Use of Tailings Industry Ceramic Tiles in the Manufacture of Triaxial Refractory

***Marcelo Dal Bó*[a*], *Dachamir Hotza*[a,b]**

[a]*Programa de Pós-Graduação em Ciência e Engenharia de Materiais – PGMAT*
[b]*Departamento de Engenharia Química – EQA*
Universidade Federal de Santa Catarina – UFSC, 88040-900 Florianópolis/SC/Brazil
**e-mail: marcelodalbo@hotmail.com*

Abstract: In this work we developed a formulation of refractory triaxial using the methodology of Mixture Design and Response Surface Analysis. This approach aims to decrease the testing laboratory and obtain a great work area, where all the characteristics necessary for the final product are obtained. Moreover, one can improve the cost / benefit in the formulation stage, and contribute significantly to a greater understanding of the interaction processing-microstructure-properties of a refractory product. Were used as tailings from the manufacture of refractory plates: coal ash, sand furnace, nail scrapings, and roll milled refractory high alumina. Based on these results, it was determined the region of triaxial diagram in which the characteristics of the product meet the specifications required for the use of refractory, such as linear shrinkage and modulus of rupture strength after firing. The optimized composition resulted in a cost 97% less than the refractory currently used.

Key-Words: Tailingss, Refratory, Mixture Design

1. Introduction and Objectives

The increasing competitiveness in ceramic and refractory industries Brazilians have driven not only improving the existing refractory linings, as well as the development of materials that are suitable for various applications.

The most the materials have a cost high due your firing conditions, which use high temperatures. The objective of this work is doing an analysis of possibility of manufacture of the plates refractory from tailings of traditional ceramic industry, decreasing the costs with refractory materials in the industry.

Several studies in the field of ceramics have reported experiences of re-use of tailings, emphasizing economic and environmental gains[1-2]. According to a preliminary study carried out in the company, were selected tailings that had the features conducive to the application in a refractory material:

- Coal ash
- Sand furnace;
- Tailings glaze;
- Refractory milled, and

- Roll-alumina.

The tailings were classified according their physical and chemical characteristics (refractoriness, flux and plasticity) and represented at the vertices of triaxial diagram.

The design and analysis of experiments were performed using the methodology of mixture design, an approach that has received great attention in the area of ceramics in recent years[3-4]. This method allows the quantitative assessment of the influence of parameters in specific properties, trough analysis of variance and the graphical representation of this effect in contour in the form of triaxial diagram.

The objective this study, therefore, was select ideal area for the manufacture of refractory plates in the company, based on the characteristics of the pieces refractory sinterized, using the technique of mixture design.

2. Materials and Experimental Methods

2.1. Methodology

The methodology for the development of this study was divided into 5 steps:

a- Physical and chemical characterization of raw materials;
b- Design of experiments to prepare the formulations refractory;
c- Preparation of the formulations in the laboratory;
d- Burning of the formulations in industrial heating curve;
e- Analysis of the properties of the refractory plates.

2.2. Materials

For the development of this research project were used materials generated or used by the company Cecrisa Revestimentos Cerâmicos S/A. Among the components listed below, only the clay PR-X and dolomitic limestone are not tailings generated by the factory. The incorporation of these components is necessary because the process of forming the refractory plates was made by pressing, which justifies the use of clay PR-X. The tailing of glazes was used to promote a sintering at lower temperature, increasing its resistance after being burned.

Below is a listing of raw materials used, assembled according to their function in a triaxial composition:

Refractories:

- Light ash coal: tailings from burning coal in the furnace that is removed by cyclones wet. Generation of 210 t/month;

- Sand furnace: tailings from burning coal into the furnace that is not fluidized, flowing beneath the furnace. Generation of 15 t/month;

- Ceramic roller: breaking the rolls of alumina ovens glaze. Generation of 0.66 t/month;

- Refractory milled: breaking of refractory parts used in cars burning cookie that are purchased from outside suppliers. Generation of 4.5 t/month, and;

- Limestone dolomitic raw material formulation of the mass of bi-burning, the basis of carbonates.

Flux:

- Glazes Tailings (Zest): loss of glazes in the factory. Generation of 12 t/month.

Plastic:

- Clay PR-X: raw material formulation of the mass of bi-burning.

2.3. Experimental Design

The mixture design used in the development of this project was based on an arrangement simplex centroid increased three axial points and three points chosen in the region is the best in preliminary tests.

The triaxial diagram, Figure 2 shows the pseudo-component used in this study and the 13 compositions according to the mass fractions of refractory materials (50 to 100%), plastic clay (0 to 50%) and tailings glazes (0 to 50 %). Each composition is represented by a point in the diagram.

As can be seen, the apex of the diagram corresponds to the refractory materials: coal ash, refractory milled, sand furnace, ceramic roller and limestone dolomitic. The percentage of each component was chosen in proportion to the amount generated from each of them. The limestone dolomitic was incorporated in addition (10%), to achieve a less linear shrinkage. Thus, the refractory composition was:

- Sand furnace: 5,86%;
- Coal ash: 82,12%;
- Refractory milled: 1,76%;
- Ceramic roller: 0,26%;
- Limestone dolomitic: 10,00%

The design of experiments for the samples was obtained as shown in Table 1.

Table 1: Composition of the formulations obtained by the design of experiments with the Statistica 7.0 software, incorporating the centroids points.

Formulation	Flux (%)	Plastic (%)	Refractory (%)
1	0,00	0,00	100,00
2	50,00	0,00	50,00
3	0,00	50,00	50,00

4	0,00	25,00	75,00
5	25,00	0,00	75,00
6	25,00	25,00	50,00
7	16,67	16,67	66,67
8	8,33	8,33	83,34
9	8,33	33,33	58,34
10	33,33	8,33	58,34
11	4,16	29,17	66,67
12	16,66	29,17	54,17
13	4,16	41,67	54,17

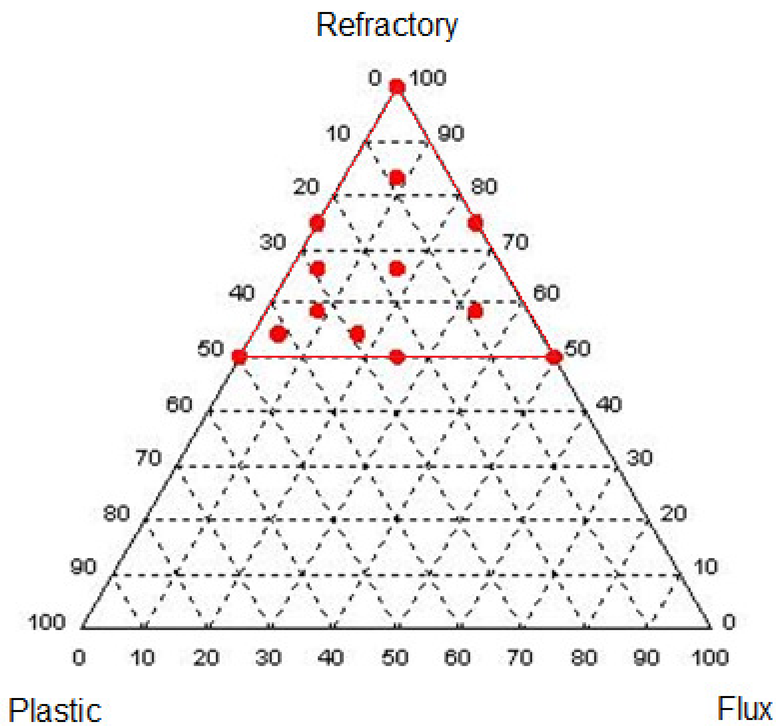

Figure 2: Simplex design showing the pseudo-component of compositions analyzed in the triaxial diagram.

2.4. Curve burning plates refractory

The refractory plates, after being shaped by the pressing process, were burned in the tunnel kiln, stacked on top of the car burning in order to provide the best possible sintering. Figure 3 shows the curve of burning used.

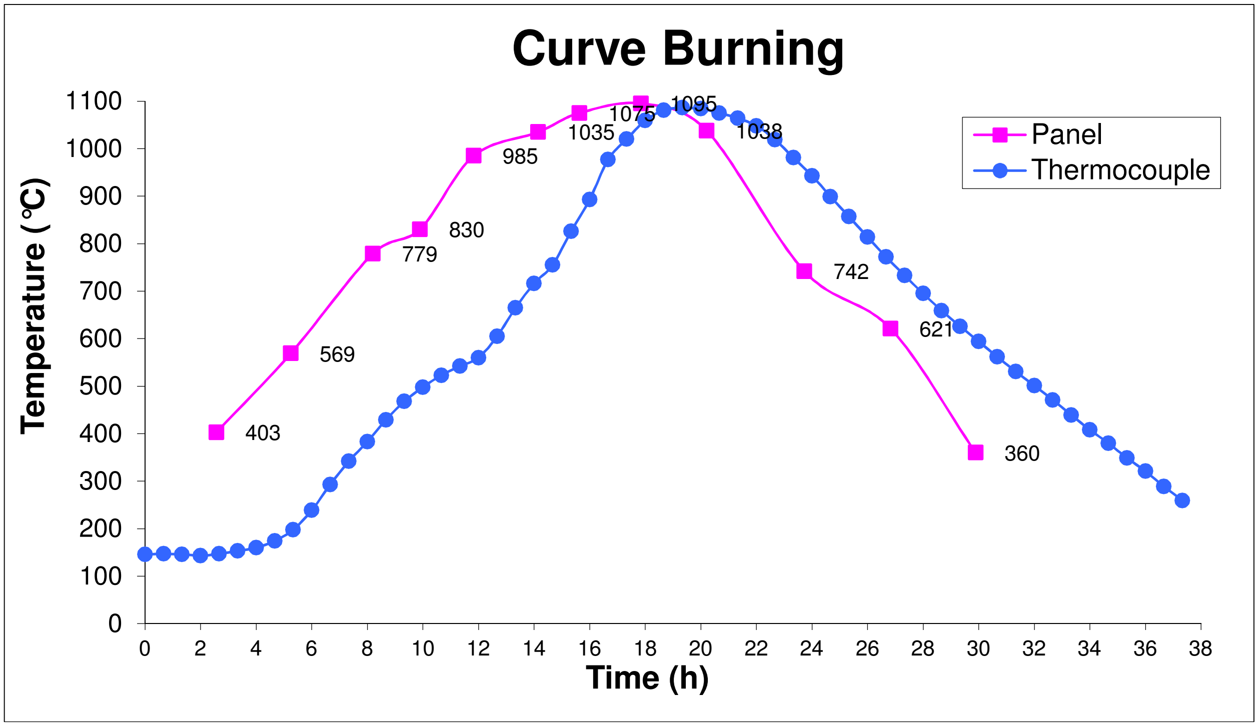

Figure 3: Show the curve burning of refractory plates.

2.5. Properties of Refractories Plates

The properties of refractory materials depend very much on environments where they will be used. The life of the product will depend, among other things, of the chemical stability of phases formed. Mechanical strength and linear shrinkage are related to sintering the material suffered when manufactured. With it the characteristics that were selected as important to be studied were:

- Linear shrinkage (%);
- Flexural green strength (Kgf/cm²);
- Flexural strength after firing (Kgf/cm²);
- Absorption of water (%);
- Bulk density (g/L).

3. Results and Discussion

3.1. Chemical characterization of raw materials.

The Table 2 show the chemical characterization of raw materials used in this study, note that between refractory materials, the ceramic roller presents high percent of Al_2O_3; the sand furnace, coal ash and refractory milled have with principal component the

SiO_2. The refractory milled has a high percentage of magnesium oxide (MgO), responsible for the high resistant shock thermal. The tailings glazes stands out for its high levels of alkalis, compounds typically flux. The plastic component, clay PR-X, had a high loss on ignition, represented mainly by fraction of organic matter.

Table 2: Show the chemical characterization of raw materials used in this study.

MATERIAL	SiO_2	Al_2O_3	Na_2O	K_2O	MgO	CaO	BaO	TiO_2	ZrO_2	Fe_2O_3	ZnO	P_2O_5	SO_3	Loss on ignition
Ceramic roller	34,98	59,37	0,50	1,28	2,59	0,20	0,00	0,33	0,00	0,69	0,00	0,04	0,00	0,00
Sand furnace	65,48	20,73	0,21	2,07	0,46	3,08	0,00	1,03	0,00	3,78	0,00	0,06	1,09	2,00
Coal ash	55,34	27,14	0,35	3,01	1,29	2,33	0,00	1,43	0,46	3,97	0,00	0,08	0,39	4,20
Refractory milled	50,92	30,35	0,93	1,52	5,21	2,44	0,00	1,08	3,19	2,06	0,00	0,06	0,52	1,70
Tailings Glazes	54,51	7,93	1,99	3,54	2,41	9,06	1,12	0,09	11,90	0,45	5,29	0,00	0,00	1,70
PR-X clay	44,23	37,45	0,00	0,24	0,25	0,19	0,00	2,03	0,00	1,05	0,00	0,03	0,00	14,50
Limestone dolomitic	13,30	2,75	0,16	0,44	17,9	30,53	---	0,11	---	0,99	---	0,03	---	33,8

3.2. Characterization of the refractory plate

3.2.1. Linear shrinkage (%)

According to the statistical tests, for the variable linear shrinkage, chose the cubic full model to simulate the behavior of this variable. Note in Figure 4 greater linear shrinkage when it has a high percentage of flux in the formula, and low linear shrinkage when it has a high percentage of refractory and clay.

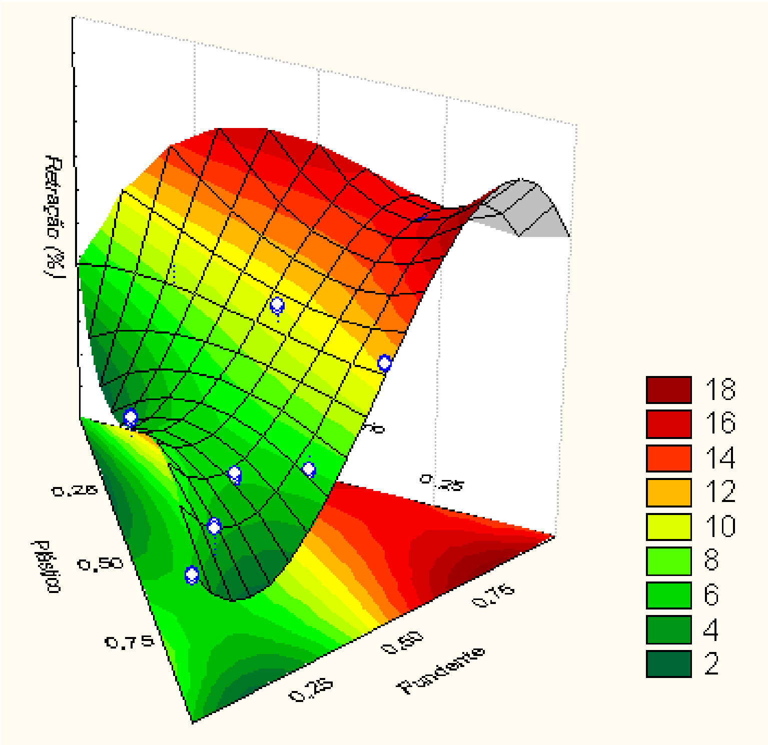

Figure 4: Show the behavior of the linear shrinkage with percent different of refractory, plastic and flux parts.

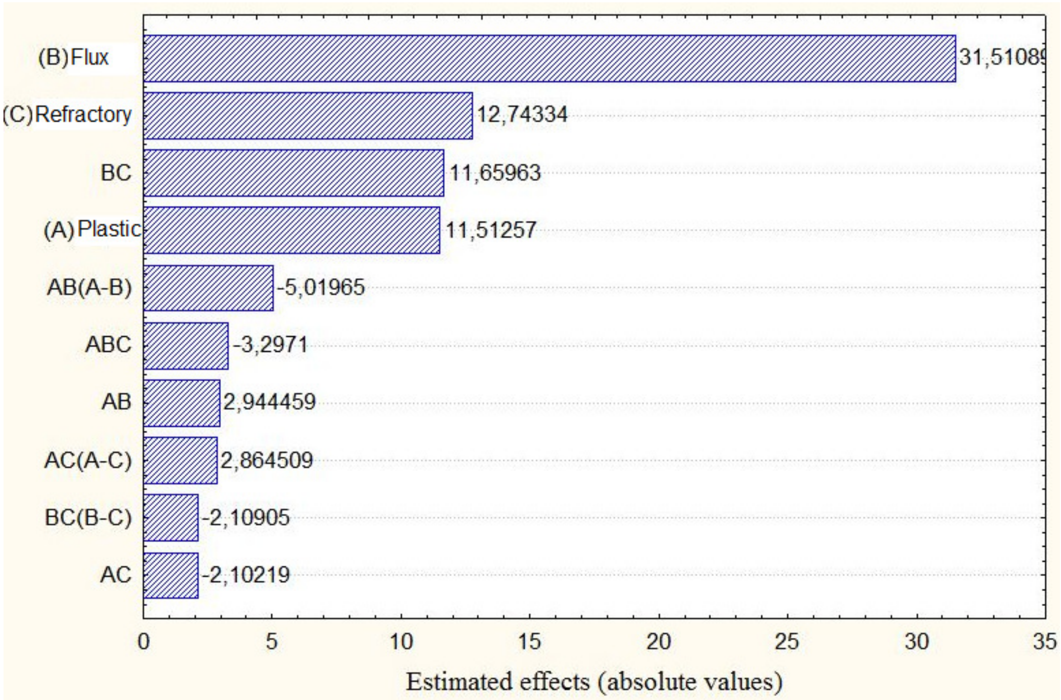

Figure 5: Pareto diagram of the cubic full model corresponding to linear shrinkage.

Analyzing the Figure 5; the flux, refractory, Plastic and interaction BC (Flux-Refractory) are variable significant. Therefore, when the percentages of these variables are modified, there is significant variation of linear shrinkage.

3.2.2. Flexural strength at green (Kgf/cm²)

The analyzing of flexural strength at green variable showed that with high percent of plastic materials, obtain a high resistance flexural at green; the result was already expected, since that clay PR-X present of the plasticity characteristic.

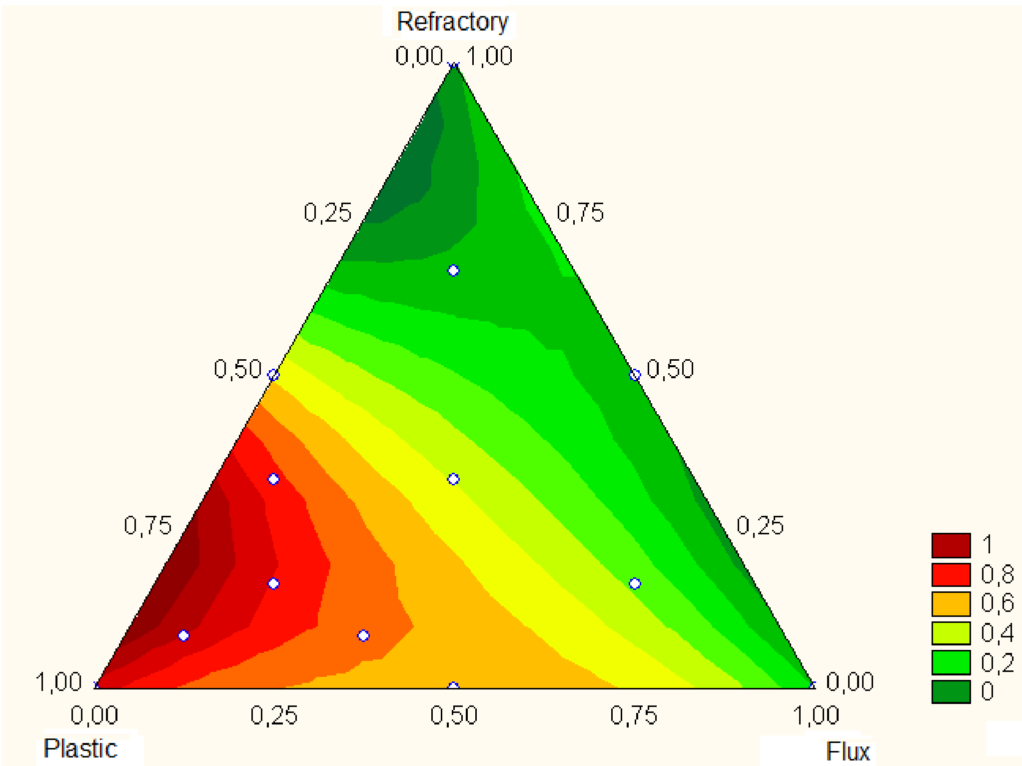

Figure 6: Response surface of the cubic full model corresponding to flexural strength at green.

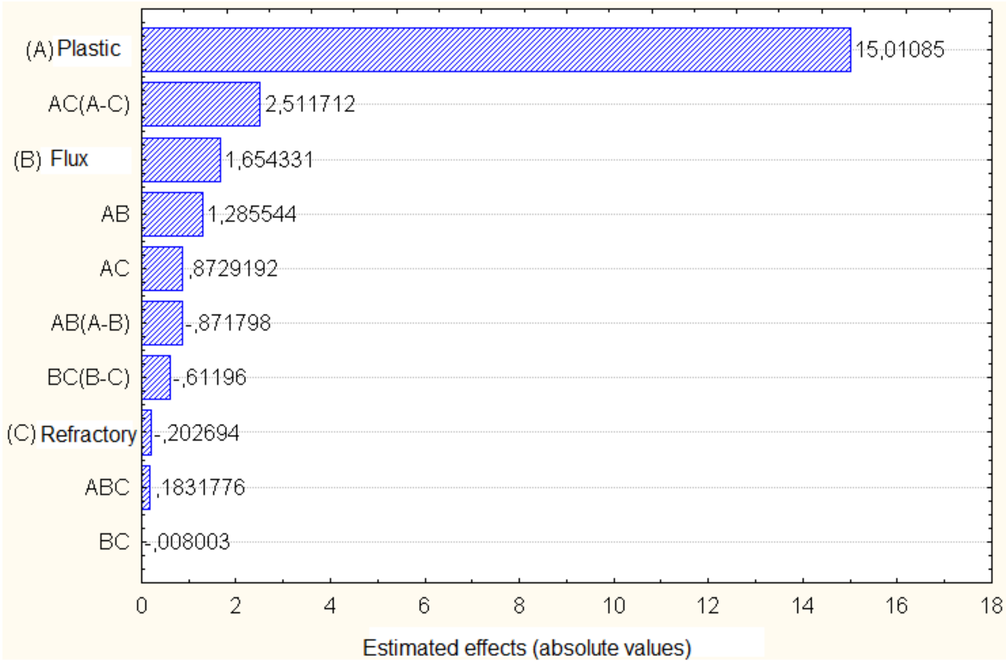

Figure 7: Pareto Diagram corresponding to flexural strength at green.

Analyzing the Figure 7, observed that only the plastic material acts significantly on the variable flexural strength at green, therefore, when we vary the percentage of plastic material, we are also varying the flexural strength at green.

3.2.3. Flexural strength after firing (Kgf/cm²)

The surface response (Figure 8) for flexural strength after firing showed that the best resistance is when we have high percent of flux, because this material has high percentage of alkalis (Table 2).

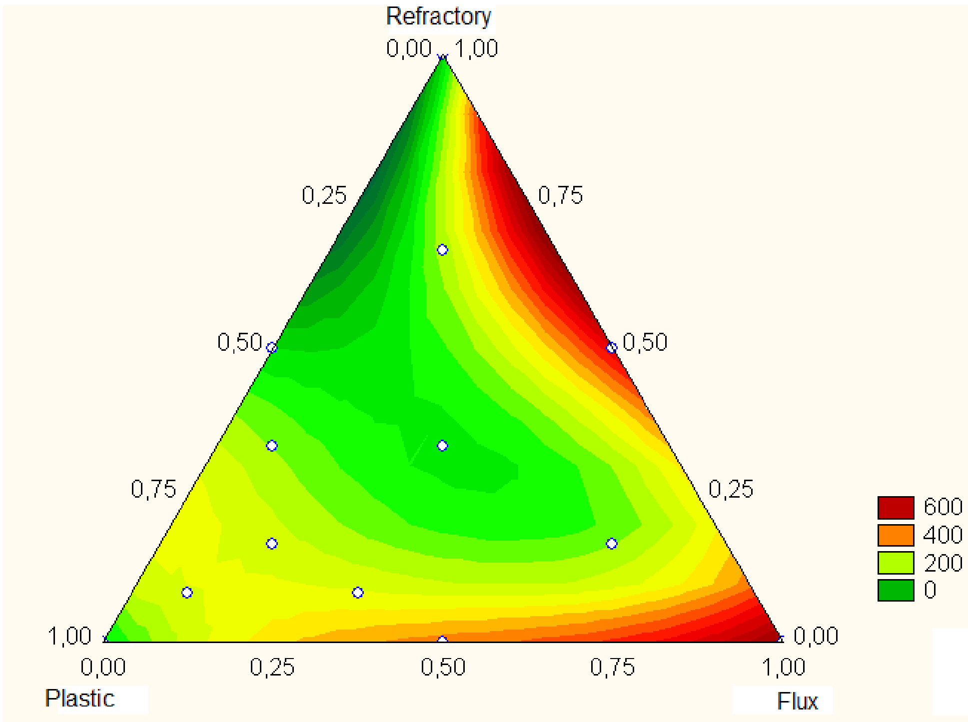

Figure 8: Response surface of the cubic full model corresponding to flexural strength after firing.

The Pareto Diagram for this variable, show the significant influence of the Flux variable and the ABC interaction, Figure 9.

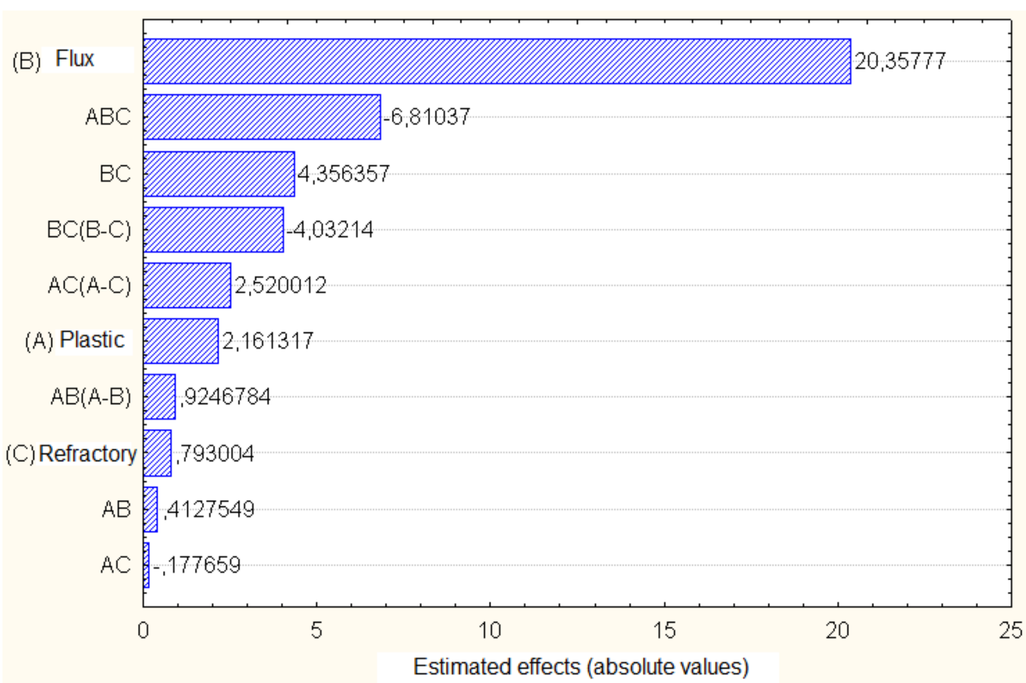

Figure 9: Pareto Diagram corresponding to flexural strength after firing.

3.2.4. Bulk density (g/L)

The Figure 10 depicts the curves of levels for the variable bulk density, according to the cubic full model. You may notice a greater density of the compositions by increasing the percentage of flux in the formula and a low density when the values of refractory and plastic fractions are larger.

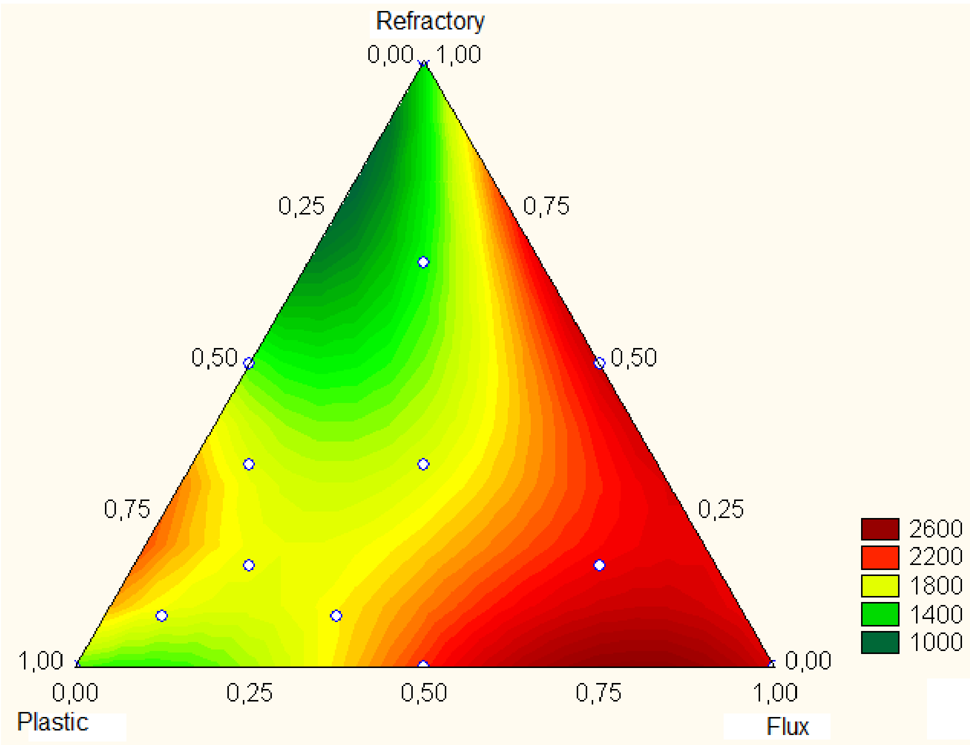

Figure 10: Response surface of the cubic full model corresponding to bulk density.

The Figure 11, show another validation for the cubic full model. The graphic represent the predict values versus residues. Wasn't observed any kind of trend or variance alternating with the level of density, thereby validating the statistical model

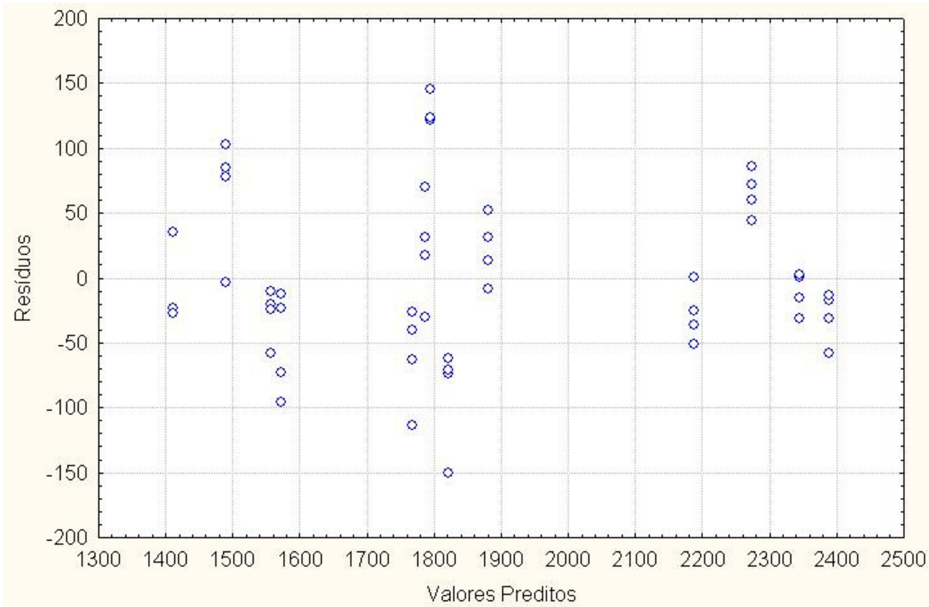

Figure 11: Show the validation of cubic full model for bulk density variable.

3.2.5. X-Ray Characterization

According to the results, the formulation number 13 showed great features as the variables studied. With it, this was characterized by diffraction of X-rays to check the phases formed in this sample. The analyzing showed that was presents crystal structure such as: quartz, mulite, anorthite and cordierite.

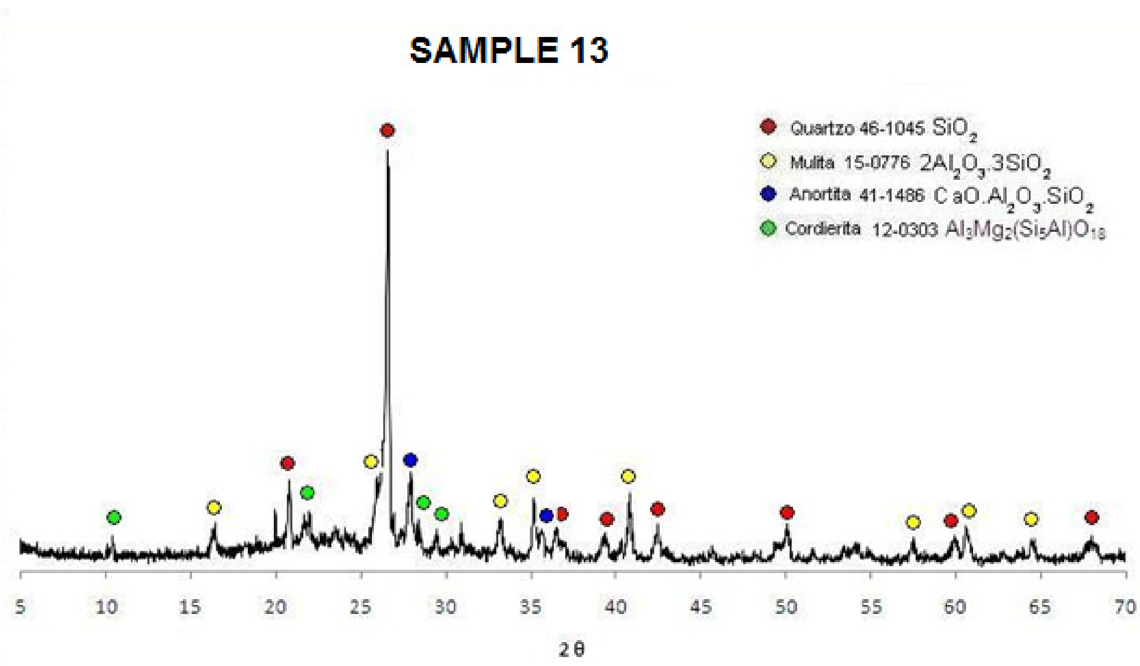

Figure 14: Show the X-Ray for the sample number 13.

3.2.6. Comparison products

According to these variables it is possible to make a comparison between the best formulation and the refractory plate currently used by the company. This comparison is show at Table 3.

Table 3: Comparing the technical properties.

Properties	**Current Refractory**		**New refractory Formula 13**	
	Mean	***STD Deviation***	**Mean**	***STD Deviation***
Linear shrinkage (%)	6,15	*0,30*	4,93	*0,15*
Flexural strength after firing (kgf/cm²)	175,55	*24,45*	203,58	*17,91*
Flexural strength at green. (kgf/cm²)	7,26	*2,20*	11,33	*0,67*
Water absorption (%)	11,82	*2,83*	11,40	*1,46*
Bulk density (g/L)	2021	*24,28*	1930	*13,30*

4. Conclusions

With the objective of using tailings from traditional ceramic industry for the processing of refractory triaxial obtained by mixture design, we can conclude:

- The application of techniques of mixture design in triaxial ceramic compositions, was an important tool that greatly facilitates the interpretation of the results of the laboratory tests;
- The studied tailings (sand furnace, ceramic roller, coal ash and refractory ground) have high refractive features, and these materials are suitable for the manufacture of refractory plates;
- In all formulations with a high percentage of flux (tailings ceramic glaze), there is a large linear shrinkage, low water absorption, high mechanical strength after sintering and high bulk density. This is due to the formation of liquid phase during sintering (sintering with liquid reactive) from high rates of alkalis contained in this tailing;
- According to the analysis of diffraction of X-ray, the formulations 9, 11, 12 and 13 were crystalline phases as quartz, mullite, anorthite and cordierite. Since these crystalline phases routinely found in refractory products;

- All the crystalline phases formed have high melting point, thereby locking the refractoriness required for the manufacturing process;
- For the variables studied, the sample number 13 showed excellent characteristics compared with the pattern plate. In this case, we obtained a large reduction of cost, and utilizing waste disposed of to date, thus contributing to the preservation of the environment.

5. Bibliography

1 **Alexandre, J., Toledo, R., Saboya, F., Pereira, M.** Utilização de planejamento simplex na previsão de propriedades de peças cerâmicas vermelhas. **Cerâmica, v. 47, n.303, p.170-174, 2001.**

2 **Bergman, R. et al.**, "Experimental design and optimization, Cheometrics and Intelligent Laboratory Systems", v. 42, p. 3-40, 1998.

3 **Bhatti, M.A.,** "Practical optimization methods with Mathematica applications". **New York: Springer Telos, 2000.**

4 **Cornell, J. A.; Ramsey, P. J.** "A Generalized Mixture Model for Categorized-Components Problems with an Application to a Photoresist-Coating Experiment", ***Technometrics*, 40 [1] p. 48-61, 1998.**

5 **Cornell, J.A.**, "Experiments with mixtures-designs, models, and the analisys of mixtures data", **2nd edition, New York: Wiley, 1990.**

6 **Correia, S.L. et al.** "Using Statistical Techniques to Model the Flexural Strength of Dried Triaxial Ceramic Bodies". **Journal of the European Ceramic Society, v. 24, n. 9, p. 2813-2818, 2004.**