



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

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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 sink. 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 concentration of 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.

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

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Nomenclature

Abbreviation	Description
AFC	Advanced Flotation Control
c	Assays of the concentrate
C	Total weight of the concentrate
C_{cr}	Concentration criterion
C_F	Concentration of the floatable minerals in the pulp
DES	Design Expert 9.0.3.1 Software
D_f	Specific gravity of the fluid medium
D_h	Specific gravity of the heavy mineral
D_l	Specific gravity of the light mineral
DMS	Dense medium separation
DOE	Design of experiments
E	Enrichment ratio
EDXRF	Energy Dispersive X Ray Fluorescence
Eh	Electrochemical potential
F	Total weight of the feed
f	Assays of the feed
g	Gram
h	Hour
HM	Heavy Minerals
IST	Instituto Superior Técnico
K	Flotation rate constant (Kinetic)
k	Constant from the Student's t-distribution for 95% confidence
L	Litter
l	Levels of DOE
LD	Limit of detection
Lm	Valuable mineral loss to the tailings
LOF	Lake of Fit
LQ	Quantification limit
Min	Minute
m_t	measurement time
N	Number of trial of DOE
n	Number of measurements under reproducibility conditions
n_k	Order of the reaction (Kinetic)
OFC	Optimizing Flotation Control
ppm	Parts per million
R	Represents an hydrocarbon chain
R_C	Ratio of concentration
Rm	% recovery of the valuable mineral
s	Standard deviation of the reference material or sample measurement under reproducibility conditions
t	Assays of the tailings
t_k	Time of reaction (Kinetic)
U	Measurement uncertainty
u_{method}	Uncertainty of the method
u_{REPRO}	Uncertainty of the measurement of the sample
u_{VL}	Uncertainty of the measurement of the reference material

u_{VR}	Uncertainty of the certified value of the reference material
V	volume
Wt	Weight
X	Factors of DOE
XRD	X-ray diffraction
Y	Response variable of the model

1. Introduction

1.1. Objectives and Motivation

The work presented intends to optimize the flotation process by manipulating three 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 require sand with iron and heavy minerals contents bellow 150ppm. The price of the sand increases with the lower iron and heavy minerals content. Sand with less than 100ppm of iron content and 100ppm of heavy minerals are considered very high quality. Iron content affects the transparency of glass, discolours ceramic products and lowers the melting point of refractory materials (Taxiarchou & al, 1997).

Today, the current ex-works market price for silica sand without treatment is 2,50€, for yellow sand or river sand semi washed is 5,50€, for calibrated washed silica sand is 12,00€, for purified silica sand with a silicon dioxide (SiO_2) content above 99,3%(Wt) is 16,00€, for purified silica sand with a silicon dioxide (SiO_2) content above 99,5%(Wt) and iron content about 0,030% (Wt) is 25,00€, for purified silica sand with a silicon dioxide (SiO_2) content above 99,8%(Wt) and iron content about 0,010% (Wt) is 60,00€. 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. Thesis outline

This work is organized as follows:

Chapter 2 presents the froth flotation, the historical evolution, fundamentals and describes the industrial process in study.

Chapter 3 describes the material and methods, the equipment, the chemical reagents, the tests and analysis methods used.

Chapter 4 shows the experimental results.

Chapter 5 explains the analysis and discussions of trials and experimental results.

Finally, chapter 6 contains the conclusions and future studies.

1.3. 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 with low commercial value, due to its abundance, but 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 silica sand deposit located in Rio Maior (Portugal) is a sedimentary deposit of continental facies plio-Pleistocene (between the upper Pliocene and Quaternary old) composed by a bottom thick layer of white sand and alternating layers of diatomite and lignite on top.

The white sands of Rio Maior are important especially due to its siliceous composition and high purity. The aggregate material contains fine well calibrated clay, kaolinite, white and yellow sands. (Galopim de Carvalho & Pereira, 1973).

Silica raw materials exist on different types of deposits; the most common sources are sands, sandstones and quartzites, among others. The extraction methods used are excavation by caterpillar excavator, dredging and rarely explosives. The majority are open pit mines. Therefore, comminution, sizing, and beneficiation are 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 (DMS), magnetic and high-tension separation, froth flotation, acid leaching and dewatering (Wills, 1977) (Corporation, Unimin, 1999) (Banza, Quindt, & Gock, 2006).

The wide variety of mineral processing techniques available should be selected in terms of grain size distribution as summarized in Wills (1997) and reproduced in Figure 1.

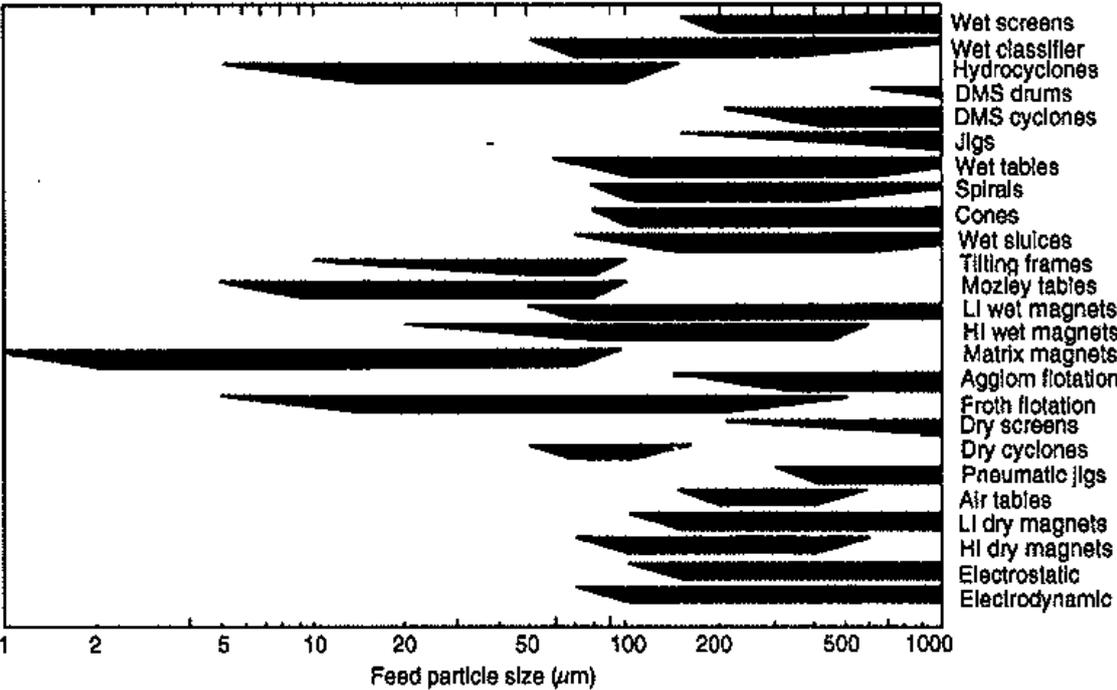


Figure 1 – Separation methods used in mineral processing as a function of raw material particle size (Wills, 1977)

In the following text some processes commonly used in the ore sand processing are listed and briefly described.

The *screening* is used to separate minerals into multiple grades by particles size. It can be used in dry or wet material.

Attrition, scrubbing and washing are used to remove clay and slimes. A higher concentration of solids is used in attrition; the washing generally removes fines.

Gravity separation is based on different specific gravity (relative density). The equipment most commonly used are conical separators, jigs, pinched sluices and cones, spirals, shaking tables and pneumatic tables. A large advantage of this technique compared to other processes is its minor environmental effects. The shaking tables have a reduced use for sand applications (Jordens, Cheng, & Waters, 2013) (Corporation, Unimin, 1999) (Wills, 1977).

The particle size distribution is important in gravity separation, as is the fluid used, usually water or air. Efficiency of gravity separation is measured by the concentration criterion (C_{cr}) as shown on Equation 1

$$C_{cr} = (D_h - D_f) / (D_l - D_f) \quad (1)$$

Where D_h is the specific gravity of the heavy mineral, D_f is the specific gravity of the fluid medium and D_l is the specific gravity of the light mineral. Efficiency increases with the concentration criterion and, commonly, when the concentration criterion falls between -2,5 and 2,5 specific gravity should not be used.

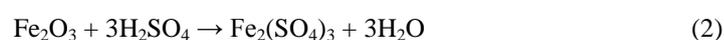
Dense medium separation (DMS) or heavy medium separation is a gravity concentration process used to separate minerals with different specific gravity using a fluid with density higher than water's. The minerals lighter than the fluid float while minerals denser than the liquid sink.

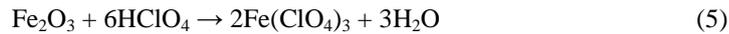
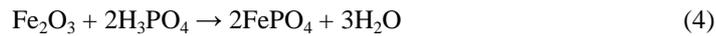
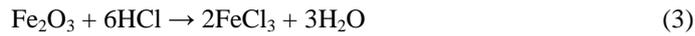
The *magnetic separation* is used to separate minerals with different behavior when placed in a magnetic field. Mineral particles that are attracted along the lines of an applied magnetic field are ferromagnetic or paramagnetic, while the mineral particles that are repelled along the lines of an applied magnetic field are diamagnetic. The paramagnetic materials can be concentrated in high-intensity magnetic separators, while low-intensity magnetic separators can separate ferromagnetic ores. The magnetic separators can be used with both dry and wet minerals and can be classified as low and high-intensity separators.

The diamagnetic minerals cannot be concentrated magnetically because the forces involved are very small (Wills, 1977) (Jordens & al, 2014).

The *high-tension separation or electrostatic separation* is used in dry materials, and separation occurs due to the difference in electrical conductivity. The requirement for low humidity and temperature makes the process expensive due the energy costs (Wills, 1977) (Jordens, Cheng, & Waters, 2013).

Acid leaching is based on the fact that some metal oxides are soluble in acid solutions (Ubal dini & al, 1996). Acid leaching is used at very low pH (1-4) and consequently has a high environmental impact that is reduced by an alkaline washing. This process is time-consuming; the first relevant results can be achieved after 10 days and can extend until 30 or 40 days (Adbelkrim, 2009). Acid leaching can be also complemented with ultrasound irradiation reducing the leaching time and the acid concentration used (Du & al, 2011). Different acids can be used in acid leaching. The chemical reactions in iron oxide removal are (Tuncuk & Akcil, 2013):





A mixture of hydrofluoric acid (HF) and hydrochloric acid (HCl) can be used to reduce the Fe_2O_3 content with efficiency around 92%.

Dewatering is a solid-liquid separation. A large amount of water is needed and the purified minerals have to be dried at the end to allow loading and transport. Dewatering process can be classified as sedimentation, filtration and thermal drying (Wills, 1977).

In this work the froth flotation separation process is used to purify minerals. The froth flotation is based on physico-chemical surface properties of various minerals and it is described in some detail in 2.2 Fundamentals.

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 allows to obtain empirical models used for optimizing the variables to obtain the desired process response (Mohanty & Das, 2010).

Experimental design has a large application in different sciences. It is generally divided into screening design (e.g. full factorial, fractional factorial, and Plackett–Burman designs), response surface design (second order symmetrical designs are the three-level factorial design, Box–Behnken design, central composite design, and Doehlert design) and mixture designs.

Depending of the number of factors to be optimized, different strategies can be used on experimental design. These strategies are represented in Figure 2.

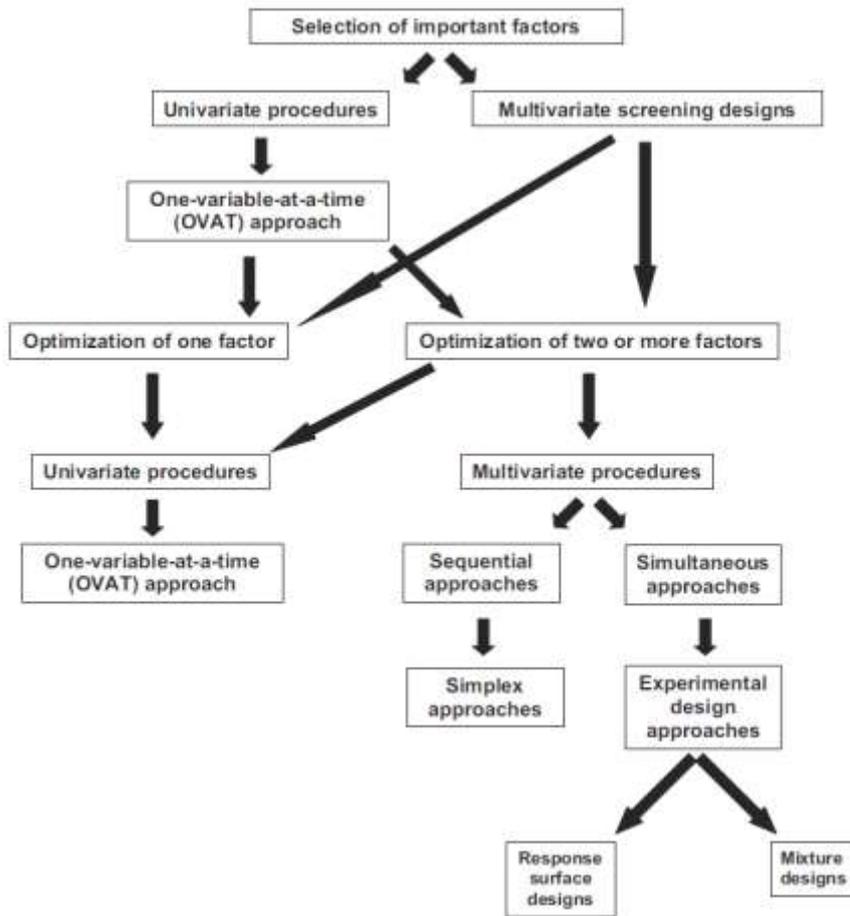


Figure 2 – Optimization of strategies in experimental design (Dejaegher & Heyden, 2011)

To find the optimal conditions for the factors it is required a high number of experiments. For two factors, it is possible to visualize the entire response surface, for three or more factors it is not possible to visualize the entire response surface.

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 $N=3^3=27$ experiments are need, including one centre point as shown in Figure 3 (Dejaegher & Heyden, 2011).

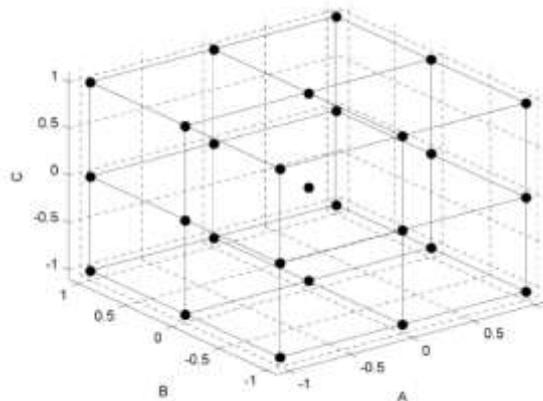


Figure 3 – Three-level full factorial design (Dejaegher & Heyden, 2011)

The empirical model obtained from design surface depends of the number of factors and levels as shown in Table 1. For three-level full factorial design the quadratic model has 10 terms as shown on Equation 6.

Table 1 – Number of runs and number of terms present in a quadratic model

Number of Factors	Treatment Combinations 3 ^j Factorial	Number of Coefficients Quadratic Empirical Model
2	9	6
3	27	10
4	81	15
5	243	21
6	729	28

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

$$Y = \beta_0 + \sum_{i=1}^p \beta_i X_i + \sum_{i=1}^p \sum_{j=1}^p \beta_{ij} X_i X_j + \sum_{i=1}^p \beta_{ii} X_i^2 + e \quad (6)$$

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

Before beginning an experimental design it is necessary to analyse and to define some points as target of experiments, to analyse the independent variables of process and select the most important variables, to define the plan of experiments, to select the experimental design and statistical software to support it.

2. Froth Flotation

2.1. Historical evolution

Flotation is a physico-chemical process used for mineral separation since the XIX century. In 1860, William 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 as fatty acids (Fuerstenau, Jameson, & Yoon, 2007). Froth flotation had a great evolution in the beginning of the 20th century. In the United States, the quantity of 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 angle 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 a result of practical and sensitive work on complex ores (Fuerstenau, Jameson, & Yoon, 2007).

2.2. Fundamentals

The ores extracted from the Earth are always a blending of different minerals. 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). Flotation is commonly used to treat sulphide, oxide and phosphate ores, but it has also been applied in removing ink in paper recycling and waste water treatment (Rahman, Ata, & Jameson, 2012).

The process takes place in an ore pulp (three-phase structure), in which the surface of one or more minerals in the finely ground pulp are 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 can be 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 kinetics and is described as follows:

$$\frac{dC_F}{dt_k} = -K C_F^{n_k} \quad (7)$$

Where C_F is the concentration of the floatable mineral in the pulp, t_k is the time of reaction, K is the flotation rate constant and n_k is the order of reaction (Hernández & 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.

2.2.1. 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. The 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 not linear; usually obeying to a square power law variation (Shean & Cilliers, 2011).

The flotation efficiency is dependent on equilibrium between reagents concentration and pH (Wills, 1977).

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 (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 (Cytac Industries, Inc., 2010).

The collectors are classified as shown in Figure 4 by their chemical nature.

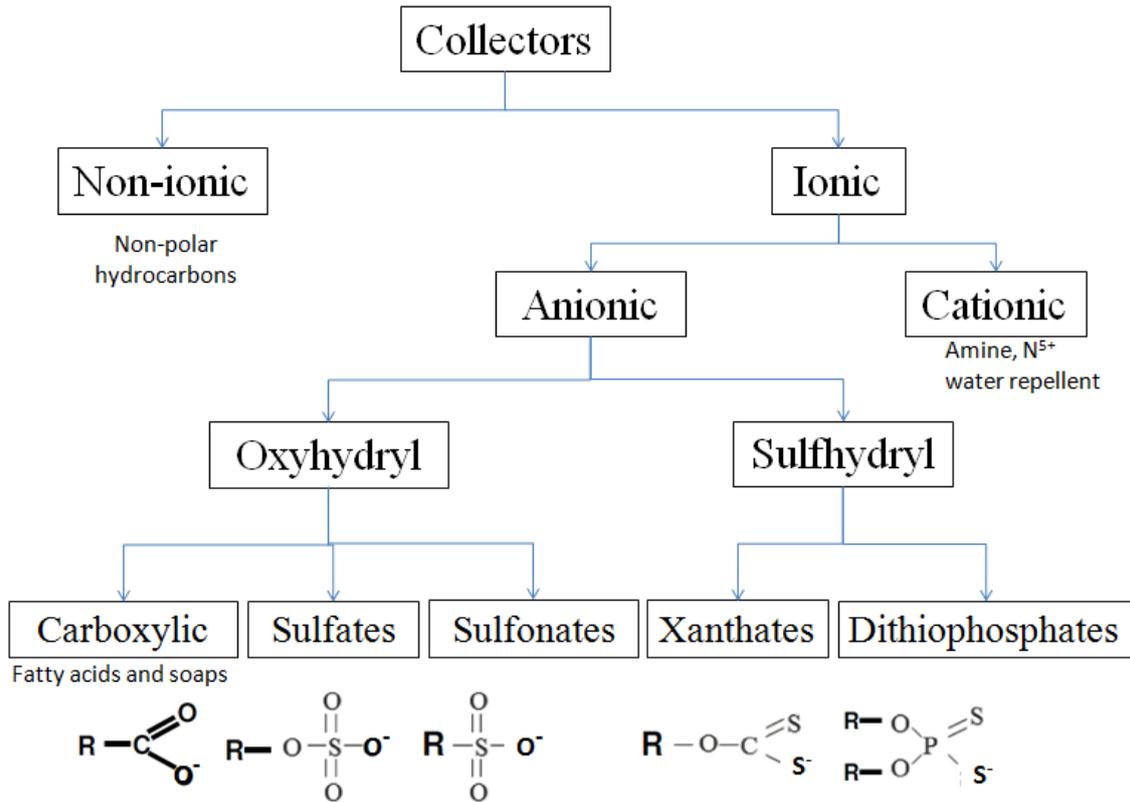


Figure 4 – Classification of Collectors [adapted from (Wills, 1977)]

In Figure 4 the “R” represents a hydrocarbon chain. The different collectors with the same classification change in the different hydrocarbons chains for “R”.

Mineral recovery is proportional to concentration of collector until it reaches a plateau, then the increase in the concentration has no effect or may occur a reduction of recovery as shown in Figure 5 (Wills, 1977).

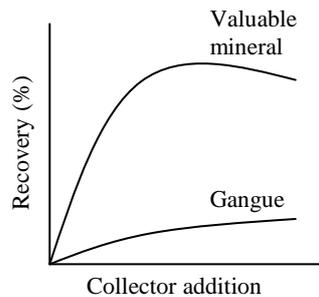


Figure 5 – Effect of collector addition on recovery (Wills, 1977)

Modifiers are compounds used to modify the properties of the pulp and can be divided in:

- Regulators of pH: in general the mineral charge surface changes 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. The pH can affect also the way of adsorption of particular collectors on mineral surfaces.
- Activators: prepare the mineral surface 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 defloculates the mineral particles aggregates (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 the air bubbles.

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

Operational 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.

Slurry flow rates are important to make the mass balance and to control the concentration of chemical reagents (Shean & Cilliers, 2011). *Slurry Density* is used to determine the concentration of solids on slurry but it is also important to the mass balance (Shean & Cilliers, 2011).

Retention time depends of the flotation kinetics as shown in Equation 7. Commonly the retention time is directly proportional with the recovery due to the linear characteristics of kinetics (Hernández & Calero, 2001).

Water quality on flotation can change by internal or external factors. The internal factors include the minerals processed, the chemicals used, reuse of internal water, locals of storage, etc. The external factors include the raw water quality, local climate, multiple sources of raw water supply, water external reuse, etc. The change of water quality can affect positively or negatively the flotation recovery (Liu, Moram, & Vink, 2013).

Pulp level in one cell can disturb the next cells level. The pulp level control is important to control the retention time and the froth depth. In theory, the higher the froth depth, the easier will the separation (Shean & Cilliers, 2011).

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

Flotation cell design can be performed in rectangular or cylindrical mechanically agitated cells or tanks and flotation columns. The volume and number of cells are important parameters due the residence time. The empirical rules from process engineers with large experience are still used today. However, flow sheet simulators are used to help on plant design to find the best economic and process options (Scheda, Zanin, & Chiarandini, 1997).

Agitation controls the turbulence in the flotation cells, its reduction creates favorable hydrodynamic conditions for coarse particles (Tao, 2004).

Air flow rate changes cause a rapid response on flotation process for bubbles of similar size. Air flow rate is a variable that can be more effectively controlled than pulp level (Shean & Cilliers, 2011).

Small bubbles increase the collision with particles increasing recovery. Larger bubbles are necessary to transport coarse mineral particles to the surface, and reduce detachment (Tao, 2004).

Several authors described *Cell Bank Control* of froth flotation. Automation of froth flotation was developed to increase process efficiency. Until the 1970s it had not significant success. In fact, the processes control of froth flotation was substantially improved with the development of appropriate and precise instrumentation (Shean & Cilliers, 2011).

As mentioned by Shean and Cilliers (Shean & Cilliers, 2011): “each flotation process is unique (e.g. cell configuration, instrumentation, ore, chemistry, etc.) a large variety of advanced flotation control (AFC) and optimizing flotation control (OFC) strategies have been developed and implemented, and a single, universal, control approach cannot be given.” This is the reason why the control of many working plants still needs human intervention. The flotation process is very complex because the numbers of variables that affect the process is very high and not precisely determined. Some correlations between parameters are non-linear which difficult the flotation control (Shean & Cilliers, 2011). 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 the variables simultaneously. Nevertheless, it is necessary to consider the effects of each variable on the flotation process (Shean & Cilliers, 2011).

2.2.2. Flotation performance

To measure the flotation performance it 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 the most common way to define the effectiveness of a separation.

$$C/F = (f-t)/(c-t) \quad (8)$$

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

Ratio of Concentration (R_C) is the inverse of weight recovery.

$$R_C = F/C = (c-t)/(f-t) \quad (9)$$

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

$$R_m = 100 Cc/Ff \quad (10)$$

Valuable Mineral loss (L_m) represents the valuable mineral loss to the tailings.

$$L_m = 100 - R_m \quad (11)$$

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

$$E = c/f \quad (12)$$

Other measurements or values can be considered at industrial level. In the case study the flotation performance was evaluate using the content in some contaminants (Fe_2O_3 and heavy minerals). As the feed composition was constant during all the study, there can be a direct relationship between contaminants content and the above listed performance indicators.

2.3. Industrial process of flotation

Flotation can be classified as direct flotation or reverse flotation. Direct flotation is the classification used when the valuable product is removed in the froth, while in reverse flotation the valuable product is 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).

2.3.1. Process description

The flow-sheet of the process is shown in Figure 6. 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. It 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 ($< 90 \mu m$). The underflow of the hydro classifier 1 is pumped to the hydro classifier 2. The hydro classifier 2 feed distribution is between 0,09 and about 1 mm. The overflow is a fine fraction of sand with average particle size of $360 \mu m$ (the product under study). The underflow is the coarse fraction with average particle size of $470 \mu m$.

In the industrial plant of Figure 6 the fine fraction or the coarse fraction passes through spirals to remove about one half of the heavy minerals present in the sand. The scheme of industrial spirals process in study is shown in Figure 7.

Each spirals group has 3 outputs, sand, middling and tailings. In Figure 7 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 sent to the 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 sent to a tailings pond.

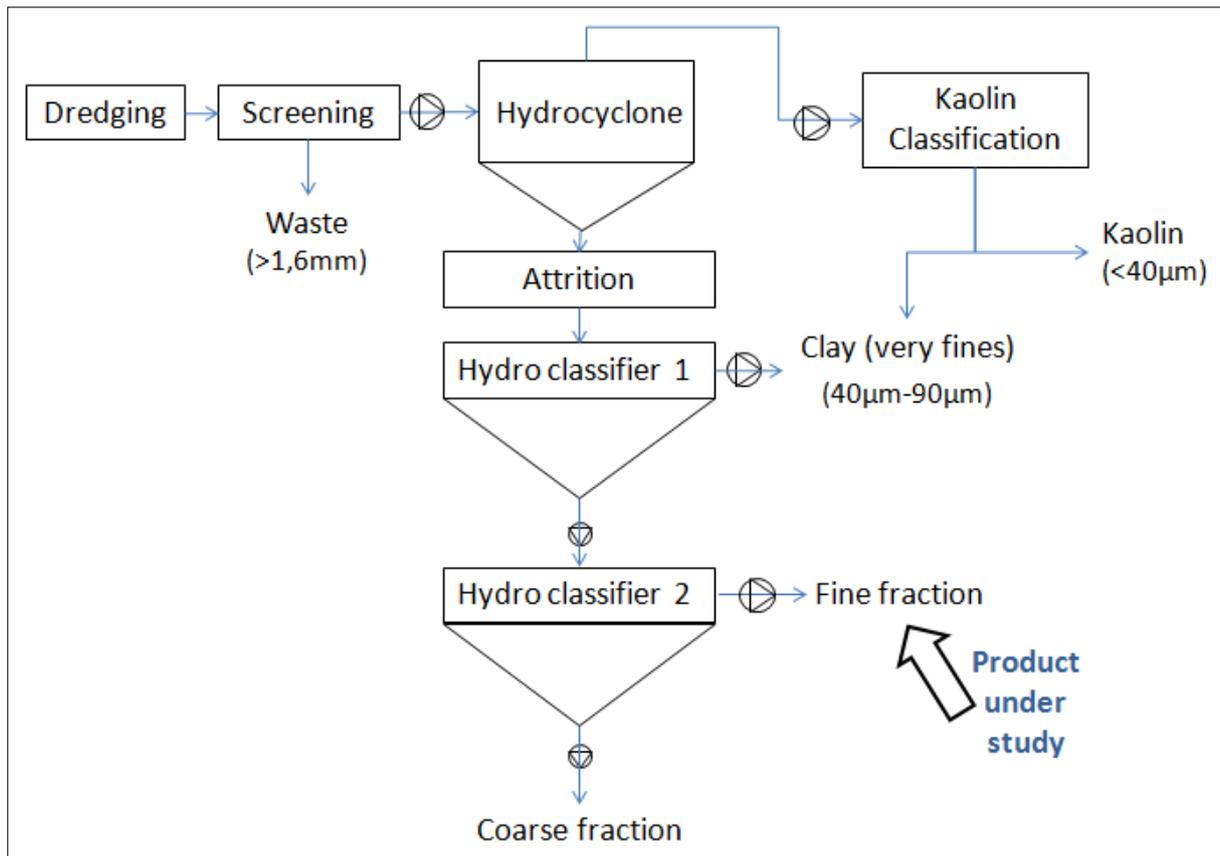


Figure 6 – Partial flow sheet of the industrial process

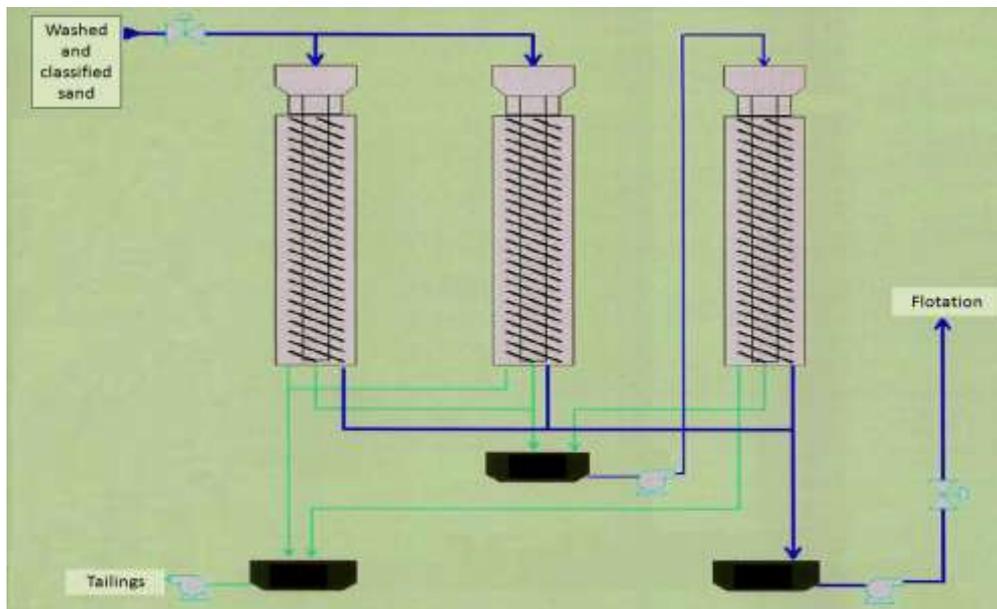


Figure 7 – Scheme of industrial spirals process in study

The first step in the flotation is the separation of water from sand by a drainage screen. Then, the recycled water from the flotation process is added. From the drainage screen, the sand enters in the first conditioner, where all the chemical reagents (frother, collector and caustic soda) are added and mixed. The pulp flows 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 8.

On the 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 tailings pond of flotation. Drainage water from the tailing pond is pumped to the flotation process to be reused.

The flotation flow rate changes with the raw material characteristics because it depends of the content in the coarse and fine fraction and also of the segregation on raw material in the silo.

The flotation cells in study are made by Sala International AB (property Metso Corporation), type AS 4,5. They have 22,5 m³ of total volume and a retention time of 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 reagents flow rate control is manual.

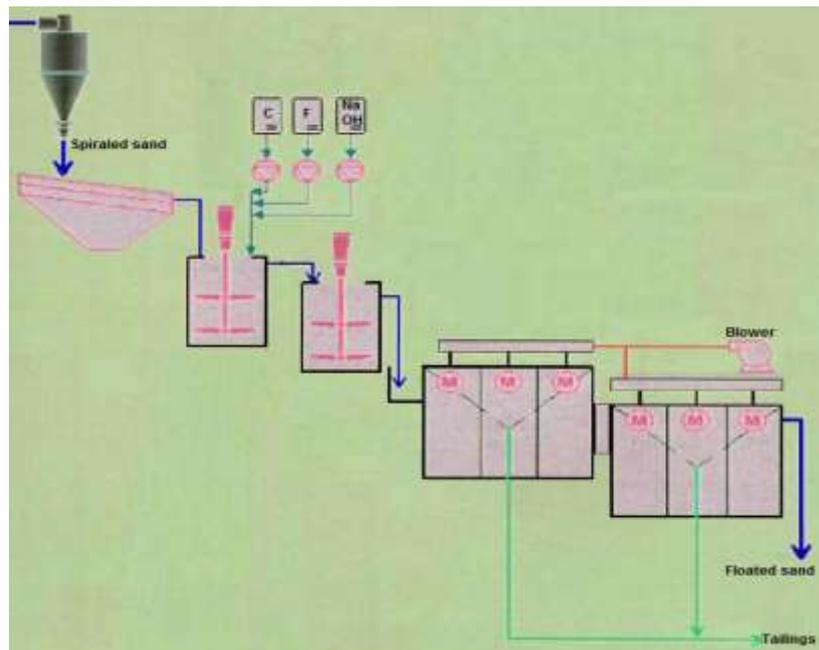


Figure 8 – Scheme of industrial flotation process in study

2.3.2. Flotation Feed

As described, the flotation feed is washed, classified and spiraled silica sand. The particle size of floated sand varies between 0,090 and about 1mm as shown in Table 2. 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.

The characterization data of the sand that feed the flotation is shown in Figure 9 and Figure 10.

Table 2 – Particle size distribution of flotation feed

Particle size (µm)	Fine Fraction		Coarse Fraction	
	Retained % (Wt)	Cumulative retained % (Wt)	Retained % (Wt)	Cumulative retained % (Wt)
>1000	0	0	0,3	0,3
1000-710	0,1	0,1	4,3	4,6
710-500	1,3	1,4	21	25,6
500-355	38,1	39,5	51	76,6
355-250	44,9	84,4	20	96,6
250-180	13,3	97,7	3,1	99,7
180-125	2,2	99,9	0,3	100
125-90	0,1	100	0	100
90-63	0	100	0	100
<63	0	100	0	100
Total	100		100	

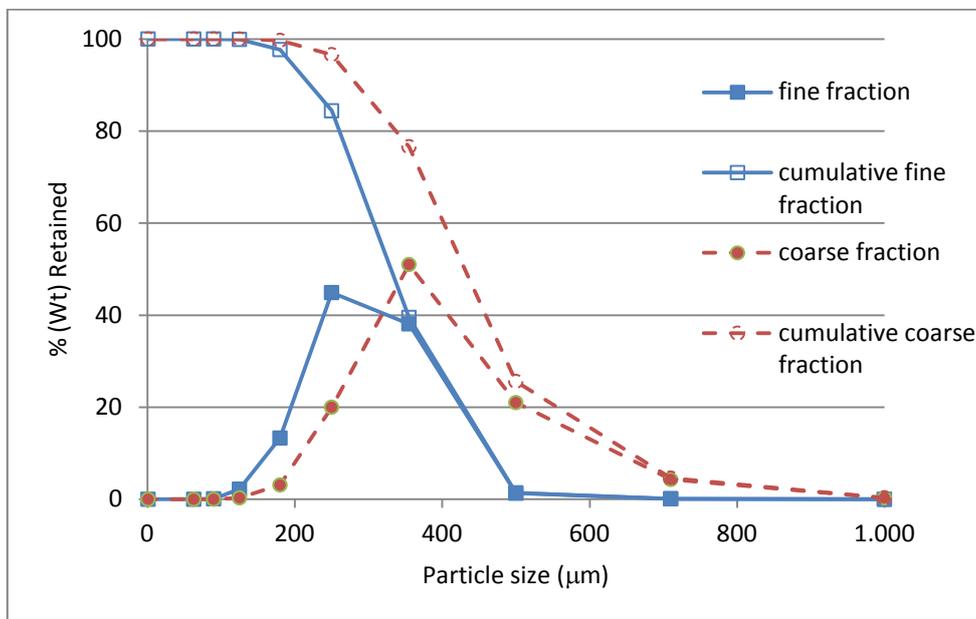


Figure 9 – Particle size distribution and cumulative oversize of flotation sand feed

Table 3 – Average chemicals composition of flotation feed

Chemical composition	Fine Fraction	Coarse Fraction
	% (Wt)	% (Wt)
SiO ₂	99,43	99,49
Fe ₂ O ₃	0,055	0,063
Al ₂ O ₃	0,324	0,289
TiO ₂	0,086	0,043
K ₂ O	0,012	0,012
CaO	0,004	0,004
MgO	0,003	0,003
Na ₂ O	0,001	0,003
Loss on Ignition	0,090	0,090
Total	100,00	100,00
Heavy Minerals	0,311	0,418

The content in SiO₂ is obtained by the difference to the total amount of the sum of all oxides measured.

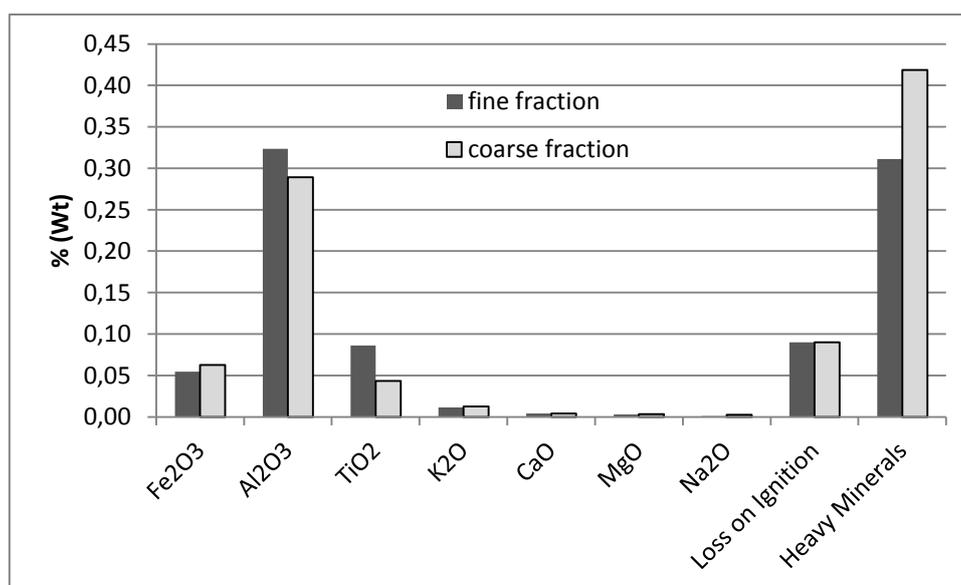


Figure 10 – Chemicals composition of flotation sand feed

2.3.3. Flotation Tailings

During the flotation process (inverse flotation), the heavy minerals are removed with paddles (overflow). The main characterization of the flotation tailings from fine fraction is shown in Table 4 and Table 5.

Table 4 – Grain size distribution of flotation tailings

Particle size (µm)	% (Wt) Retained	% (Wt) Cumulative retained
>1000	0,0	0,0
1000-710	2,0	2,0
710-500	9,6	11,6
500-355	38,0	49,6
355-250	33,7	83,3
250-180	11,4	94,7
180-125	3,1	97,7
125-90	0,9	98,6
90-63	0,7	99,3
<63	0,7	100,0
Total	100,0	

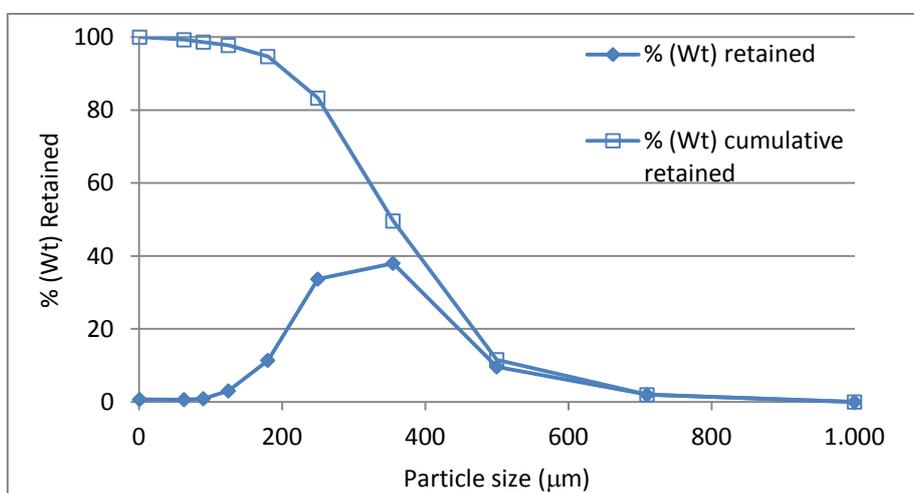


Figure 11 – Particle size distribution and cumulative oversize particle size distribution of tailings

Table 5 – Chemicals composition of tailings

Chemical composition	% (Wt)
SiO ₂	91,845
Fe ₂ O ₃	1,000
Al ₂ O ₃	6,200
TiO ₂	0,641
K ₂ O	0,020
CaO	0,160
MgO	0,000
Na ₂ O	0,036
Loss on Ignition	0,098
Total	100,00
Heavy Minerals	17,503

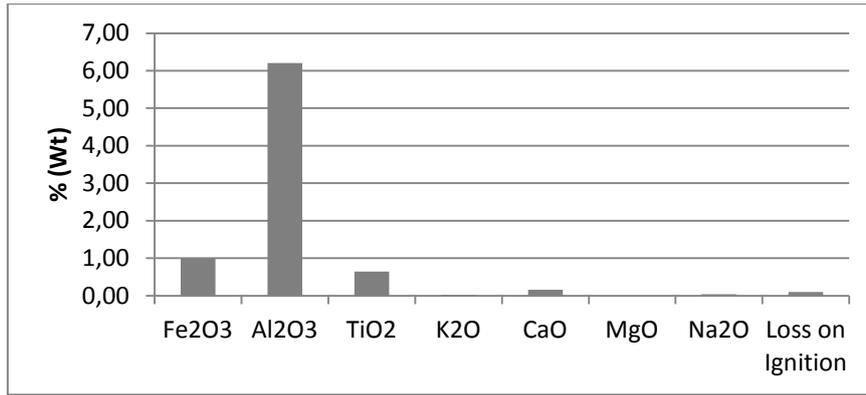


Figure 12 – Chemical composition of tailings

2.3.4. Mineralogy of floated sand

The mineralogical analysis of the floated sand is shown in Table 6. The analysis was obtained by X-ray diffraction (XRD)

Table 6 – Mineralogy of floated sand

Mineral	Concentration (%)
Andalusite (Al ₂ SiO ₅)	61
Mullite (Al ₆ Si ₂ O ₁₃)	6
Pyrope (Mg ₃ Al ₂ (SiO ₄) ₃)	10
Tourmalin (Na(Mg,Fe,Li,Mn,Al) ₃ Al ₆ (BO ₃) ₃ Si ₆ O ₁₈ (OH,F) ₄)	8
Quartz (SiO ₂)	10
Rutile (TiO ₂)	3
Magnesioferrite (Mg(Fe ³⁺) ₂ O ₄)	2
Total	100

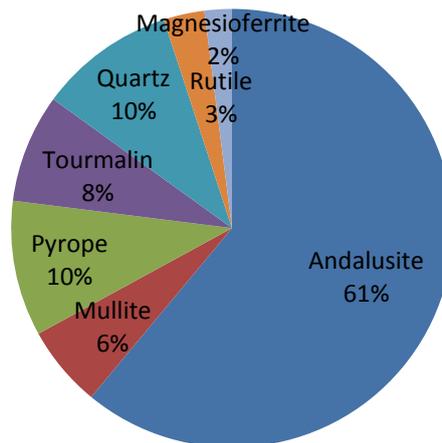


Figure 13 – Mineralogy of floated sand

2.3.5. Flotation chemical reagents

The plant in study uses 3 chemical reagents in flotation: collector, frother and pH regulator. These chemical reagents are described on section 3.1.2 Chemical reagents.

3. Material and Methods

The present section describes the materials, equipments and methods used in the experimental work. The trials were made in laboratory. On the previous section it was described the industrial process. The lab trials represent only a part of the whole industrial process. The lab trials only represent the industrial process when the fine fraction is the fraction treated by flotation. During the production of spiraled fine fraction it was collected a sufficient sample of the 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.

3.1.1. 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 7 and Table 8.

Table 7 – 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 8 – Chemical analysis of feed on lab trials

Chemical composition	% (Wt)
SiO ₂	99,637
Fe ₂ O ₃	0,023
Al ₂ O ₃	0,213
TiO ₂	0,020
K ₂ O	0,011
CaO	0,004
MgO	0,003
Na ₂ O	0,000
Loss on Ignition	0,089
Total	100,00
Heavy Minerals	0,1686

3.1.2. Chemical reagents

Although the chemical reagents are collected from the industrial process, at lab level it is difficult to use such small quantities. The dilution used on chemical reagents and the levels choose for each variable (concentration of collector and frother and pH) are explained in Annex III – Confidential data.

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 9 are shown the 3 variables (factors) at 3 levels.

Table 9 – Variables 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.

3.1.3. 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 Leeds flotation cell is shown in Figure 14.



Figure 14 – (a) Frontal view and (b) lateral view of Leeds flotation cell

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. The laboratory flotation machine used is shown in Figure 15.



Figure 15 – Denver laboratory flotation cell

pH meter

The pH was considered key variable of the process. The pH was measured by Crison instruments SA, pH 2000 during all runs. The equipment used is shown in Figure 16. The electrode is made by Hanna Instruments, model HI1312.



Figure 16 – Crison pH meter

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 response 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 possible variables considered as constants were the impellers speed because in the industrial process the impellers speed is constant, the volume of flotation cells because the equipment used was the same, the air flow rate because the Denver lab cell is self aerated, the feed sand quality and the solids concentration. The process water can change at industrial and laboratorial level, but this possible variation of quality was not accounted owing the water analysis limitation (economical, equipments, methodology and available time), anyway the company in study made weekly analysis due to the discharge of waste water license, and the changes are negligible.

3.2.1. 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 kinetic trials were also important to program the DOE trial. It was necessary about one hour to perform a trial, after wait about 12 hours to sample drying on oven, and one more hour to perform the chemical and heavy minerals analysis.

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 flotation times are shown in Table 10.

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), in this case it was not added pH regulator, but it was measured. After adding the chemical reagents wait for 3 minutes or 5 minutes depending of trial number, as shown in Table 10. Then, the air flow was opened at 110 L/h, and during 1 to 8 minutes the froth was removed with blades manually, according with Table 10.

Table 10 – Kinetic trials conditions

Trial	Conditioning time (min) [no air flow]	Flotation time (min) [air flow at 110 L/h]	Total time (min)
K1	3	1	4
K2	5	2	7
K3	3	3	6
K4	5	4	9
K5	3	5	8
K6	5	6	11
K7	3	7	10
K8	5	8	13

3.2.2. Design of experiments (DOE)

Target of experiments was to find the best conditions to minimize the iron content and heavy minerals on silica sand in a flotation process. From flotation variables analysis, from industrial experience in accord with references used, the factors considered with more importance were the chemical reagents concentration and pH.

Considering 3 factors, with probable correlations between them, the strategy used to evaluate the flotation performance in different conditions was the response surface design.

For the statistical treatment data and analysis was used the software Design Expert 9.0.3.1 from State-Ease Inc. Because there are 3 levels for each factor, and other studies indicate a non linear answer, it was chosen the quadratic model to the first data treatment.

In Design-Expert, full factorial 3-level designs are available. The number of experiments will be 3^3 plus some replicates of the center point.

As shown in Table 9 the factors (A, B and C from Figure 3) considered were pH and concentration of collector and frother with the levels described in the same table.

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 the 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, according to the volumes calculated on Annex III – Confidential data. The pH used was controlled with sodium hydroxide to reach the desired pH for each trial, except on trials for pH (-1), in this case it was not added pH regulator, but it was measured. The air flow valve was closed.

The chemical reagents were conditioned for 5 minutes. The air flow was completely opened; water was added until reached the maximum level to have a flotation solids concentration about 35%. During more 8 minutes the froth was manually removed with blades.

The trials were made in 3^3 different conditions as described in Table 11.

The run or order to perform the trials was made randomly to ensure the independence of observations. The real run is shown in Table 11.

Table 11 – Trials description

Trial	Run	Collector conc. (g/ton)	Frother conc. (g/ton)	pH
1	27	-1	-1	-1
2	8	0	-1	-1
3	18	1	-1	-1
4	1	-1	0	-1
5	11	0	0	-1
6	20	1	0	-1
7	2	-1	1	-1
8	14	0	1	-1
9	24	1	1	-1
10	28	-1	-1	0,5
11	9	0	-1	0,5
12	17	1	-1	0,5
13	4	-1	0	0,5
14	12	0	0	0,5
15	21	1	0	0,5
16	6	-1	1	0,5
17	15	0	1	0,5
18	23	1	1	0,5
19	3	-1	-1	1
20	10	0	-1	1
21	19	1	-1	1
22	5	-1	0	1
23	13	0	0	1
24	22	1	0	1
25	7	-1	1	1
26	16	0	1	1
27	25	1	1	1
28	26	0	0	0,5
29	29	0	0	0,5
30	30	0	0	0,5
31	31	0	0	0,5
32	32	0	0	0,5

To find out the trials error there are 5 extra trials on center points. The trials results between trial 1 and 27 are an average of two replicates (this replicates aren't suggested by the model of DOE). 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 as shown in Figure 17. The dense liquid was bromoform (Chem-Lab NV, 99% CHBr_3), Density of 2,89 g/mL and molar weighting of 252,73 g/mol. The analytical weighing machine used to quantify the heavy minerals content was made by Mettler instrumente AG, model AE100, calibrated by ISQ in June 2014 with an error on grade 0-0,1g of $\pm 0,0002\text{g}$.



Figure 17 – Separatory funnel to separate heavy minerals from quartz sand

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. The EDXRF spectrometer is showed in Figure 18. The calibration conditions are described on Annex I – EDXRF spectrometer calibration .



Figure 18 – EDXRF spectrometer

Measurement uncertainty methodology

The limit of detection (L_D) can be measured in accordance with the International Union of Pure and Applied Chemistry (IUPAC) as defined by Gazulla (2013). However there is no available sample with a concentration 0.5 times the concentration of the lowest standard in the calibration curve (Gazulla & al, 2013).

The L_D can also be measured using the inverse of measurement time (Fellin, Negri, & Zanuttini, 2013).

The measurement time (m_t) used was 120 seconds. The L_D of the EDXRF measurement is 0,008% using Equation 13.

$$L_D = 1/m_t \quad (13)$$

The quantification limit (L_Q) presents the quantifiability of an analysis, and in accordance with IUPAC guidelines is calculated by multiplying the number of times (n) of measurements of a sample in the same reproducibility conditions, usually 10, by the standard deviation (s) of that measurements as shown on Equation 14 (Gazulla & al, 2013).

$$L_Q = n \times s \quad (14)$$

The Measurement uncertainty (U) is obtained by the product of k (constant from the Student's t -distribution for 95% confidence) and uncertainty of the method (u_{method})

$$U = k \times u_{method} \quad (15)$$

Where the u_{method} can be achieve by the Equation 16, and where u_{VR} is the uncertainty of the certified value of the reference material, u_{VL} is the uncertainty of the measurement of the reference material and u_{REPRO} is the uncertainty of the measurement of the sample (Gazulla & al, 2013).

$$u_{method}^2 = u_{VR}^2 + u_{VL}^2 + u_{REPRO}^2 \quad (16)$$

The measurement uncertainty for the EDXRF measures is 0,0018% (wt) or 18 ppm and is described on Annex I – EDXRF spectrometer calibration

4. Experimental Results

Although the flotation performance is often measured by Equation 8 to Equation 12, at industrial process the results are evaluated in terms of Fe₂O₃ 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 Fe₂O₃ and heavy minerals.

4.1. Kinetic trials results

The Table 12 and Table 13 show the kinetic results for Fe₂O₃ content (wt) and heavy minerals content (wt) respectively for different flotation time.

Table 12 – Kinetic results for 3 minutes of conditioning time

Trial	Conditioning time (min) [no air flow]	Flotation time (min) [air flow at 110 L/h]	Total trial time (min)	Fe ₂ O ₃ content (%)	Heavy minerals content (%)
K1	3	1	4	0,015	0,058
K3	3	3	6	0,015	0,032
K5	3	5	8	0,014	0,022
K7	3	7	10	0,013	0,021

Table 13 – Kinetic results for 5 minutes of conditioning time

Trial	Conditioning time (min) [no air flow]	Flotation time (min) [air flow at 110 L/h]	Total trial time (min)	Fe ₂ O ₃ content (%)	Heavy minerals content (%)
K2	5	2	7	0,014	0,036
K4	5	4	9	0,014	0,027
K6	5	6	11	0,013	0,021
K8	5	8	13	0,012	0,022

4.2. DOE trials results

The results of DOE trials 1 to 27 for 2 replicates are listed in Table 14. The Table 15 lists the results of trial 28 to 32, made under the same conditions (these trials were not replicated).

Table 14 – Results of Fe₂O₃ content and heavy minerals content for 27 trials

Trial	Collector conc. (g/ton)	Frother conc. (g/ton)	pH	Fe ₂ O ₃ content % (wt) Replicate 1	Fe ₂ O ₃ content % (wt) Replicate 2	HM content % (wt) Replicate 1	HM content % (wt) Replicate 2
1	-1	-1	-1	0,013	0,012	0,0031	0,0040
2	0	-1	-1	0,012	0,013	0,0059	0,0029
3	1	-1	-1	0,012	0,013	0,0048	0,0037
4	-1	0	-1	0,013	0,013	0,0052	0,0017
5	0	0	-1	0,012	0,012	0,0020	0,0048
6	1	0	-1	0,013	0,012	0,0026	0,0054
7	-1	1	-1	0,013	0,012	0,0021	0,0022
8	0	1	-1	0,012	0,013	0,0022	0,0048
9	1	1	-1	0,012	0,011	0,0050	0,0049
10	-1	-1	0	0,012	0,013	0,0055	0,0063
11	0	-1	0,5	0,013	0,013	0,0056	0,0036
12	1	-1	0,5	0,013	0,012	0,0051	0,0036
13	-1	0	0,5	0,014	0,014	0,0073	0,0060
14	0	0	0,5	0,012	0,013	0,0061	0,0064
15	1	0	0,5	0,012	0,012	0,0035	0,0042
16	-1	1	0,5	0,012	0,014	0,0020	0,0053
17	0	1	0,5	0,013	0,014	0,0015	0,0052
18	1	1	0,5	0,014	0,013	0,0019	0,0046
19	-1	-1	1	0,013	0,013	0,0075	0,0071
20	0	-1	1	0,015	0,013	0,0053	lost sample
21	1	-1	1	0,013	0,012	0,0070	0,0066
22	-1	0	1	0,014	0,014	0,0122	0,0102
23	0	0	1	0,013	0,013	0,0075	0,0079
24	1	0	1	0,013	0,013	0,0033	0,0047
25	-1	1	1	0,013	0,014	0,0017	0,0049
26	0	1	1	0,013	0,013	0,0041	0,0159
27	1	1	1	0,013	lost sample	0,0100	0,0078

Table 15 – DOE trial results for trial 28 to 32

Trial	Run	Collector conc. (g/ton)	Frother conc. (g/ton)	pH	Fe ₂ O ₃ content % (wt)	Heavy Minerals content % (wt)
28	26	0	0	0,5	0,013	0,0064
29	29	0	0	0,5	0,013	0,0082
30	30	0	0	0,5	0,013	0,0059
31	31	0	0	0,5	0,012	0,0105
32	32	0	0	0,5	0,012	0,0050

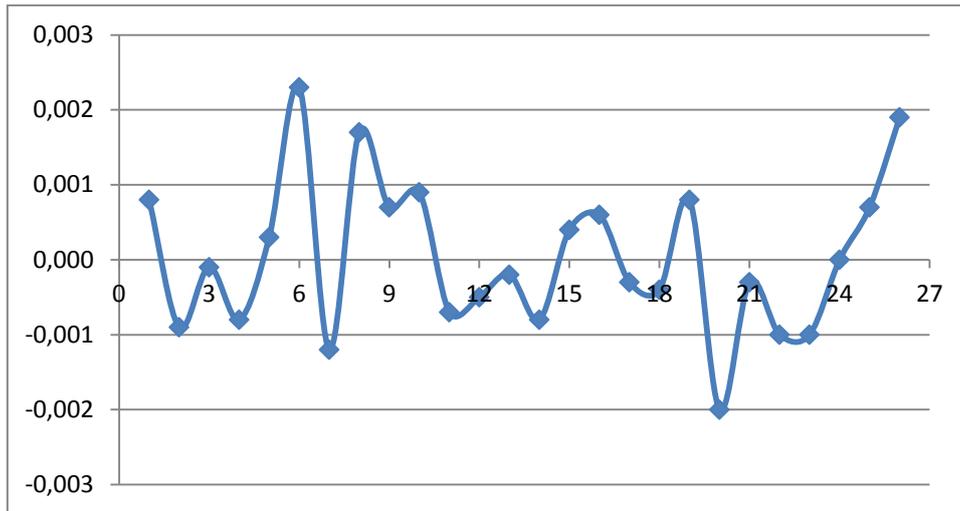


Figure 19 – Difference between 2 replicates results for Fe₂O₃ content

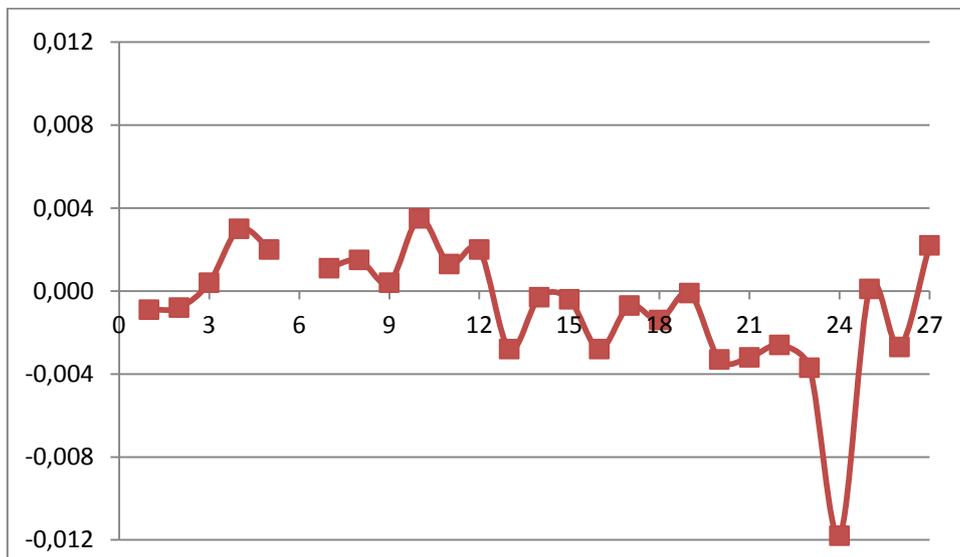


Figure 20 – Difference between 2 replicates results for heavy minerals content

The trial 24 has a difference between 2 replicates larger than usual, but there was no opportunity to repeat the trial.

5. Analysis and discussion of results

In analysis and discussion of results section it is analyzed the kinetic results, the possible correlation between variables, the Fe_2O_3 content response, the heavy minerals content response and the optimization.

The variation of results, in general was small, because the range work was defined based on experience of industrial process, and the industrial process is already empirically optimized.

5.1. Analysis and results discussion of kinetic trials

The kinetic trials were very important to perform the DOE trial. The results show the flotation kinetics and the time needed for the attachment of particles to air bubbles.

The 13 minutes of trial time were adequate to the heavy minerals removal as shown in Figure 22, the minimum values were achieved after 11 minutes of trial, but for the Fe_2O_3 content the Figure 21 shows that it will be necessary to use more flotation time, until find a repeat of minimums or even a small rise of values as shown in Figure 5.

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

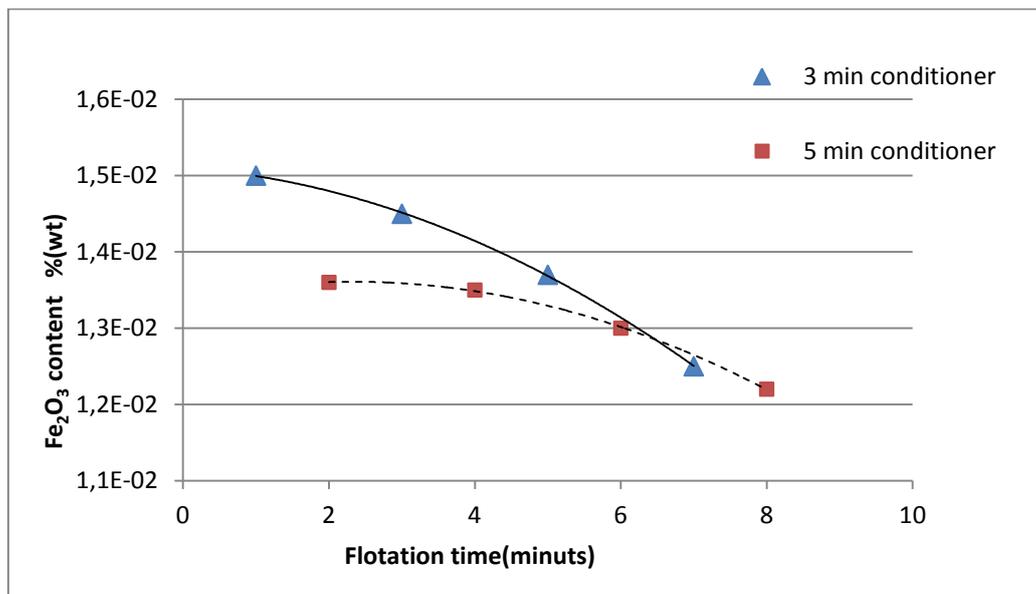


Figure 21 – Fe_2O_3 content on sink product for different condition of residence time

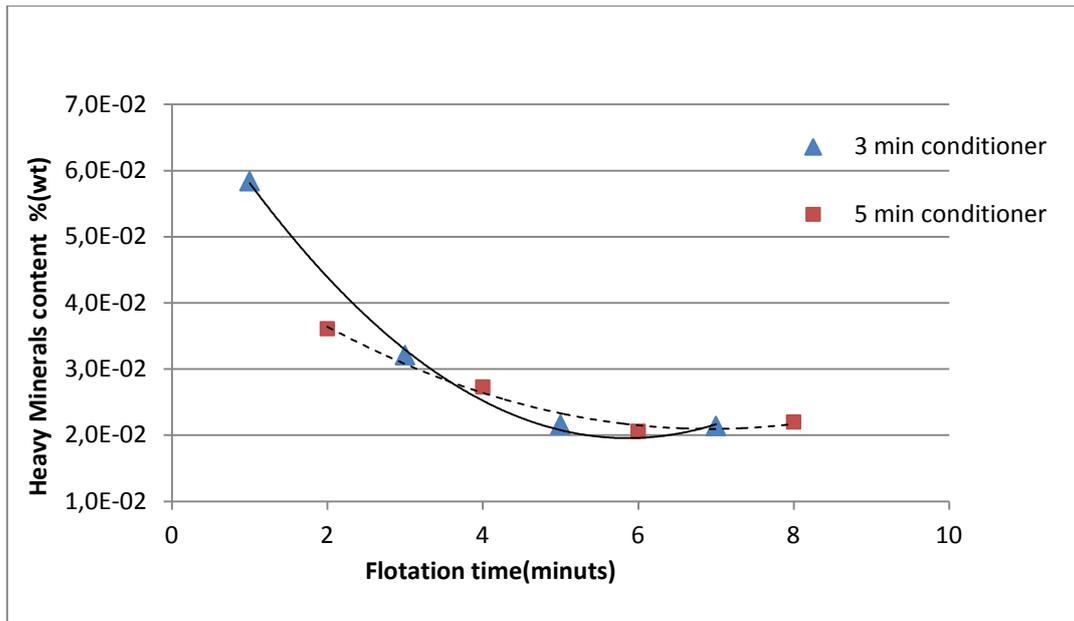


Figure 22 – Heavy minerals content in the sink product for different conditions of residence time

5.2. 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, coefficients are shown in Table 16. The larger correlations are between pH and response variables.

Table 16 – Pearson's correlation coefficient

	Run	Collector Conc.	Frother Conc.	pH	Fe ₂ O ₃ content	HM content
Run	1,000					
Collector Conc.	0,478	1,000				
Frother Conc.	-0,032	0,000	1,000			
pH	0,090	0,000	0,000	1,000		
Fe ₂ O ₃ content	-0,439	-0,328	0,135	0,483	1,000	
HM content	0,188	-0,051	-0,062	0,540	0,150	1,000

The correlation between response variables Fe₂O₃ content and heavy minerals content is low, only 0,15, which contradicts what was expected. The Figure 23 has shown the dispersion of correlation between response variables of experimental DOE trials.

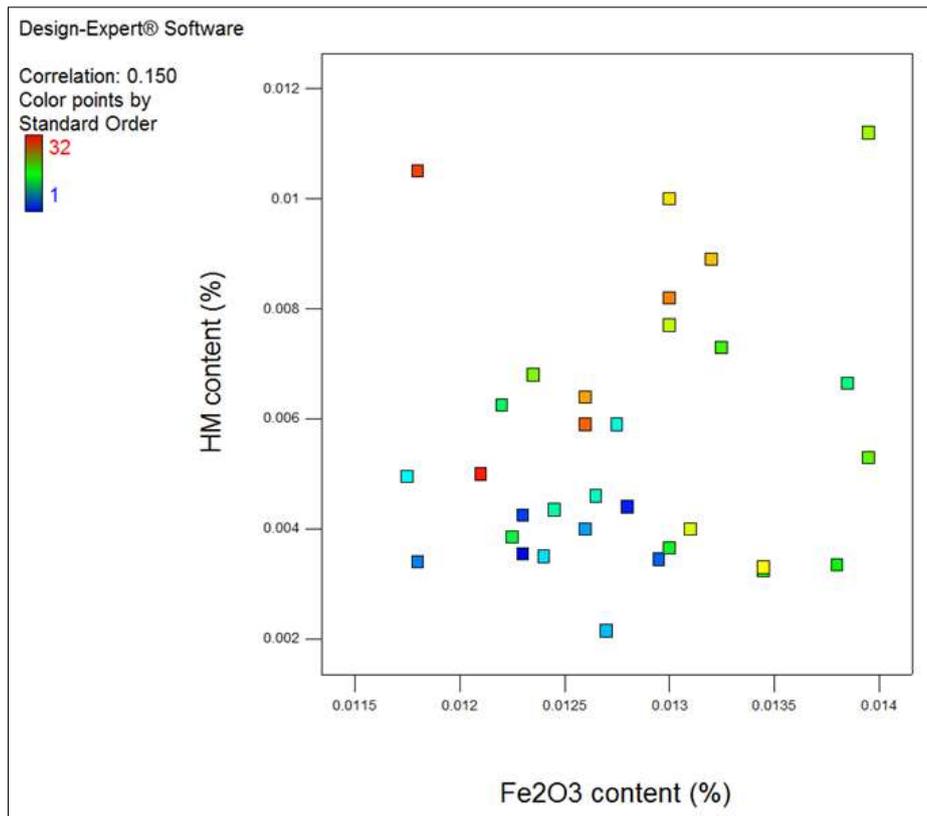


Figure 23 – Correlation between Fe₂O₃ content and heavy minerals content

However, using a large grade of Fe₂O₃ content and heavy minerals content the correlation between them is about 0,8 as it can see observed in Figure 24, where it was used industrial results from different types of beneficiated silica sand, even so at low grade of contents the correlation between Fe₂O₃ content and heavy minerals content is also low.

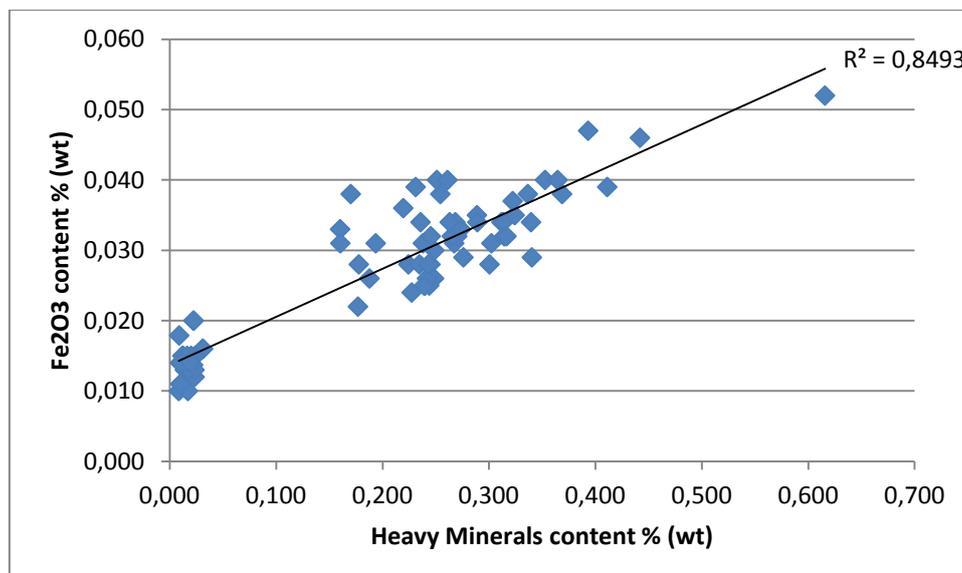


Figure 24 – Correlation between Fe₂O₃ content and heavy minerals content using industrial data from sand with different levels of beneficiation

5.3. Analysis and results discussion of Fe₂O₃ content

For the trials under the same conditions (28 to 32) the average result for Fe₂O₃ content was 0,012% and the variance was 2E⁻⁷, which indicates a low error on lab methodology. These trials were made in average conditions of industrial process and the results are in line with the average results of industrial production.

For the trials 1 to 27 the average results for Fe₂O₃ content was 0,013% and the variance was 6E⁻⁷, these results indicate a small variability of results.

The replicates have always differences caused by random factors (handling, measurements, and analysis). As the DOE only suggest one replicate for each trial, except for centre point, and it was made 2 trials for each condition, in statistical treatment data it was used the average results between the 2 replicates.

To create a model to predict the response variable in function of the results it is necessary to evaluate which variables or interactions between variables have statistical significance.

The first step was to identify the best model to predict the response. The most appropriate model was the linear model.

After analysis of variance (partial sum of squares) it was obtained the ANOVA table for response surface model shown in Table 17.

Table 17 – ANOVA for Fe₂O₃ content of selected model

Source	Sum of Squares	Degrees of freedom	Mean Square	F Value	p-value	
					Prob > F	
Model	4E-06	3	1E-06	5.2	0,005	Significant
<i>A-collector conc.</i>	1E-06	1	1E-06	4.7	0,039	Significant
<i>B-frother conc.</i>	2E-07	1	2E-07	0.8	0,380	Not significant
<i>C-pH</i>	3E-06	1	3E-06	10.2	0,004	Significant
Residual	7E-06	28	3E-07			
<i>Lack of Fit</i>	6E-06	23	3E-07	1.5	0,339	Not significant
<i>Pure Error</i>	9E-07	5	2E-07			
Cor Total	1E-05	31				

The F-test applied to the model indicates the level of significance of the model prediction. The model has a p-value ≤ 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.

The frother concentration is not significant. The coefficients of variables defined as significant and their confidence intervals are shown in Table 18.

Table 18 – Coefficients of linear regression model for Fe₂O₃ content

Factor	Coefficient Estimate	Degrees of freedom	Standard Error
Intercept	0,013	1	9E-05
A-collector conc.	-3E-04	1	1E-04
C-pH	4E-04	1	1E-04

The model equation from linear regression to predict Fe₂O₃ content is shown on Equation 17.

$$\text{Fe}_2\text{O}_3 \text{ content} = 0,013 - 3 \times 10^{-4} \times A + 4 \times 10^{-4} \times C \quad (17)$$

The comparison between the experimental and estimated Fe₂O₃ content is shown in Figure 25.

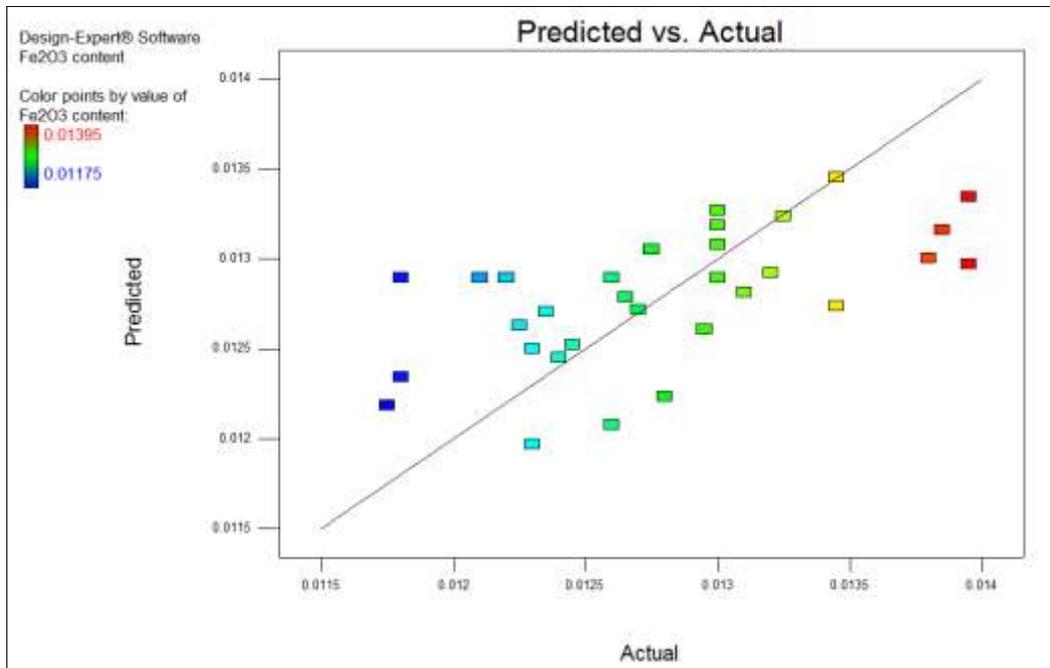


Figure 25 – Comparison of experimental and predicted Fe₂O₃ content

To validate the model 3 tools were used to analyse the residuals shown in Figure 26, Figure 27 and Figure 28. The normal plots of the difference between the observed and predicted values of Fe₂O₃ content (or residuals) are shown in Figure 26.

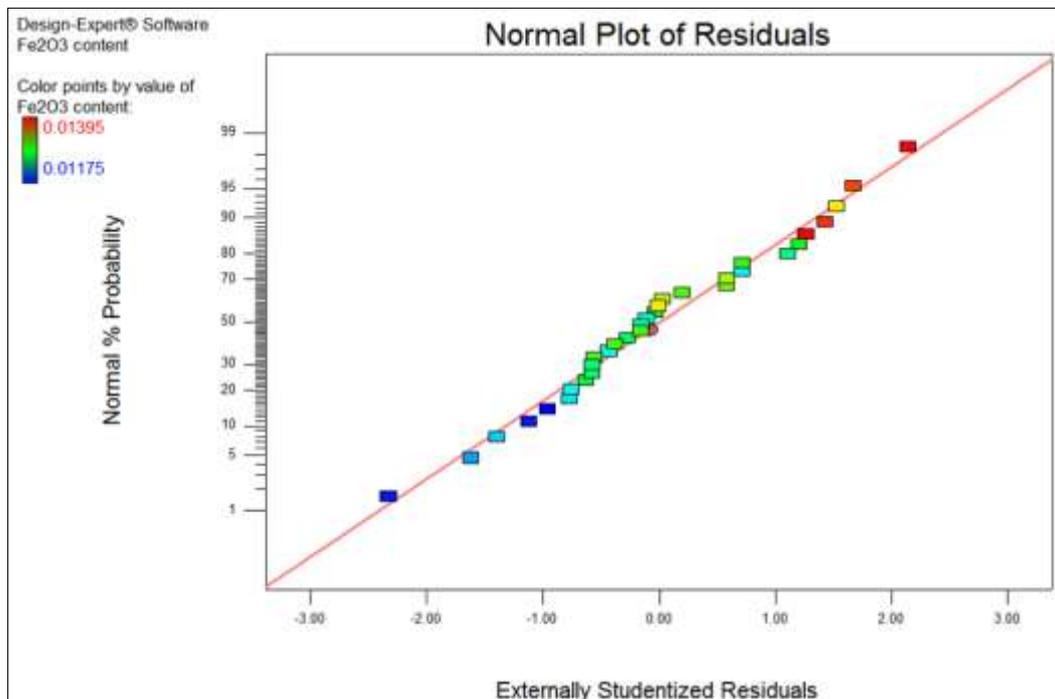


Figure 26 – Normal plot of residuals for Fe₂O₃ content

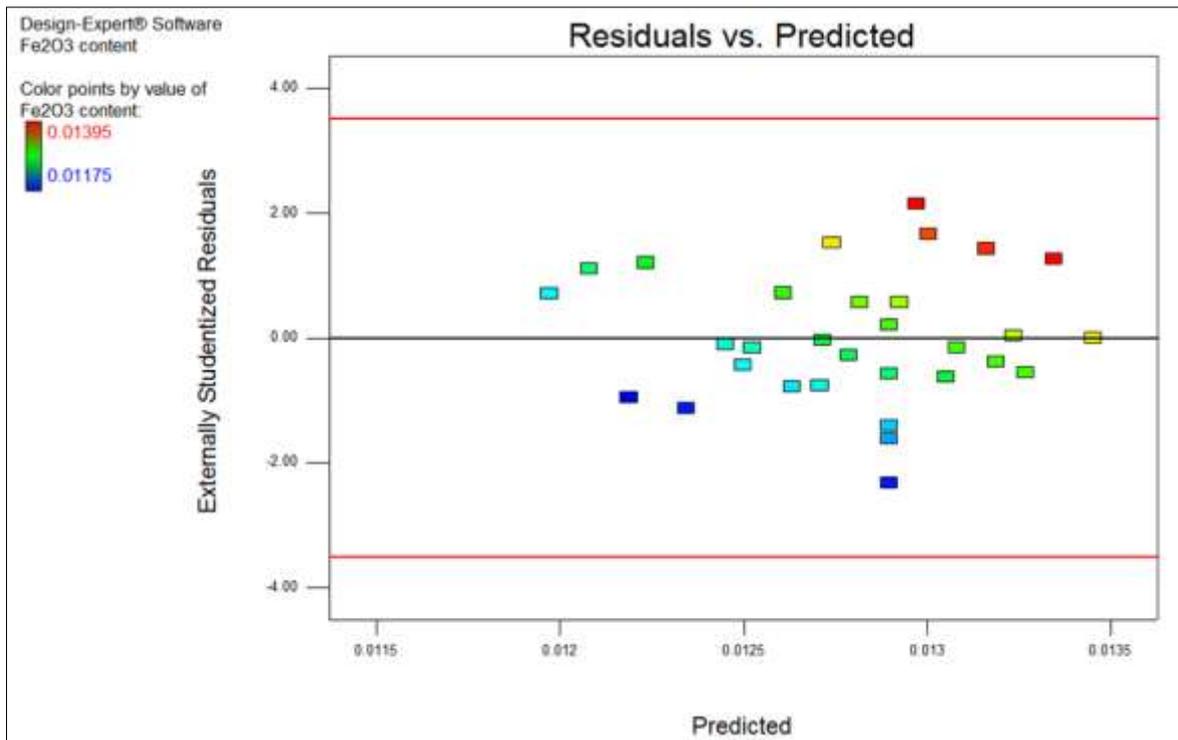


Figure 27 – Predicted values for Fe₂O₃ content vs residuals

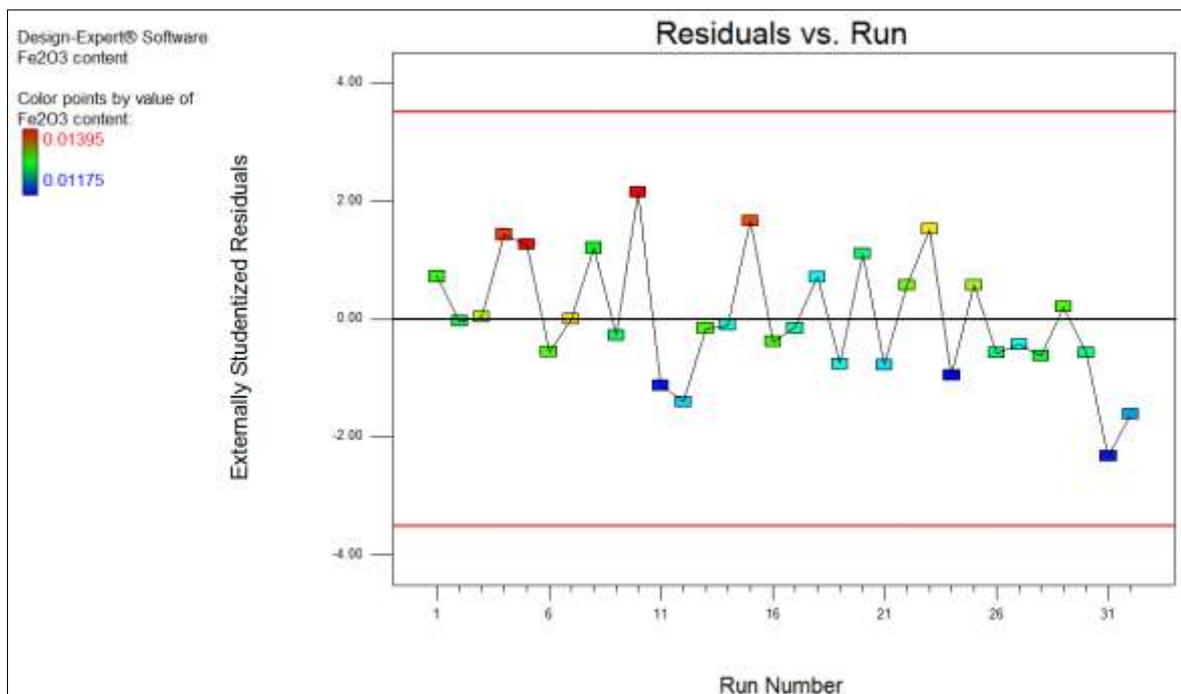


Figure 28 – Analysis of residuals versus run for Fe₂O₃ content analysis

In these conditions the model was accepted to predict the process in study.

5.4. Analysis and results discussion for heavy minerals content

Considering the trials carried out under the same conditions (trials 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 (see Table 15). These trials were made in standard conditions of industrial process and the 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 indicate a larger variability of results.

The replicates have always differences caused by random factors (handling, measurements, and analysis). As the DOE only suggest one replicate for each trial, except for centre point, and it was made 2 trials for each condition, in statistical treatment data it was used the average results between 2 replicates.

To create a model to predict the response variable in function of factors it is necessary to evaluate which variables or interactions between variables have statistical significance.

The first step was to identify the best model that predicts the response. The most appropriate model was the linear model.

After the analysis of variance (partial sum of squares) it was obtained the ANOVA table for the response surface model shown in Table 19. 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 on DES with Box-Cox Plot support recommends transforming the statistical model with an inverse square root as shown in Figure 29 to predict the heavy minerals content.

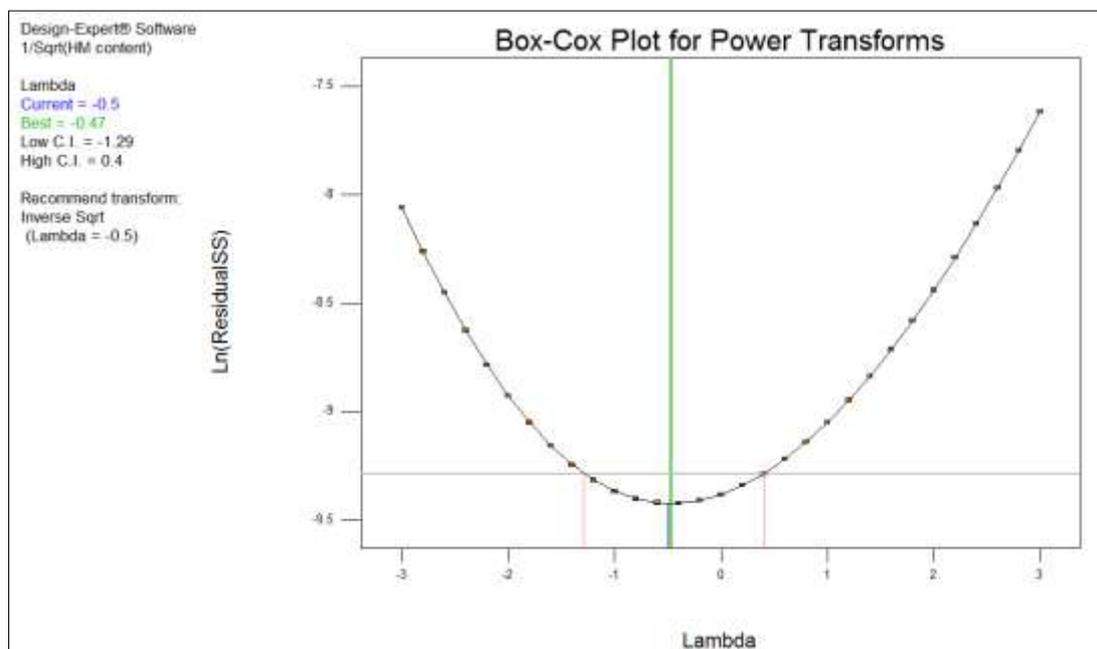


Figure 29 – Box-cox plot for power transforms on heavy minerals model analysis

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 considering these variables inside the levels studied.

Table 19 – ANOVA for heavy minerals content of selected model

Source	Sum of Squares	Degrees of freedom	Mean Square	F Value	p-value	
					Prob > F	
Model	91,7	3	30,6	5,53	0,004	Significant
<i>A-collector conc.</i>	0,5	1	0,5	0,09	0,762	Not significant
<i>B-frother conc.</i>	11,5	1	11,5	2,08	0,161	Not significant
<i>C-pH</i>	79,7	1	79,7	14,43	0,001	Significant
Residual	154,7	28	5,5			
Lack of Fit	142,7	23	6,2	2,58	0,148	Not significant
Pure Error	12,0	5	2,4			
Cor Total	246,5	31				

The model has a p-value $\leq 0,05$, it means that the model is significant and 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 coefficients of variables defined as significant and their confidence intervals are shown in Table 20.

Table 20 – Coefficients of linear regression model for heavy minerals content

Factor	Coefficient Estimate	Degrees of freedom	Standard Error
Intercept	14,7	1	0,43
C-pH	-2	1	0,53

The model equation from linear regression to predict heavy minerals content is shown on Equation 18.

$$\frac{1}{\sqrt{HM}} = 14,7 - 2 \times C \quad (18)$$

The comparison between the experimental and estimated heavy minerals content is shown in Figure 30.

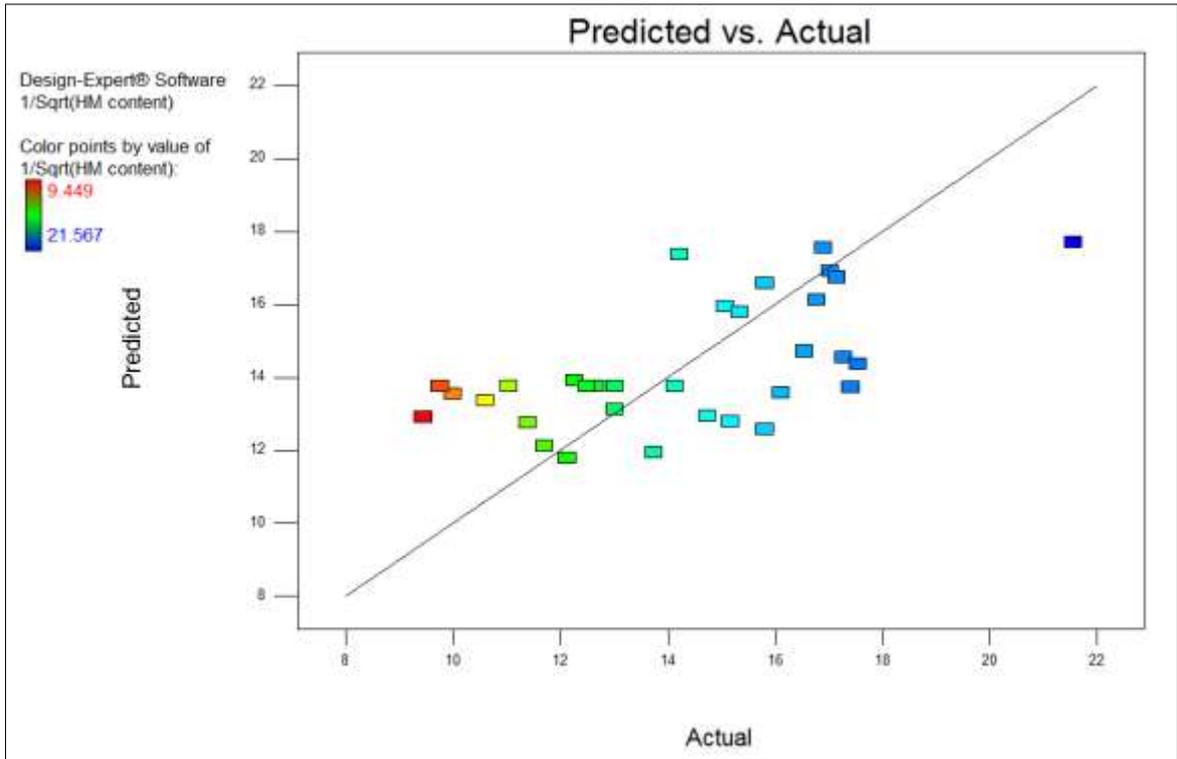


Figure 30 – Comparison of experimental and predicted heavy minerals content

To validate the model 3 tools were used to analyse the residuals shown in Figure 31, Figure 32 and Figure 33. The normal plots of the difference between the observed and predicted values of heavy minerals content (or residuals) are shown in Figure 31.

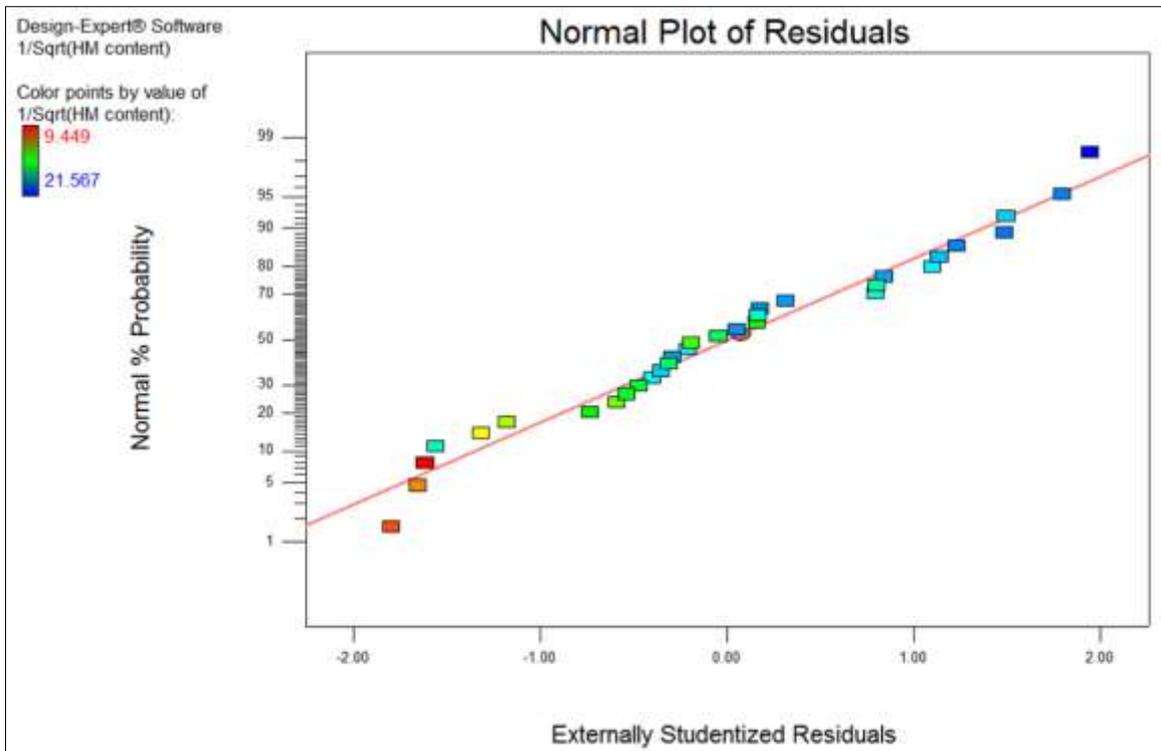


Figure 31 – Normal plot of residual for heavy minerals content

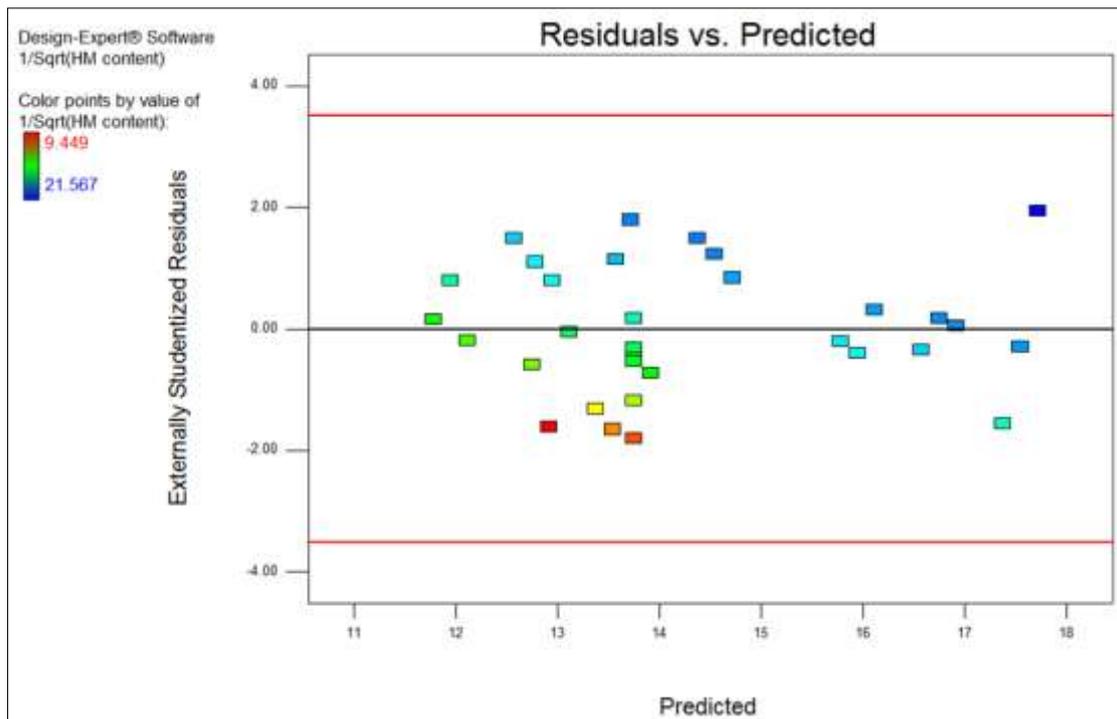


Figure 32 – Predicted values for heavy minerals content vs residuals

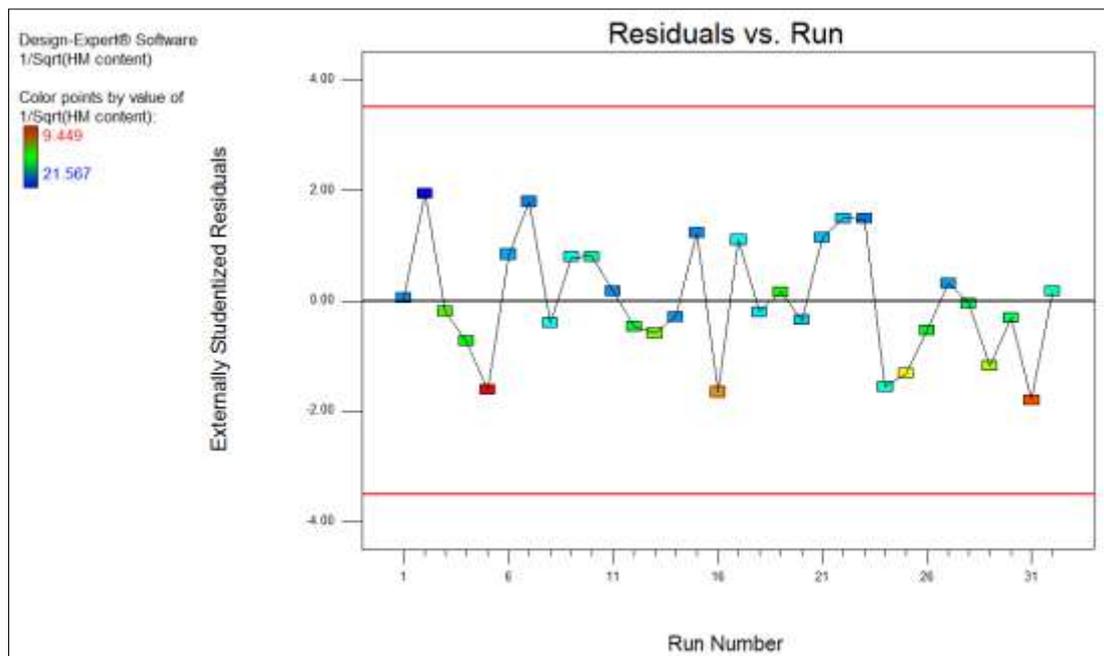


Figure 33 – Analysis of residuals versus run for heavy minerals content

5.5. Design optimization

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

Fe₂O₃ content minimization

The overview of the surface model response is shown in Figure 34, and to predict the response in different conditions, the Equation 17 is used for Fe₂O₃ content. To predict the response, the factors A and C should be replaced by collector concentration and by pH in coded factors [-1,1] respectively, considering values inside the levels tested on the trials, because the extrapolation is not validate.

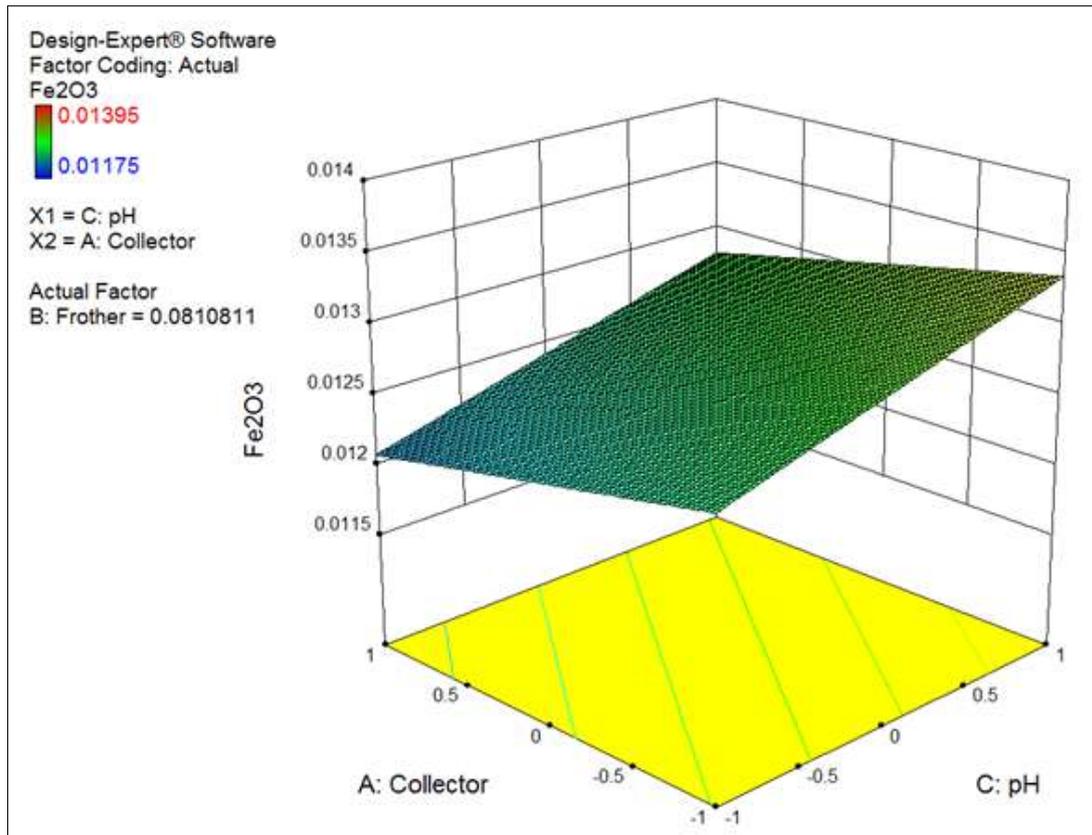


Figure 34 – 3D Surface model to Fe₂O₃ content

From the Equation 17 it is possible to understand that the Fe₂O₃ content will be proportional to pH and inversely proportional to collector concentration. Looking to this model, and as the limits are the levels used on trials, the optimized conditions will be the pH at coded level -1 and collector concentration at coded level 1.

Heavy minerals content minimization

For heavy minerals content the overview of model response is shown in Figure 35, and to predict one response in different conditions the Equation 18 can be used. To predict the response, the factor C on Equation 18 should be replaced by pH in coded factors [-1,1].

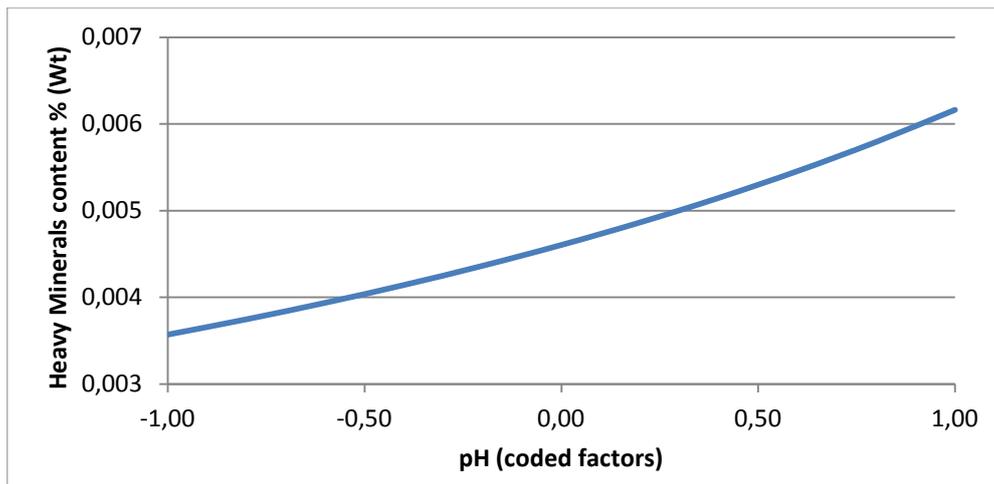


Figure 35 – Model response for heavy minerals content

From the Equation 18 it is possible to understand that the heavy minerals content will be proportional only to pH. Looking to this model, and as the limits are the levels used on trials, the optimized conditions will be pH on minimum value.

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. These criteria allow find the conditions shown in Figure 36.

From Figure 37 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%.



Figure 36 – Optimization solution with priority for Fe_2O_3 content minimization



Figure 37 – Expected optimization results using the model of DES

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.

6. 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.

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Annexes

Annex I – EDXRF spectrometer calibration and calculus of measurement uncertainty

The measurement uncertainty is shown in Table 21. The measurement uncertainty of standards used is described in Figure 38 and Figure 39.

Table 21 – EDXRF calculus of measurement uncertainty

n=	10	
K=	1,833	From t-student table
s=	9E-05	
$u_{\text{method}}^2 = u_{\text{VR}}^2 + u_{\text{VL}}^2 + u_{\text{REPRO}}^2$		
$u_{\text{VR}} =$	0,001	From BAS
$u_{\text{VL}} =$	$8\text{E-}5/\text{sqr}(10) =$	2,53E-05
$u_{\text{REPRO}} =$	$9\text{E-}5/\text{sqr}(10) =$	2,85E-05
$u_{\text{method}} =$	$\text{sqr}(1\text{E-}6+6,4\text{E-}10+8,1\text{E-}10)$	
U =	1,833 x 1E-3	
U =	1,8E-03	



BUREAU OF ANALYSED SAMPLES LTD.

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- R.P. MEERES, *B.A.*, (Oxon)
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BRITISH CHEMICAL STANDARD CERTIFIED REFERENCE MATERIAL

CERTIFICATE OF ANALYSIS
BCS-CRM No. 313/1
HIGH PURITY SILICA

Prepared under rigorous laboratory conditions and, AFTER CERTIFICATION ANALYSIS IN GREAT BRITAIN, issued by the Bureau of Analysed Samples Ltd.

The Material for this CRM was supplied by Pilkington Brothers plc, St. Helens. It was graded to pass a 125 micrometre (120 mesh) sieve and the sieved material was passed over a magnetic separator.

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ANALYSES

Mean values — mass content in %. All results relate to the dried (110°C) sample

Analyst No.	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MnO	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	Li ₂ O	Loss on Ignition
1	99.69	0.040	0.012	0.012	0.00010	0.006	0.0013	0.004	0.005	<i><0.0001</i>	0.0008	0.12
2	99.70	0.039	0.016	0.012	0.00017	0.006	0.0014	0.003	0.004	<i>0.0002</i>	0.0004	0.09
3	99.72	0.042	0.022	0.012	...	0.006	0.003	0.0001	...	0.09
4	...	0.037	0.014	0.010	...	0.005	0.0014	0.002	0.006	0.07
5	99.82	0.031	0.016	0.012	0.00012	0.003	...	0.0002	0.0002	0.04
6	99.86	0.038	0.017	0.011	0.00012	0.006	0.0015	0.004	0.006	<i><0.0001</i>	0.0009	0.07
7	99.84	0.035	0.008	0.11
8	99.76	0.033	0.020	0.012	0.00010	0.007	0.0013	0.002	0.004	0.0002	0.0004	0.12
9	99.83	0.031	0.018	0.012	0.00015	0.007	0.0010	0.004	0.005	<i><0.0001</i>	...	0.05
M _M	99.78	0.036	0.017	0.012	0.00013	0.006	0.0013	0.003	0.005
S _M	0.07	0.004	0.003	0.001	0.00003	0.001	0.0002	0.001	0.002

M_M: Mean of the intralaboratory means. S_M: Standard deviation of the intralaboratory means.

The above figures are those which each analyst has decided upon after careful verification.

Figures in bold type certified, figures in small italic type only approximate

The following additional information was supplied - Analyst No. 6: SO₂ 0.006%, ZrO₂ 0.002%

P.T.O.

Figure 38 – Page 1 of analysis certification of standard used for EDXRF calibration

BCS-CRM No. 313/1 HIGH PURITY SILICA

NOTES ON METHODS USED

SILICA

Analysts Nos. 1 and 7 determined silica by XRF according to the procedure in BS 1902:Part 9.2. Nos 2, 3, 5, 6 and 9 determined silica gravimetrically by direct treatment of the ignited sample with hydrofluoric and sulphuric acids. No. 8 fused the ignited sample with sodium carbonate, extracted with hydrochloric acid and determined the insoluble silica gravimetrically after evaporating to dryness. The residual silica in the filtrate was determined photometrically.

ALUMINA

Analysts Nos. 1, 2, 4, 6, 8 and 9 decomposed the sample by evaporation with hydrofluoric and mineral acid, Nos. 1, 2, 8 and 9 with sulphuric acid, No. 4 with hydrochloric acid and No. 6 with perchloric acid. Nos. 1, 2, 4 and 6 dissolved the residue in hydrochloric acid. No. 1 determined alumina by ICP-AES, Nos. 2, 4 and 6 used AAS. No. 8 fused the residue with sodium carbonate/tetraborate and used a titrimetric method with EDTA. No. 9 fused with potassium hydrogen sulphate and used a photometric method with solochrome cyanine R. Nos. 3, 5 and 7 determined alumina by XRF.

Analysts Nos. 1, 4 and 8 also used XRF and obtained mean values of 0.032%, 0.03% and 0.036% respectively.

TITANIA

All analysts, except Nos. 3 and 5, determined titania on samples decomposed with hydrofluoric and sulphuric or perchloric acids. No. 1 used ICP-AES, Nos. 2, 8 and 9 used photometric methods with hydrogen peroxide. Nos. 4 and 6 used AAS. Nos. 3 and 5 used XRF.

Analysts Nos. 1, 4 and 8 also determined titania by XRF and obtained mean values of 0.017%, 0.02% and 0.020% respectively. Analyst No. 6 also used a photometric method with hydrogen peroxide and obtained a mean value of 0.016%.

IRON OXIDE

Analysts Nos. 1, 2, 4, 6, 8 and 9 decomposed the sample as for the alumina determination. No. 3 used a similar procedure. No. 1 determined iron oxide by ICP-AES. Nos. 2 and 4 used AAS. Nos. 3, 6, 8 and 9 used photometric methods. Nos. 3, 6 and 8 with 1:10-phenanthroline and No. 9 with 2-2' bipyridyl. No. 5 used XRF.

Analysts Nos. 1, 4 and 8 also used XRF and obtained mean values of 0.012%, 0.012% and 0.013% respectively. Analyst No. 6 also used AAS and obtained a mean value of 0.012%.

MANGANESE OXIDE

All analysts, except No. 5, determined manganese oxide on samples from which the silica had been removed by treatment with hydrofluoric and mineral acid. No. 5 fused the sample with a mixture of sodium and potassium carbonates and dissolved the melt in hydrochloric/sulphuric acid. No. 1 determined manganese oxide by ICP-AES. Nos. 2, 6, 8 and 9 by AAS. No. 5 used a photometric method after oxidation with periodate.

CALCIUM OXIDE

Analysts Nos. 1, 2, 4, 6, 8 and 9 decomposed the samples as for alumina. No. 1 determined calcium oxide by ICP-AES. Nos. 2, 4, 6, 8 and 9 by AAS. Nos. 3 and 7 determined calcium oxide by XRF.

MAGNESIA

All analysts determined magnesia on samples decomposed by treatment with hydrofluoric and mineral acid to remove silica. No. 1 used ICP-AES, the remainder used AAS.

SODIUM OXIDE

All analysts decomposed the sample with hydrofluoric and mineral acid and extracted the residue with hydrochloric acid. Nos. 1, 2, 5 and 9 used AES. The remainder used AAS.

POTASSIUM OXIDE

All analysts except No. 3 decomposed the sample as for sodium oxide. Nos. 1, 2 and 9 used AES, Nos. 4, 6 and 8 used AAS. No. 3 used XRF.

Analysts Nos. 1, 4 and 8 also used XRF and obtained mean values of 0.006%, 0.01% and 0.007% respectively.

CHROMIUM OXIDE

All analysts decomposed the sample with hydrofluoric acid. Nos. 1, 2 and 3 extracted the residue with hydrochloric acid. Nos. 3, 5 and 8 fused the residue with sodium carbonate. No. 1 used ICP-AES. Nos. 2 and 6 used AAS. Nos. 3, 5, 8 and 9 used photometric methods with 1:5-diphenylcarbazide.

LITHIUM OXIDE

All analysts used the same techniques as for the determination of sodium oxide.

LOSS ON IGNITION

All analysts ignited the sample at 1025° ± 25°C.

References:

1. Specification for and recommended procedure for the testing and analysis of glass making sands. Glass Technology, Vol 19, 1978 p.93-101.

Abbreviations:

AAS : Atomic absorption spectrometry ICP-AES : Inductively Coupled Plasma-Atomic Emission Spectrometry
AES : Atomic emission spectrometry XRF : X-ray fluorescence spectrometry, fused bead technique

NEWHAM HALL,
MIDDLESBROUGH
ENGLAND.

For BUREAU OF ANALYSED SAMPLES LTD,
P.D. RIDSDALE,

Managing Director

Preliminary Edition May, 1987
Main Edition April, 1989

Figure 39 – Page 2 of analysis certification of standard used for EDXRF calibration

Table 22 – Calculation program for EDXRF calibration

Channel	Fe
K factor	0,00140
RMS	0,00047%
Correlation	0,99842
Nr Std - coeff	5 - 2
Concentration range	0,0102 - 0,0288 (%)
Relative RMS (%)	2,42

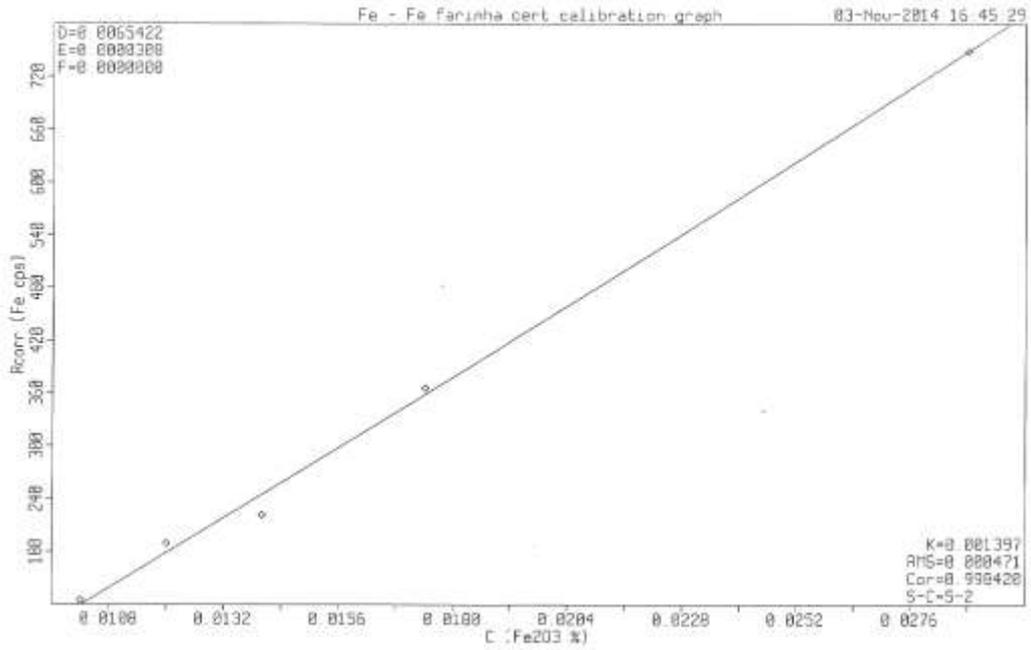


Figure 40 – Calibration graph of EDXRF

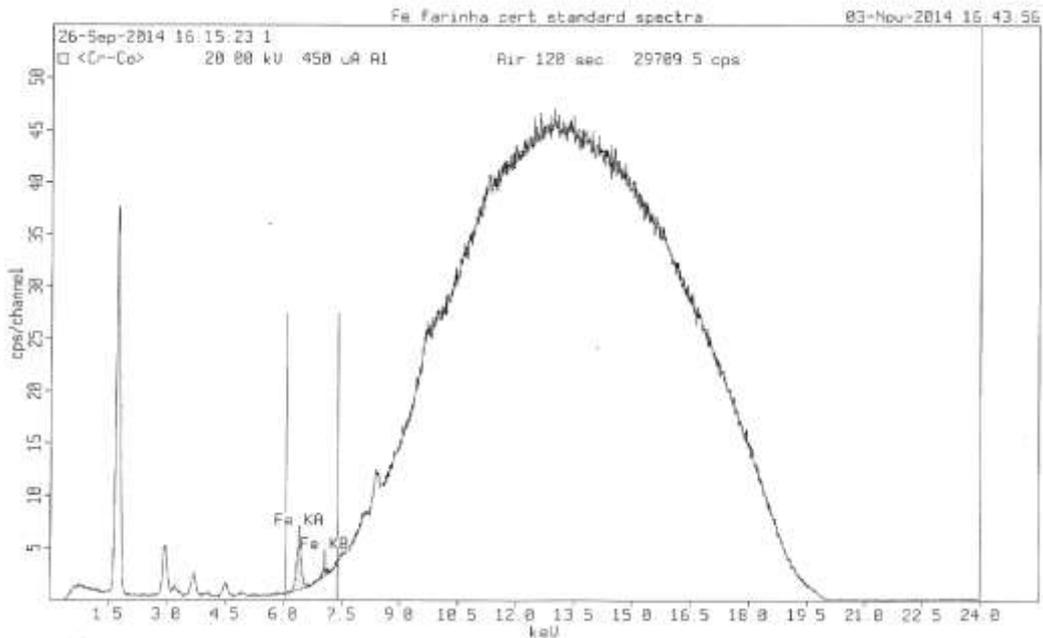


Figure 41 – Standard spectra for EDXRF

Annex II – Statistical data

Variance

For the variance was used the following equations:

$$s^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2$$

Where s^2 is the variance, n is the number of observations, x_i the experimental value of i^{th} observations and \bar{x} is the average of i^{th} observations

The Design expert software was used, but this section explain the statistical models used in the treatment data, in the evaluation of fitted model and in the determination of optimal conditions.

Pearson's correlation coefficient

The Pearson's correlation coefficient, ρ is calculated by the following equation:

$$\rho = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^n (x_i - \bar{x})^2} \cdot \sqrt{\sum_{i=1}^n (y_i - \bar{y})^2}}$$

Where x_1, x_2, \dots, x_n and y_1, y_2, \dots, y_n are measured values of 2 variables.

Data treatment (Bezerra & al, 2008)

The estimation of γ and β parameters of Equation 6 requires a matrix notation described in the following equation:

$$y_{m \times 1} = X_{m \times n} b_{n \times 1} + e_{m \times 1}$$

Where y is the response vector, m represent the numbers of lines of matrix, X is the matrix used in experimental design runs, n represent the numbers of columns of matrix, b is the vector constituted by parameters of the model and e is the residual

ANOVA statistical test (Mohanty & Das, 2010)

For the ANOVA calculations is used the following methodology:

The sum of Squares for the model is calculated using the following equation:

$$\text{Model sum of squares} = \sum_{i=1}^n y_i^2 - \frac{(\sum_{i=1}^n y_i)^2}{n}$$

Where y_i is the model prediction of i^{th} observations and n is the number of observations

The residual sum of Squares is calculated using the following equation:

$$\text{Residual sum of squares} = \sum_{i=1}^n (x_i - y_i)^2$$

Where x_i is the experimental value for the i^{th} observations.

For the model, the F-value is calculated using the following equation:

$$F\text{-test} = \frac{\text{Estimate of model variance}}{\text{Estimate of residual variance}}$$

For the lack-of-fit, the F-value is calculated using the following equation:

$$F\text{-test} = \frac{\text{Estimate of residual-corrected-for-pure-error variance}}{\text{Estimate of pure error variance}}$$

Box-Cox λ (Osborne, 2010)

The general procedure is to:

- divide the variable into at least 10 regions or parts,
- calculate the mean and standard deviation (s.d.) for each region or part,
- Plot log (s.d.) vs. log(mean) for the set of regions,

Estimate the slope of the plot, and use the slope (1-b) as the initial estimate of λ

Annex III – Confidential data