado por vários parâmetros do processo. Neste estudo, considerando que grande parte das variáveis, como a dimensão das células de flutuação, a velocidade de agitação, o tempo de retenção, a variabilidade da alimentação, entre outras, são determinadas pela própria instalação industrial, foram mantidas fixas. Para o processo de otimização foram selecionadas as variáveis: pH do meio, concentração de coletor e concentração do espumante ou tensoativo. Os resultados dos ensaios mostraram que para os intervalos de variabilidade selecionados não existem correlações entre as variáveis. As condições que minimizam o teor em Fe_2O_3 são a minimização do pH e maximização da concentração de coletor.

Palavras-chave: Flutuação, minerais densos, areia siliciosa, coletor, tensoativo, design experimental.

Abstract

The target of this study is the optimization of an industrial froth flotation process of silica sand to minimize the Fe_2O_3 and heavy minerals content. Multiple laboratory tests were made, following the technique of experimental design to define the optimum work conditions that enable the minimization of Fe_2O_3 and heavy minerals contents in the sunk. Flotation is a complex process with multiple factors that may influence the minerals purification. In this study, as the majority of variables associated with froth flotation are difficult to change in the industrial process e.g.: size of the flotation cells, impellers speed, retention time, variability of feed and others were kept constant. For optimization the variables selected were pH, concentration of collector and frother. The test results do not showed correlation between variables. Conditions to minimize the Fe_2O_3 are the pH on minimum tested and collector concentration on maximum tested.

Key words: Flotation, heavy minerals, silica sand, collector, frother, experimental design.

1. Introduction

1.1. Objectives and Motivation

This work intended to optimize multiple variables (pH, concentration of collector and frother) for the implementation of the best conditions on industrial process in order to obtain more purified silica sand. The industry involved extracts and transforms non metallic minerals from Rio Maior (Portugal).

The market demands different silica sand quality according with diverse applications. Industries of flat glass, engineering stone and ceramic wants sand with iron contents and heavy minerals bellow 150ppm. The price of sand increases with the lower iron and heavy minerals content. Sands with 100ppm of iron content and 100ppm of heavy minerals are considered very high quality. Iron content affects transparency of glass, discolours ceramic products and lowers the melting point of refractory materials (Taxiarchou & al, 1997).

The current ex-works market price for silica sand can change between 2,50€ and 60,00€ per ton depending his beneficiation and purity. High purity silica sand is uncommon but required for added-value applications. To develop this attractive market it was made the present work.

1.2. Background

Ore deposits of the Earth crust consist of a mixture of different minerals that change in grain size, quality and nature depending on their geological origin and history. The largest group of minerals constituting the Earth crust is the silicates with over 90% of the Earth's crust. Sand is a naturally occurring granular material composed by finely divided rock and mineral particles. The composition of sand is highly variable, depending on the local rock sources and conditions, but the most common constituent of sand is silica (silicon dioxide, or SiO_2), usually in the form of quartz. Silica sand is a non metallic mineral very important on human day life. Silica sand is used on glass industries, foundry, ceramics, paint and rubber, abrasives, construction (energy and stone engineering including), cement, sport and leisure.

The extraction methods used are excavation by caterpillar excavator, dredging and rarely explosives. The majority are open pit mines. Therefore, beneficiation is usually necessary to improve the quality of the raw material. To remove impurities several processes (single or combined) are usually needed: screening, attrition, scrubbing and washing, gravity concentration, dense medium separation, magnetic and high-tension separation, froth flotation, acid leaching and dewatering (Wills, 1977)

(Corporation, Unimin, 1999) (Banza, Quindt, & Gock, 2006).

Presented work use an experimental plan to analyze the froth flotation performance with process variables changing.

Experimental design is a formal plan of experiments defined by a matrix composed by the different level combinations of the factors (independent variables) in study widely used for optimization of processes, supporting the definition of best process parameters. This methodology allows finding the interaction between different variables, based on statistical analysis (Dejaegher & Heyden, 2011) (Bezerra & al, 2008).

The statistical data analysis is based on variance analysis (ANOVA) that quantifies the significance of each independent variable and possible interaction with other variables and obtain empirical models used for optimizing the variables to obtain the desired process response (Mohanty & Das, 2010).

A three-level full factorial design includes N trials that represent all possible combination between factors (X) and levels (l). For 3 factors $N = l^X$, so at 3 factors are need $N = 3^3 = 27$ experiments, including one centre point (Dejaegher & Heyden, 2011).

The Taylor series are polynomial equations that are used to predict the response variable:

$$Y = \beta_0 + \sum_{i=1}^{p} \beta_i X_i + \sum_{i=1}^{p}\sum_{j=1}^{p} \beta_{ij} X_i X_j + \sum_{i=1}^{p} \beta_{ii} X_i^2 + e \quad (1)$$

Where Y is the estimate answer, β_0 is the overall mean response, β_i the main effect for factor (i= 1, 2,..., p), β_{ij} the two-way interaction between the ith and j^{th} factors, β_{ii} the three-way interaction between i^{th} factors, X is input factors and ε is the experimental error, i≠j (Bezerra & al, 2008) (Telford, 2007).

2. Froth Flotation

2.1. **Historical evolution**

Flotation is a physic-chemical process used for mineral separation since the XIX century. In 1860, Willian Haynes patented a process for separating sulfide from gangue mineral particles using oil and named it bulk-oil flotation - British Patent 488/1860 (Miller & Parekh, 1999) (Ahmad, 1951). Later, in 1877, the Bessel brothers patented and built the first commercial flotation plant in Dresden, Germany to clean graphite ore - German Patent 42, Class 22. The froth flotation process was invented in 1905 simultaneously by A.H. Higgins in England and G.A. Chapman in Australia using as flotation reagents naturally occurring chemicals such fatty acids (Fuerstenau, Jameson, & Yoon, 2007).

Froth flotation undergoes a great evolution in the beginning of the 20th century. In the United States, the quantity ore treated by this method increases by 4 times between 1926 and 1960 and doubles between 1960 and 1980 (Du H. , 2008).

Investigation of sulfide minerals flotation began before 1930, while the flotation of non metallic minerals began only near 1950. The flotation process was studied and reviewed by several authors, considering the development of flotation reagents, type, size and flow of gas bubbles, contact angles and properties of interfacial films, grain size distribution of ores, interaction between reagents and minerals surface, zeta potential, adsorption density, pH, reagent interactions, etc. However, the flotation process evolution was also as a result of practical and sensitive work on complex ores (Fuerstenau, Jameson, & Yoon, 2007).

2.2. **Fundamentals**

The flotation process uses differences in the surface properties of particles of minerals to effectively separate the particles with different economic value, by inducing 'froth', that is three-phase structures comprising air bubbles, solids and water (Farrokhpay, 2011).

The process takes place in an ore pulp in which the surfaces of one or more minerals in the finely ground pulp transformed in water-repellent (hydrophobic) by adding specific chemical reagents. These chemical reagents are attracted to some mineral particles surface through physical or chemical adsorption. The nature and extent of this adsorption are dependent on several variables, namely on the density and type of the surface charges of the mineral particles in the aqueous pulp (Corporation, Unimin, 1999) (Cummins & Given, 1973).

The hydrophobic particles are transported to the froth layer by air bubbles, and removed as floated product. As the flotation process is not perfect, the bubble-attached particles can drop to the pulp and unattached particles are drag to the froth. Consequently, the particles of all types of minerals will be present in both the froth and the pulp. The rate of flotation, keeping the variables constants, varies with the flotation time; using the analogy between chemical reactions and flotation processes, this approach is defined as flotation kinetic and is described as follows:

$$\frac{dC_F}{dt_k} = -K C_F^{n_k} \quad (2)$$

Where C_F is the Concentration of the floatable minerals in the pulp, t_k is the time of reaction, K is the flotation rate constant and n_k is the order of reaction (Hernáinz & Calero, 2001) (Somasundaran & Lin, 1973). In flotation, the kinetic is generally of first order.

The rate of flotation is dependent of large number of variables that can be grouped in three major components according to Kawatra (Kawatra, 2011): chemical, operational and equipment variables. The optimization and control of these variables is keys to the froth flotation process.

2.3. **Flotation variables**

Chemical reagents are used to change the surface chemical properties. Their nature, concentration and

interactions are very significant on flotation process performance.

The selection of reagents depends of the specific mineral mixture to be purified. Chemical reagents used are the key variable of flotation process, as well as the concentration used (Rahman, Ata, & Jameson, 2012) (Bayat & Akarsu, 2002). The control of concentration of reagents is very important because the relation between reagents concentration and recovery is no-linear; usually obeying a square power law variation (Shean & Cilliers, 2011).

Collectors or promoters are reagents that create favorable conditions to the attachment of selected mineral particles to the air bubbles while the others remain unattached. The collector changes the particles surface creating a hydrophobic film that will increase the contact angle between air bubble and mineral particle promoting a strong bubble attachment and the transport of hydrophobic particles to surface. The collectors are commonly classified by their ionic charge: non-ionic and ionic (anionic or cationic) (Kawatra, 2011).

Anionic collectors are used on mineral ores with a positive surface charge, generally tall oil fatty acids, while the cationic collectors are used on mineral ores with a negative surface charge, generally amines (Cytec Industries, Inc., 2010).

The concentration of collector is proportional to mineral recovery until reach a plateau, and then increase the concentration has no effect or it may occur a reduction of recovery as shown in Figure 1 (Wills, 1977).
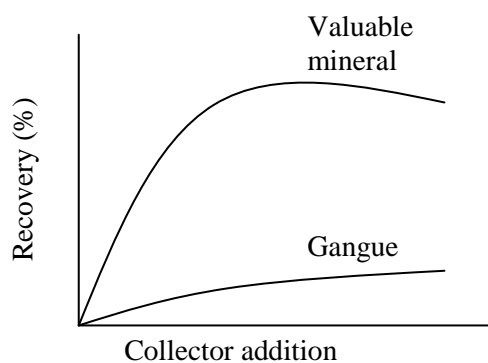

Figure 1 – Effect of collector addition on recovery (Wills, 1977)

Modifiers are compounds used to modify the properties of the pulp and can be divided in:
− Regulators of pH: in general the mineral changes the charge surface under different pH conditions (negative charge under alkaline conditions and positive charge under acid conditions), this phenomena is used to manipulate the attraction of collectors to mineral surfaces.
− Activators: prepare the mineral surfaces to improve the action of collector.
− Depressants: Important to differentiate two mineral particles in order to inhibit the flotation of one maintaining the flotation properties of the others.
− Dispersants: the dispersant helps on the cleaning of mineral surface, dispersing slimes and deflocculates

the mineral particles agregates (Corporation, Unimin, 1999).

Frothers are used to stabilize the froth phase. The frothers reduce the interfacial surface tension to enhance the attachment of the mineral particle to air bubbles.

Oils are used to extend collector properties. Kerosene and others tall oils are nonpolar and hydrophobic (Cummins & Given, 1973).

Operation conditions as slurry flow rate, slurry properties (pulp density and solids content), retention time, froth wash water quality and rate and pulp levels in cells can change flotation performance.

Equipment used in flotation determines the cell design (cells bank configuration), agitation (speed and type), air flow rate into cells, and cells bank control are also important to flotation performance.

The froth flotation is a complex engineering process, where various phenomena are interrelated; for which the change of one parameter will influence the performance of other parameters (Kawatra, 2011).

Good control of a flotation process does not imply the manipulating or measuring all these variables simultaneously. Nevertheless, it is necessary to consider the effects of each variable on the flotation process (Shean & Cilliers, 2011).

2.4. **Flotation performance**

To measure the flotation performance is necessary to measure and control some important variables of the process. The performance of flotation can be measured by different methods (Kawatra, 2011) (Wills, 1977):

Weight Recovery is most common ways to define the effectiveness of a separation.

$$C/F = (f-t)/(c-t) \tag{3}$$

Where F is the % weight of the feed, C is the % weight of the Concentrate, c is the assays of the concentrate, t is the assays of the tailings and f is the assays of the feed.

Valuable Mineral Recovery (Rm) is the percentage of valuable mineral in the feed that is recovered in the concentrate.

$$Rm = 100 \, Cc/Ff \tag{4}$$

Enrichment Ratio (E) is the ratio between assays of concentrate and assays of the feed.

$$E = c/f \tag{5}$$

Others measurements or values can be considered at industrial level. In the cases study was evaluate using the content in some contaminants.

2.5. **Industrial Process of flotation**

Flotation can be classified as direct flotation or reverse flotation. Direct flotation is when the valuable product is removed in the froth, while in reverse flotation the valuable product is on the sunken (Corporation, Unimin, 1999). The following description is about a

reverse flotation inserted in a complete beneficiation process of silica sand installed in Rio Maior (Portugal).

Process description

The flow-sheet of process is showed in Figure 2. The extraction of white sand is made by dredge. The feed is screened to remove rocks and other solids larger than 1,6mm. Then the slurry is pumped to a hydro cyclone that separates the sand from kaolin and water. The overflow of the hydro cyclone (water, kaolin and very fine sand) is processed in the kaolin classification. The underflow is mainly sand and is stocked in a silo with 1000 ton of capacity. The sand extracted from the silo is pumped to hydro cyclones to increase solids concentration and is discharged in the attrition process. After the attrition process the pulp is processed in the hydro classifier 1, which removes in the overflow the residual kaolin and very fine fraction of sand (< 90 μm). The underflow of hydro classifier 1 is pumped to the hydro classifier 2. In hydro classifier 2, all particles size distribution are between 0,09 and about 1 mm. The overflow is a fine fraction of sand with average particle size of 360μm (the product under study). The underflow is the coarse fraction with average particle size of 470μm. The fine fraction or the coarse fraction of Figure 2 passes through spirals to remove about one half of the heavy minerals present in the sand.
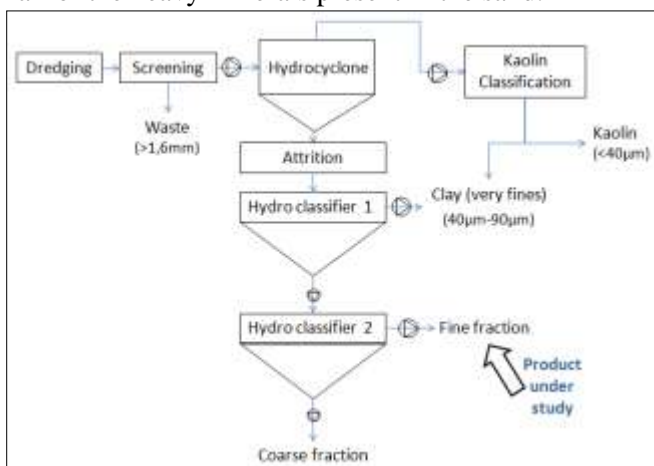

Figure 2 – Flow sheet of industrial process until classification

The scheme of industrial spirals process in study is shown in Figure 3.
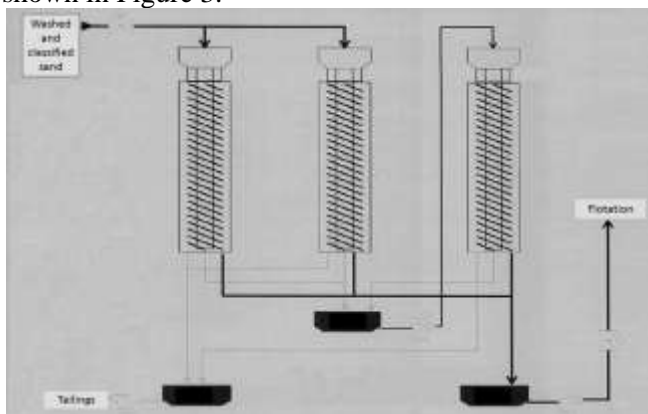

Figure 3 – Scheme of industrial spirals process in study

Each spirals group has 3 outputs, sand, middling and tailings. In Figure 3 the bold line represents the feed, and the light line represents the middling and the tailings. The purified sand from the 3 groups of spirals is send to flotation process or stored in a pile. The middling products of the 3 groups of spirals are treated in the third group of spirals and the tailings are sending to a tailings pond of spirals.

The first step in flotation is the separation of water from sand by a drainage screen. Then, recycled water from flotation process is added. From the drainage screen, the sand enters in the first conditioner, where all the chemical reagents (frother, collector and caustic) are added and mixed. The pulps flow to the second conditioner to increase the retention time and to be homogenized. The scheme of industrial flotation process in study is shown in Figure 4.

On cells bank, the air from blower helps to create the froth. It has mechanical cells with impellers to promote agitation and paddles to remove the tailings that are sent to the tailing pond of flotation.

The flotation cells in study was made by Sala International AB (property Metso Corporation), type AS 4,5. They have 22,5 m^3 of volume and a retention time about 12 minutes. The speed of impellers is constant and the air flow rate is controlled by valves. Dosing pumps make the addition, but the control flow is manual.
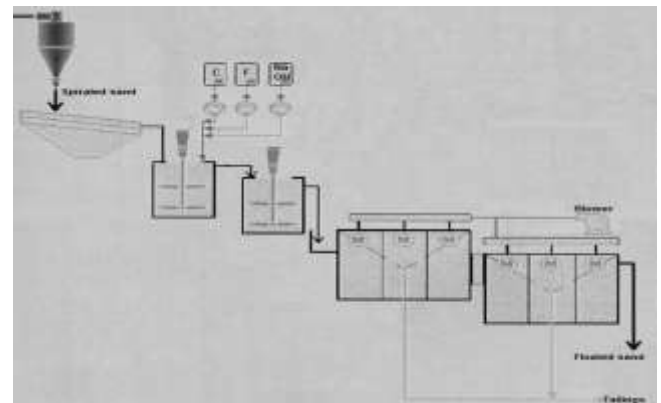

Figure 4 – Scheme of industrial flotation process in study

Flotation Feed

As described, the flotation feed is washed, classified and spiralled silica sand. The average particle size of floated sand varies between 0,090 and about 1mm. The characterization data of the sand that feed the flotation is shown in Figure 5 and Figure 6.
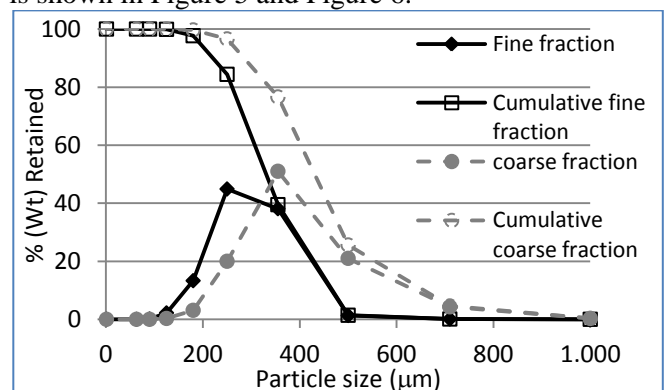

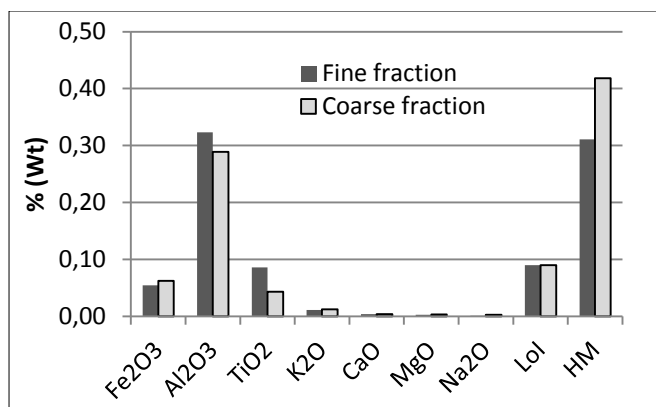Figure 5 – Particle size distribution and cumulative oversize of flotation sand feed

Figure 6 - Chemicals composition of flotation sand feed

The sand produced in major quantity is a coarse fraction, with an average particle size of 470μm, but the sand with major economical value is a fine fraction, with average particle size of 360μm.

As the beneficiation process is continuous, the flotation processes one fraction at each time. The production of fine sand to feed the flotation represents about 50% of the raw material sand, while the coarse fraction processed in flotation represents about 70% of the raw material sand.

3. Material and Methods

The present section describes the materials, equipments and methods used to optimize the flotation conditions. The trials were made in laboratory.

On the previous section was described the industrial process. The lab trials only represent the industrial process when the fine fraction is the fraction treated by flotation. During a production of spiraled fine fraction was collected sufficiency final product to eliminate the variability in the "feed quality".

3.1. Materials

The materials used are the same that are used on industrial process, the sand comes from the process, and the chemical reagents are collected from a specific batch to ensure the same quality.

Chemical Reagents

Although the chemical reagents are collected from the industrial process, at lab level it is difficult to use such small quantities. At lab level chemical reagents were diluted. The collector used is classified as carboxylic.

Levels of factors are described and analysed in coded between [-1,1], where (-1) represent the lower level used and (1) represent the higher level used. In Table 1 are shown the 3 variables (factors) at 3 levels.

Table 1 – Factors variations

Parameters (Coded factors)	Minimum	Center point	maximum
pH	-1	0,5*	1
Collector concentration (g/ton)	-1	0	1
Frother concentration (g/ton)	-1	0	1

The center point for pH was different of "0" because the objective was generally to use as experimental design center point the average conditions in the industrial process and to use levels above and below the average conditions, considering the collector supplier pH recommendations.

Sand

The trials were made with the same sample; around 500kg of sand were reserved and kept all the time with process water to maintain the quality. The properties of feed sand used on lab trials are shown in Table 2 and Table 3.

Table 2 – Particle size analysis of feed on lab trials

Particle size (μm)	% (Wt) Retained
>1000	0,0
1000-710	0,0
710-500	1,5
500-355	41,4
355-250	44,3
250-180	11,8
180-125	0,8
125-90	0,0
90-63	0,0
<63	0,0
Total	100,0

Table 3 – Chemical analysis of feed on lab trials

Chemical composition	% (Wt)
SiO_2	99,637
Fe_2O_3	0,023
Al_2O_3	0,213
TiO_2	0,020
K_2O	0,011
CaO	0,004
MgO	0,003
Na_2O	0,000
Loss on Ignition	0,089
Total	100,00
Heavy Minerals	0,1686

Laboratory equipment

Flotation cells

The kinetics trials were made on cell lab of CERENA in IST (Leeds). This cell has an air flow meter and a controlled impeller rotation at the bottom, keeping all surfaces free to remove the froth with the paddle.

The design of experimental (DOE) lab trials was made using the laboratory flotation machine, Denver equipment Co., size D12 with controlled impeller rotation. The paddle works manually. The air flow is self- aerated and depends of impeller speed.

pH meter

The pH was measured by Crison instruments SA, pH 2000 during all runs. The electrode is made by Hanna Instruments, model HI1312.

Oven

The samples were dried in an oven EcoCell made by MMM Medcenter Einrichtungen GmbH, Model LSIS-B2V/EC 55.

3.2. Lab Trials methods

The trials methodology was twofold, the kinetic trials and the design of experiments (DOE) trials. The kinetic trials were made to define the best retention time, acquire some training on trials and find some limitations. The DOE trials were made to analyse statistically the effect of independent variables on

process answer and finding the interaction between different variables, based on statistical analysis.

Different variables can be considered, analyzed and evaluated. On this approach, there are a lot of variables that were considered as constants, but the key of the study was to choose the best key variables to optimize the process.

Considering the industrial and laboratorial process restrictions and needs to reduce as must as possible the variables, the variables considered as constants were operation and equipment variables.

Kinetic trials

The kinetic trials were made in first place. The collector and frother concentration are defined by the target on industrial process, the air flow and speed rotation was adjusted to control the turbulence on surface.

The chemical reagents concentration used was different from centre level of DOE trial, because the average consumption on industrial plant was updated at the end of kinetic trials.

The kinetics trials were also important to program the DOE trial.

On industrial process the total residence time is about 12 minutes. On kinetic trials it was tested 2 different conditioning residence times and different flotation times. The conditioning residence times used were 3 and 5 minutes without air flow.

The kinetic trials were made using a Leeds flotation cell with volume of 3 litres. A 1,1kg of dry sand was inserted on cell with water of industrial process from Rio Maior until reaches the maximum cell level, to have a solids concentration of 30%. The impeller speed was regulated at 1000 rpm. Then it was added 3mL of diluted (1:10) collector and 1mL of diluted (1:400) frother. The pH used was -1(coded value). After adding the chemical reagents wait for 3 minutes or 5 minutes depending of trial number. Then, the air flow was opened at 110 L/h, and during 1 to 8 minutes the froth was removed with blades manually.

Design of experiments trials

Because there are 3 levels for each factor, and other studies indicate a non linear response, it was chosen the quadratic model to the first data treatment.

For the statistical treatment data and analysis was used the software Design expert 9.0.3.1 from State-Ease Inc. In Design-Expert, this design is located under the Response Surface, Miscellaneous design mode. Full factorial 3-level designs are available. The number of experiments will be 3^3 plus 5 replicates of the center point.

The DOE trials were made using a Denver laboratory flotation cell with volume of 3 litres. A 1,4kg of dry sand was inserted on cell with 0,7L of water tap from Rio Maior, to have a solids concentration about 65%. The impeller speed was regulated at 1000 rpm. Then it was added diluted (1:10) collector and diluted (1:400) frother. The pH used was controlled with sodium

hydroxide to reach the desired pH for each trial, except on trials for pH -1, in that case it was no addition of pH regulator, but it was measured. The air flow valve was closed. After adding the chemical reagents wait for 5 minutes. Then, the air flow was opened (self aerated), water was added until reach the maximum level to have a flotation solids concentration about 35%. During more 8 minutes the froth was removed with blades manually.

The 5 trials on center points were made to find out the trials error. The trials results between trial 1 and 27 are an average of two replicates. The trials between 28 and 32 were 5 replicates in same conditions with 5 different analyses.

3.3. Analysis methods

Heavy minerals analysis

The heavy minerals (HM) content was evaluated using a dense liquid in a separatory funnel. The dense liquid was bromoform (Chem-Lab NV, 99% $CHBr_3$), Density of 2,89 g/mL. The analytical weighing machine used to quantify the H.M. content was made by Mettler instrumente AG, model AE100, calibrated by ISQ in June 2014 with an error on grade 0-0,1g of ±0,0002g.

Energy Dispersive X Ray Fluorescence spectrometer

The Fe_2O_3 content was determined by energy dispersive X-ray fluorescence (EDXRF) using a Panalytical, model Minipal 4 spectrometer.

4. Analysis and Discussion Results

Although the flotation performance is often measured by equation 3 to equation 5, at industrial process the results are evaluated in terms of Fe_2O_3 content (wt) and heavy minerals content (wt). The trials results are also presented using this methodology because the feed sand has a constant content of Fe_2O_3 and heavy minerals.

4.1. Kinetic trials

The kinetic trials were very important to perform the DOE trial. The results shown in Figure 7 and Figure 8 evidence the flotation kinetic and the time needed for the attachment of particles to air bubbles.
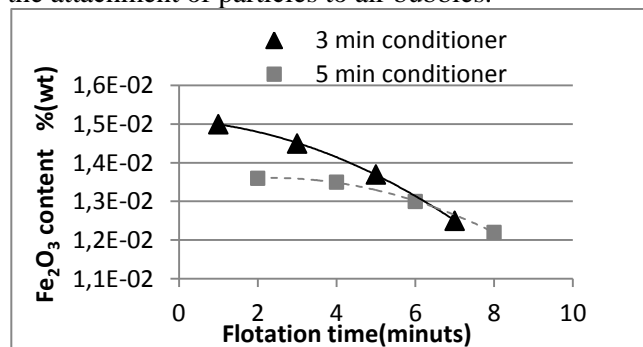

Figure 7 – Fe_2O_3 content on sink product for different condition of residence time

The 13 minutes of trial time were adequate to the heavy minerals (H.M.) removal as shown in Figure 8,

the minimum values were achieved since the 11 minutes of trial, but for the Fe_2O_3 content the Figure 7 shown that it will be necessary to evaluate more flotation time, until find a repeat of minimums or even a rise of values as shown in Figure 1.
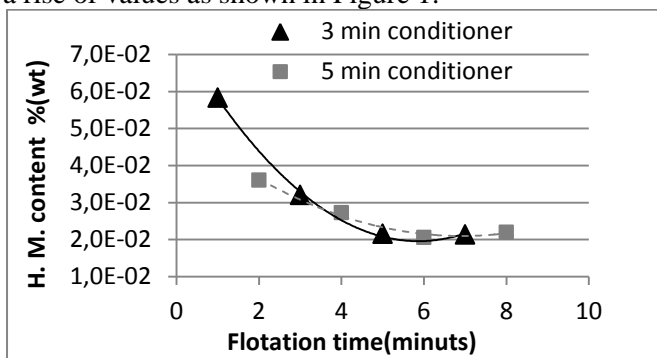

Figure 8 – Heavy minerals content in the sink product for different conditions of residence time

The adjustment made to the kinetic trial results have a coefficient of determination larger than 0,98.

4.2. Analysis of correlation for response surface quadratic model

To a first data approach the Pearson's correlation coefficients were calculated for independent variables and response variables. The larger correlations are between pH and response variables.

The correlation between response variables Fe_2O_3 content and heavy minerals content is low, only 0,15, which contradicts what was expected. However, using a large grade of Fe_2O_3 content and heavy minerals content the correlation between them is about 0,8 as it can see observed in Figure 9.
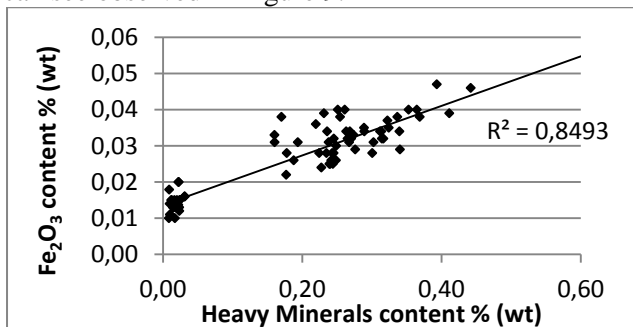

Figure 9 – Correlation between Fe_2O_3 and H.M. content using industrial data from sand with different levels of beneficiation

In Figure 9 were used industrial results from different types of beneficiated silica sand, even so at low grade of contents the correlation between Fe_2O_3 content and heavy minerals content is also low.

4.3. Analysis and results discussion of Fe_2O_3 content

For the trials under the same conditions (28 to 32) the average result for Fe_2O_3 content was 0,012% and the variance was $2E^{-7}$, which indicates a low error on lab methodology. These results are in line with the average results of industrial production.

For the trials 1 to 27 the average results for Fe_2O_3 content was 0,013% and the variance was $6E^{-7}$, these

results indicates a small variability of results. The replicates have always differences caused by random factors (handling, measurements and analysis).

To create a model to predict the response variable in function of results it is necessary to evaluate which variables or interactions between variables have statistical significance. From variance analysis (partial sum of squares) it was identifying the best model to predict the responses. The most appropriate model was the linear model. From ANOVA table was obtained the F-test for the model indicates the level of significance of the model prediction, the model has a p-value $\leq 0,05$, it means that the model is significant, and has 0,5% probability that the predicted response is due to noise. The F-test indicates also that the lack of fit is not significant.

Frother concentration has no significance to the model. The model equation from linear regression to predict Fe_2O_3 content is shown on Equation 6.

$$Fe_2O_3 \text{ content} = 0,013 - 3 \times 10^{-4} \times A + 4 \times 10^{-4} \times C \qquad (6)$$

Where A is the collector concentration and C the pH in coded values between -1 and 1.

The comparison between the experimental and estimated Fe_2O_3 content is shown in Figure 10.
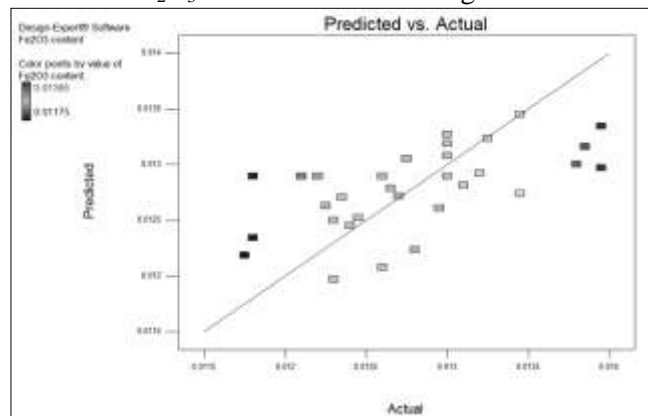

Figure 10 – Comparison of experimental and predicted Fe_2O_3 content

To validate the model tools were used to analyse the residuals. The normal plots of the difference between the observed and predicted values of Fe_2O_3 content (or residuals) are shown in Figure 11.

In this conditions the model was accept to predict the process in study.
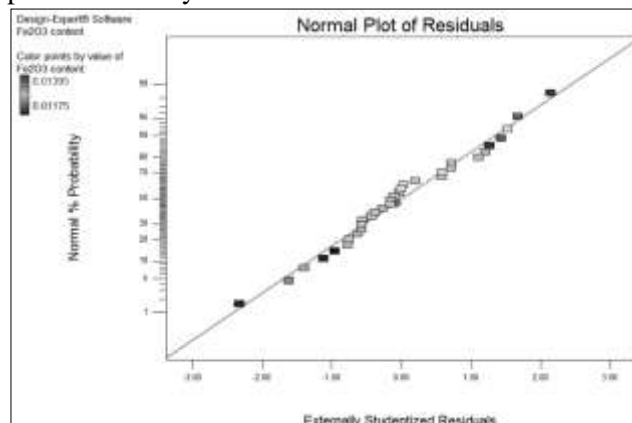

Figure 11 – Normal plot of residuals for Fe_2O_3 content

4.4. Analysis and results discussion for heavy minerals content

For the trials under the same conditions (28 to 32) the average result for heavy minerals content was 0,007% (wt) and the variance was $5E^{-6}$, which indicates a larger error on lab methodology comparing with Fe_2O_3 content methodology. These trials results are in line with the average results of industrial production.

For the trials 1 to 27 the average results for heavy minerals content was 0,005% (wt) and the variance was $7E^{-6}$, these results indicates a larger variability of results.

To create a model to predict the response variable in function of results it is necessary to evaluate which variables or interactions between variables have statically significance. First step was identifying the best model to predict the answers. The most appropriate model was the linear model.

After analysis of variance it was obtained the ANOVA table for response surface model, the only variable with statistical significance is the pH and it is not possible to identify correlations between variables, so it was made an adjustment to simplify the model. As the error terms has no a normal distribution, it is useful to transform the results

The analysis with Box-Cox Plot support recommend transform the statistics model with an inverse square root as showed in Figure 12 to predict the heavy minerals content.
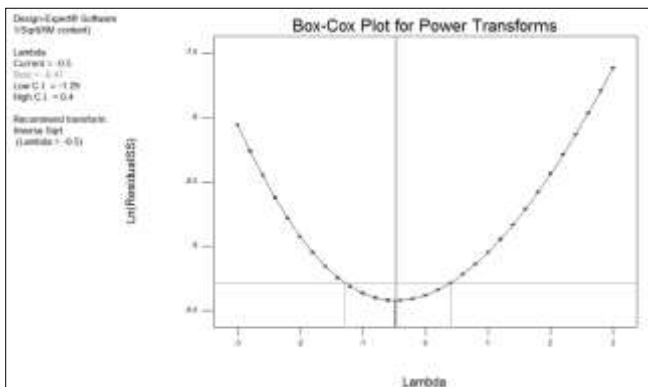

Figure 12 – Box-cox plot for power transforms on heavy minerals model analysis

Although the collector and frother concentration do not have significance, froth flotation do not works without these chemical reagents, and the model cannot be used without consider these variables inside the levels studied.

The model has a p-value $\leq 0,05$, it means that the model is significant has 0,4% probability that the predicted response is due to noise. The F-test indicates also that the lack of fit is not significant.

The model equation from linear regression to predict heavy minerals content is shown on equation 7.

$$\frac{1}{\sqrt{HM}} = 14,7 - 2 \times C \tag{7}$$

Where C is the pH in coded value between -1 and 1. The comparison between the experimental and estimated heavy minerals content is shown in Figure 13.

To validate the model tools were used to analyse the residuals. The normal plots of the difference between the observed and predicted values of heavy minerals content (or residuals) are shown in Figure 14.
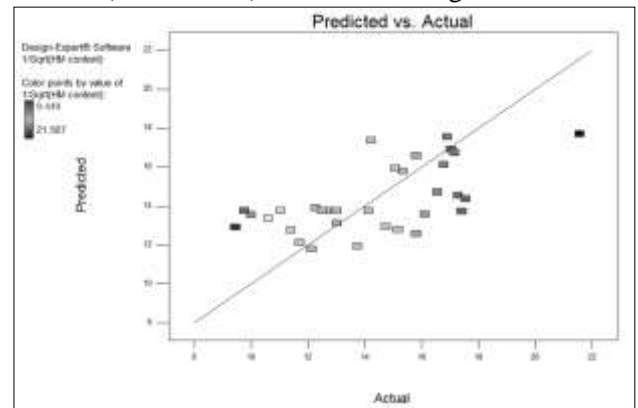

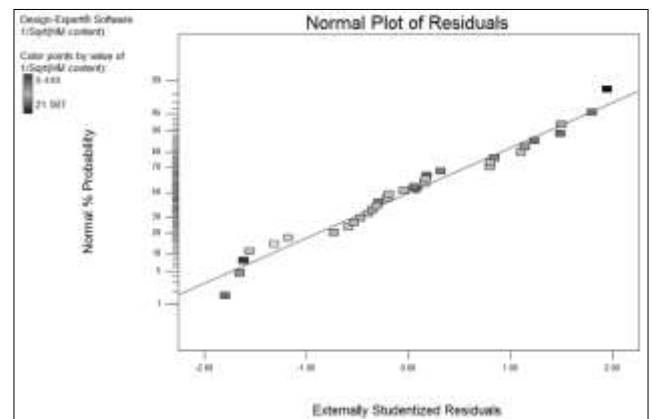Figure 13 – Comparison of experimental and predicted heavy minerals content

Figure 14 – Normal plot of residual for heavy minerals content

4.5. Design optimization

After have the model validation, the model can be used to optimize the process.

Fe_2O_3 content minimization

An overview of surface model response, as shown in Figure 15, and predicts our response in different conditions by equation 6 for Fe_2O_3 content.
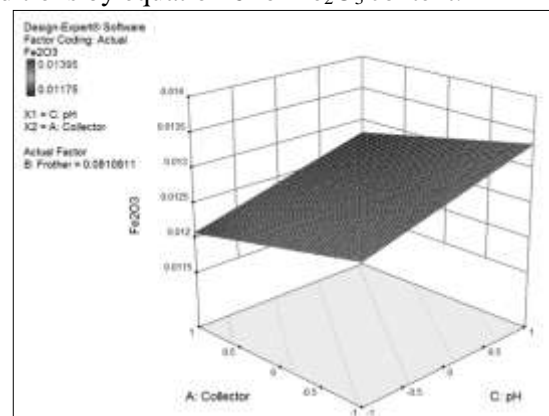

Figure 15 – 3D Surface model to Fe_2O_3 content

From the equation 6 is possible to understand that the Fe_2O_3 content will be proportional to pH and inversely proportional to collector concentration. Looking this

model, and as the limits are the levels used on trials, the optimized conditions will be the pH on minimum, frother concentration inside the levels and collector concentration on maximum tested.

Heavy minerals content minimization

For heavy minerals content the overview of model response, is shown in Figure 16, and predicts our response in different conditions by equation 7.
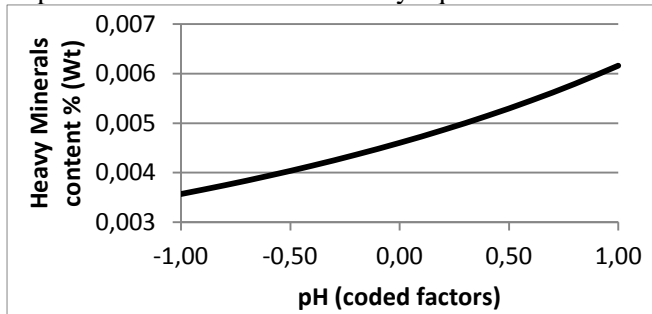

Figure 16 – Model response for heavy minerals content

From the equation 7 is possible to understand that the heavy minerals content will be proportional only to pH. Looking this model, and as the limits are the levels used on trials, the optimized conditions will be pH at minimum.

Process optimization

The major target of these trials was to find the best conditions to reduce Fe_2O_3 content to produce at industrial level silica sand with Fe_2O_3 contents below 0,010% for special applications. The response variables criteria to optimize the conditions, was to minimize Fe_2O_3 content with higher priority and heavy minerals minimization also. The expected results for the trial with pH at coded factor -1 and collector concentration at 1 will be Fe_2O_3 content 0,012% and heavy minerals content 0,004%.

The results from optimization solution indicate that the optimization point will be in the tested limits. The design of experiments does not recommend extrapolating outside the design space due to no validation of model.

5. Conclusions and future studies

The aim of the work carried out was to perform an experimental work that could help in the decisions on the optimization of an industrial flotation process running in a plant, located in Rio Maior, that beneficiates sand by reducing the content in the contaminants. These are mainly heavy minerals, such as tourmaline, rutile and magnesioferrite.

The plant produces currently a product with 120 ppm of Fe_2O_3 content used in value added applications, and desires to produce sand with 90-100ppm. The objective was therefore to study the flotation process and to determine experimentally the effects of the main chemical operational variables in the performance of the process.

In the state of the art carried out it was found that the three variables that mostly influence the flotation of the heavy minerals are the type of collector, the collector and frother concentrations and pH. In the study, the same reagents used in the industrial plant were used. The results were evaluated in terms of the content in heavy minerals and in Fe_2O_3, which are the performance indicators used in the industrial plant.

Firstly, a kinetic study was performed, with the same operational conditions used in the industrial plant, to calculate the flotation time that should be used in the following stage of tests. The value of 8 minutes maximizes, in the conditions tested, the recovery of the heavy minerals in the floated product. The conditioning time was evaluated as well and the value of 5 minutes was used since then.

Then, an experimental design was carried out where the base levels of variables were the operational conditions used in the industrial plant. The variables manipulated were the collector and frother concentrations and the pH. A full factorial design, representing all possible combinations between the levels of variables, with 3^3=27 tests, was carried out. The high and low levels of the variables tested were the increase and decrease of 11% in the collector concentration and 14% in the frother concentration. In the case of pH the modifications were not symmetrical. The asymmetry is explained by industrial conditions and the range of pH recommended by the collector supplier.

The experimental trials were carried out and the floated product was analyzed by XRF for the Fe_2O_3 content determination while the heavy minerals content was determined by dense liquid analysis. Then the results were analyzed to identify which of the variables and interactions mostly affect the heavy minerals and Fe_2O_3 contents. The variance analysis showed that the collector concentration and the pH have the highest influence in the Fe_2O_3 content and the pH is the only variable that significantly affects the heavy minerals content.

The linear regression models obtained are very simple. The commercial software Design Expert 9.0.3.1 (State-Ease Inc) was used to obtain the optimal solution. It was determined that this was the minimum value of pH and maximum collector concentration tested showing that the amplitude of the variables range tested was too small. Nevertheless, it should be pointed out that an acid pH cannot be considered because the equipment in the plant is not prepared for acidic pulps and the collector used is effective only in neutral or alkaline conditions.

The best results obtained were 0,011% in Fe_2O_3 content and 0,002% in heavy minerals content, values of the same order of magnitude of the current values of the plant, taking into account the measurements uncertainty.

The work carried out contributed to a better understanding of the froth flotation process namely the process used to beneficiate sand by flotation of the heavy minerals. It was shown that, considering the conditions used the pH at minimum (coded value -1) is the best value to be used. The frother has not a significant effect on the minerals recovery in the floated product. In fact, the frother is adsorbed in the air-water interface, so, it can be concluded that the flotation was carried out in conditions of sufficient air-water surface for particles flotation. The collector concentration should be increased in further laboratory work.

Future work should be done in the testing of other reagents. Today, there is a predisposition of companies to comply with environmental best practices, so, environmentally friendly reagents, collectors and frothers, should be tested. Other environmentally friendly solutions, like magnetic separation, today effective in particles with very small size, should be tested too.

6. References

Ahmad, H. S. (1951). Flotation of low-grade gold ores. Zurich: Dissertatlonsdruckerei Leemann AG.

Banza, A. N., Quindt, J., & Gock, E. (2006). Improvment of the quartz sand processing at Hohenbocka. *International journal of mineral processing , 79*, pp. 76-82.

Bayat, O., & Akarsu, H. (2002). Evaluation of new collectors for silica/glass sand and statistical analysis of plant trials. *Minerals engineering , 15*, pp. 293-296.

Bezerra, M., & al, e. (2008). Reponse surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta , 76*, pp. 965-977.

Corporation, Unimin. (1999). The theory and industrial practice of silica beneficiation by flotation.

Cummins, A., & Given, I. (1973). *SME mining engineering handbook.* New York: The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc,.

Cytec Industries, Inc. (2010). *Mining Chemicals Handbook.* USA.

Dejaegher, B., & Heyden, Y. V. (2011). Experimental designs and their recent advances in set-up, data interpretation, and analytical applications. *Journal of pharmaceutical and biomedical analysis , 56*, pp. 141-158.

Du, H. (2008). Flotation Chemistry of selected alkali halide salts and naturally hydrophobic minerals. Utah: ProQuest LLC.

Farrokhpay, S. (2011). The significance of froth stability in mineral flotation - A review. *Advances in colloid and interface science* , pp. 1-7.

Fuerstenau, M. C., Jameson, G. J., & Yoon, R.-H. (2007). *Froth flotation: a century of innovation.* Littleton (USA): SME.

Hernáinz, F., & Calero, M. (2001). froth flotation: kinetic models based on chemical analogy. *Chemical engineering and processing , 40*, pp. 269-275.

Kawatra, S. (20 de 07 de 2011). *Froth flotation - fundamental principles*. Obtido em 15 de 02 de 2014, de Michigan Technological University: http://www.chem.mtu.edu/chem_eng/faculty/kawatra/Flotation_Fundamentals.pdf

Miller, J. D., & Parekh, B. (1999). *Advances in flotation techology.* Denver: SME.

Mohanty, S., & Das, B. (12 de 01 de 2010). Optimization studies of hydrocyclones for beneficiation of iron ore slimes. *Mineral processing and extractive metallurgy review , 31*, pp. 86-96.

Rahman, R. M., Ata, S., & Jameson, G. J. (2012). The effect of flotation variables on the recovery of different particle size fractions in the froth and the pulp. *International Journal of Mineral Processing* , 70-77.

Shean, B., & Cilliers, J. (2011). A review of froth flotation control. *International Jornal of Minerals Processing* , 57-71.

Somasundaran, P., & Lin, I. (June de 1973). Method for evaluating flotation kinetics parameters. *Society of Mining Engineers , 254*, pp. 181-184.

Stat-Ease. (2014). *Design-Expert Software Version 9*. Obtido em 19 de 9 de 2014, de Stat-Ease: http://www.statease.com/

Taxiarchou, M., & al, e. (1997). Removal of iron from silica sand by leaching with oxalic acid. *Hydrometallurgy 46* , pp. 215-227.

Telford, J. K. (2007). A brief introduction to design of experiments. *Johns Hopkins APL Technical Digest , 27*, pp. 224-232.

Wills, B. A. (1977). *Mineral Processing Technology.* England: Butterworth Heinemann.