CARBON ANALYSIS AT FERROATLÁNTICA I+D

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ABSTRACT

Some years ago, Ferroatlantica developed a new type of electrode known as the ELSA electrode. In this electrode there is a central graphite core that provides support, surrounded by an annulus of Søderberg paste that gets baked during operation. This technology has been implemented on several silicon furnaces around the world, and was reported on during the previous Infacon conference.

In all electrodes, but particularly in the ELSA electrode, the quality and consistency of the paste are important for correct operation. As the type of paste varies between customers and between countries, Ferroatlantica has developed a quality control procedure for their customers of this technology. This procedure is geared to the point of view of the customer rather than the paste producer. The analysis is based on the desired flow pattern of the raw paste and on the desired mechanical and electrical properties of the baked paste, as experience has shown that these are the most important parameters to monitor in order to avoid having problems with the resulting electrodes. This paper discusses these methods of paste analysis in the light of complementary studies that have been done when there has been an electrode breakage in the different plants.

1. INTRODUCTION

To ensure a good furnace operation in a ferroalloy or silicon plant, the electrode paste consistency in the different quality parameters is one of the more important factors. The same furnace can operate well with different kinds of paste adapting others parameters like slippages, current, furnace load and so on. Physical parameters, like electrode diameter, casing and fins design and type of furnace (open or close), must be also taken into account in the correct selection of the paste. When all this parameters are adjusted, the more important factor is the paste consistency to ensure a good furnace operation. Periodic analyses of the Soderberg paste are important to assure this consistency. The main objective of this analysis is to control that the properties of the paste, which is being fed into the electrode, are constant. Apart from analysing the paste as a whole, some parameters of the raw materials of the paste are occasionally checked to detect possible fluctuations on their characteristics.

Furthermore, when there is an electrode breakage in the furnace, a complete set of analysis is done to obtain valuable information which, together with the data obtained from the furnace control system, is used to understand better the furnace operation.

2. ANALYSIS OF THE ELECTRODE PASTE

The main goal of the analysis is to guarantee that the properties of the paste are constant and to detect fluctuations in these properties. The analysis is composed of two main parts. The first part, which uses raw paste, is chiefly focused on the plastic behaviour of the paste during the liquid stage. The second part, which analyzes baked paste at 900ºC, studies the mechanical and electrical properties of the paste when it is baked at the same temperature of the contact shoe area.

A standard paste analysis carried out at Ferroatlántica´s Sabon plant, including the main parameters controlled is shown in table 1.

Table 1: Paste standard analysis

Identification	*Paste 1*	*Paste 2*	*Paste 3*
Raw paste			
Apparent density (g/cm^3)	1,58	1,55	1,62
% Ash	2,1	3,9	1,9
%Volatile matter (900ºC, 1h)	12,3	12,7	13,5
% Plasticity	53	45	31
% Deviation plasticity	15	14	5
Briquette compaction by heating (%)			
Apparent density in g/cm^3 at 100ºC	1,19 (75%)	1,07 (67%)	1,48 (90%)
" " " 150ºC	1,36 (86%)	1,44 (90%)	1,53 (94%)
" " " 200ºC	1,36 (86%)	1,45 (90%)	1,61 (98%)
" " " 250º	1,42 (90%)	1,47 (91%)	1,62 (99%)
" " " 300ºC	1,45 (92%)	1,50 (93%)	1,63 (99%)
Penetration on cone test (%)	52	60	23
Baked paste at 900ºC			
Apparent density (gr/cm^3)	1,35	1,32	1,34
Flexural strength (MPa)	3,7	4,1	5,2
Compression strength (MPa)	9,4	9,9	12,5
Young Modulus (GPa)	3,2	1,8	5
Segregation index (%)	4,7	9,4	4
Shrinkage (500-950ºC) (%)	0,5	0,1	0,5
Resistivity (microohms m)	104	84	89

2.1 Analysis in raw electrode paste

The main parameters taken into account are:

2.1.1 Apparent density, ash and volatile content

All this parameters are determined with standard carbon laboratory techniques and give first important information, for example:

Apparent density is an indication of paste composition. Pastes with low densities normally are anthracitic (paste 2) and pastes with coke in the mix have higher values of density (pastes 1 and 3). Polarized light microscopy can confirm the presence of each raw material on the composition of the paste.

Ash content gives information about the type of anthracite used because anthracite is the most contributing material to the total ash content. For example, an important variation in the ash content, normally suggests a change in the type of the anthracite used.

Volatile content is a useful parameter to control deviations in the pitch content of the mix or a change in the type of pitch. In a smaller proportion changes in the baking process of the anthracite or in the anthracite quality can affect the volatile content.

2.1.2. Plasticity behaviour of the raw paste

The desirable behaviour of the raw paste implies to obtain good compaction and little segregation during the liquid stage of the paste, from 100 to 500ºC. The tests of plasticity, and briquette (or cylinders) compaction are the two analyses used to know the plastic behaviour of the paste. The test of plasticity consists of a slow heating of a conformed cylinder of paste. At the end of the heating, the final diameter of the sample is measured to determine the percentage of deformation. The test is similar to the one used by the paste producers, but they do the test in hot paste as it leaves the mixer, while the users must do the trial starting with cold paste. This can introduce some differences in the values obtained, but if the trial is done always in the same way you can obtain valuable information. Plasticity is a good index to control the consistence in the fabrication of the paste during a period of the time. Problems during mixing can be detected by a deviation in the plasticity values in different samples. For example, few years ago, a paste producer changed its mixers and decided to add some oil to the paste. Figure 1 shows the deviation observed in the plasticity of the paste after those changes. The two samples shown are from the same mixing cycle. Obviously, that paste was out of range in plasticity and caused problems in the electrodes.

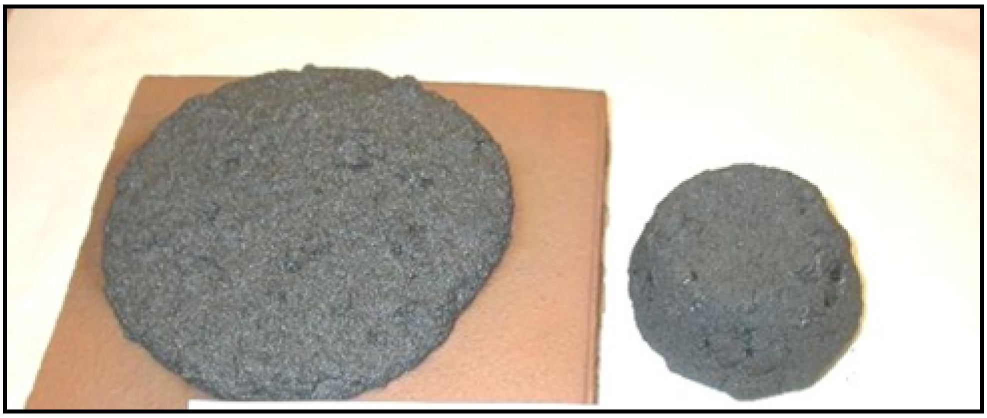

Figure 1: Deviations on plasticity

There is a range of pitch content in which the plasticity is under control. Out of that range, problems normally appear. If the plasticity is very high the material flows like if there were no dried aggregates in the formulation and segregation is prone to occur in baked samples as can be seen in figure 2.

Segregation can cause a lot of problems, especially when the paste is charged in the shape of cylinders. One cylinder of paste with its properties out of range can generate a damaged zone enough to cause an electrode breakage. When the segregated area reaches the contact clamp, the holes in the electrode make the casing withstand a great current flow what causes it’s melting and, consequently, a paste leakage and an electrode breakage, as shown in figure 3.

On the other hand, low plasticity can produce bad paste compaction because the paste does not flow enough to fill the casing and then, holes appear in the structure of the baked electrode. These holes can produce electric arcing and overheating on contact shoes area. To study the compaction behaviour of the paste a briquette (or cylinder) compaction trial is carried out.

2.1.3. Briquette compaction by heating

In this trial, a sample of paste (briquette or cylinder) is heated under fixed low pressure, as it is shown in figure 4. This pressure represents the weight of the briquette charge over the liquid paste in the real electrode.

When temperature is increased, the paste begins to flow and fills the mould. The apparent density of the sample is increased during the experiment and can eventually reach the maximum achievable density of the paste. The percentage of compaction reached at each temperature is calculated in relation to the maximum apparent density of the raw paste

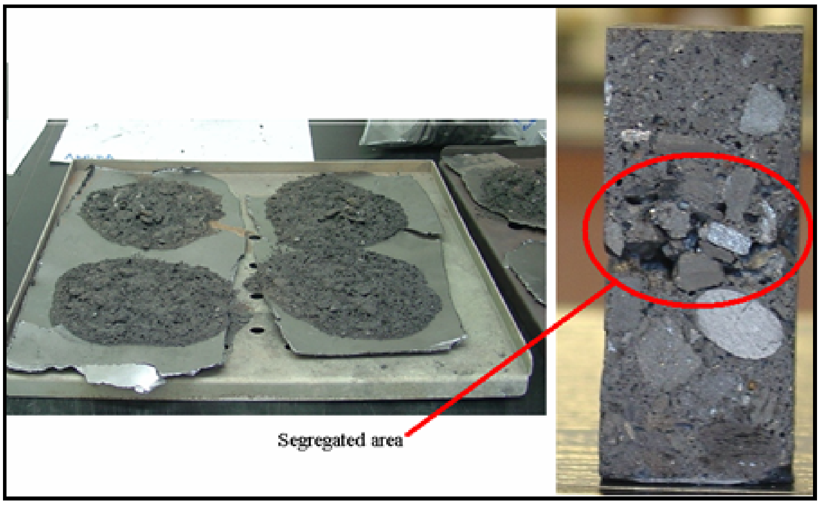

Figure 2: High plasticity and segregation

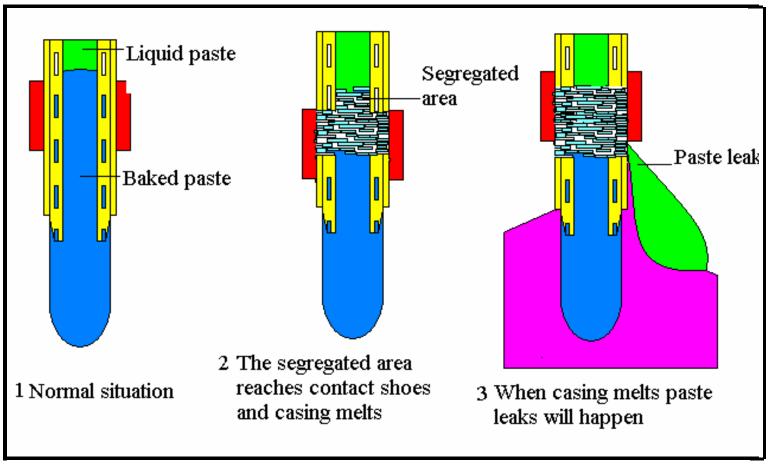

Figure 3: Scheme of segregation

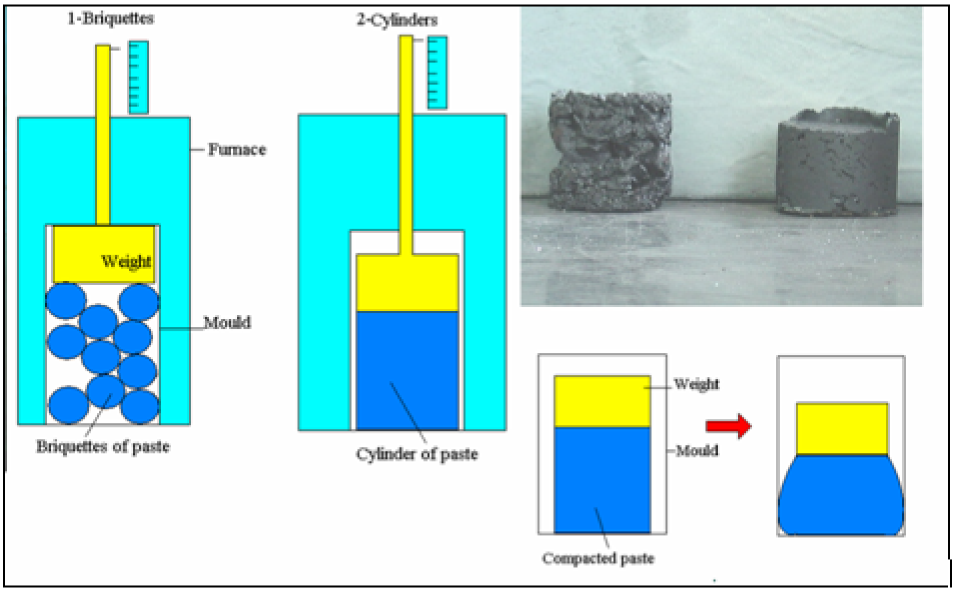

Figure 4: Compaction trial of the paste

By this method we can have information about what kind of paste compacts better in the column and we measure that in percentage at each temperature, as shown in table 1.

2.1.4. Viscosity

When the density reached in the compaction trial is equal or higher than 90% maximum achievable density, the binder content of the mixture provides enough fluency to fill the casing of the electrode. After being guarantee the compaction of the paste, the viscosity study is important in order to estimate the segregation properties of the paste because the more viscous a paste is, the less it is the tendency to segregate. Normally viscosity depends on pitch content too. Pitch in the paste must provide plasticity enough to compaction, but the amount of pitch must be the minimum possible in order to avoid segregation.

The viscosity test consists of heating a conformed sample under a cone, like the represented in figure 5. In the graphs of figure 6, the penetration of the cone into the paste at each temperature is expressed as a percent-

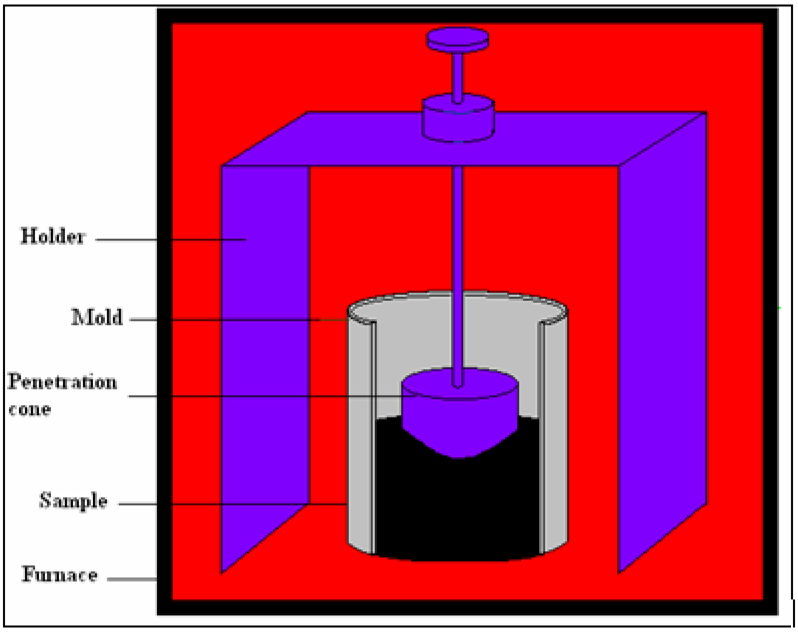

Figure 5: Penetration cone

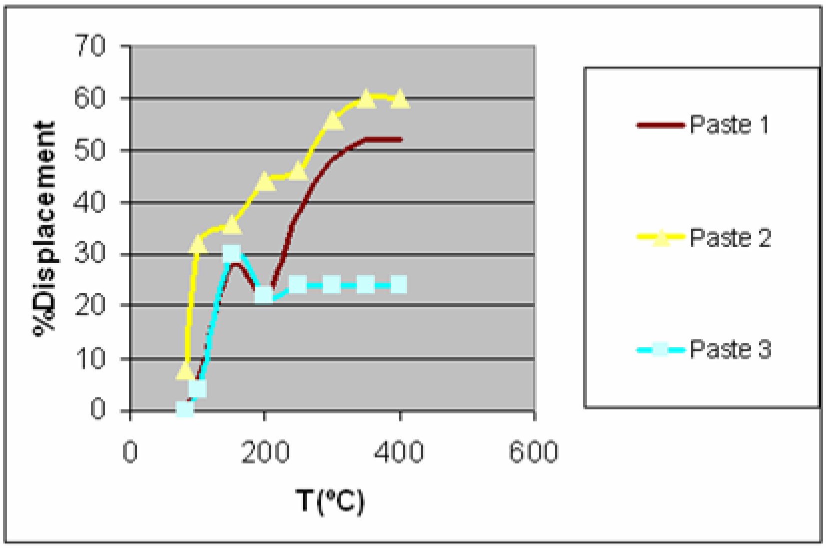

Figure 6: Viscosity curves

age of the displacement with respect to the total height of the cone. Pastes with values of penetration higher than 70%, are little viscous and more likely to segregate, so they are not recommendable, at least for the ELSA electrode.

This test is also used to determine the starting temperature of the melting of the paste which must be different depending on the kind of furnace (close, semi close) and the kind of ferroalloy production (very hot like silicon metal or less hot like ferromanganese)

2.2 Analysis in Baked paste

The measurement of the mechanical and electrical properties of the baked paste at 900ºC give valuable information to estimate the stress resistance and the capacity of transporting electrical current of the baked electrode.

To obtain baked samples, two types of processing are carried out: pressed and not pressed baked paste samples, as shown in figure 7. The pressed sample is moulded by heating the paste to 160ºC and then pressing it under high pressure. After that, the sample is baked slowly to 500ºC. The not pressed sample is obtained by putting paste in a mould and heating it slowly to 500 ºC under constant low pressure. Then, the samples are baked to 900 ºC Normally, if the compaction is good there are not important differences between these samples but sometimes the not pressed sample does not compact well and, consequently, the mechanical properties of this sample are poor. This is another indication that the plasticity of the paste is in the low range, what can generate problems in the electrode.

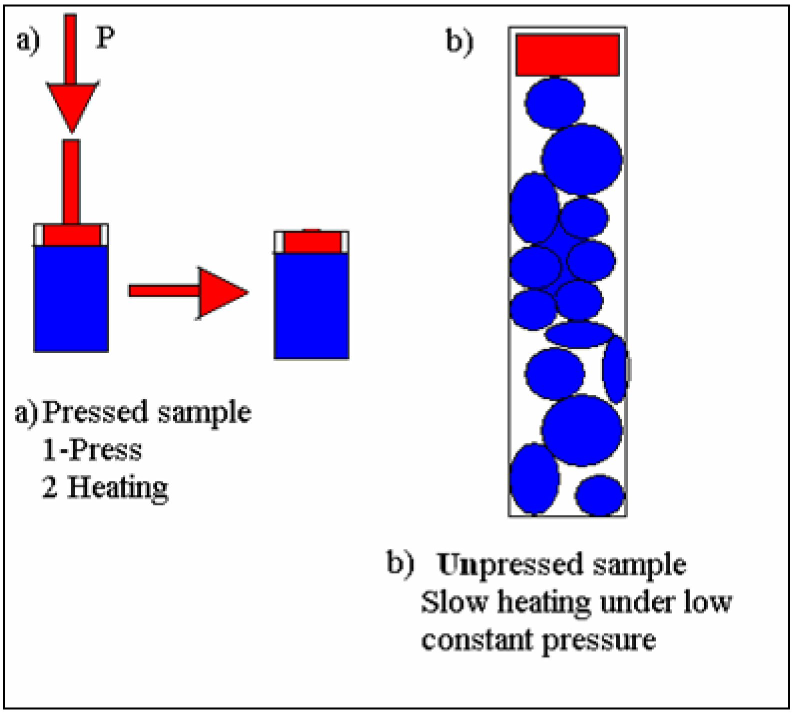

Figure 7: Paste compaction methods

2.2 1. Mechanical properties and electrical conductivity

The electrode must have enough strength and flexibility to withstand the stresses generated during the normal running of the furnace. In most of the commercial pastes, strength and flexibility are opposite terms, so they must be balanced correctly.

Electrical conductivity of the paste in the baked area should be enough to transport the current from the contact shoes to the tip of the electrode. The assemblies utilized to measure flexural strength and resistivity is shown in figures 8 and 9.

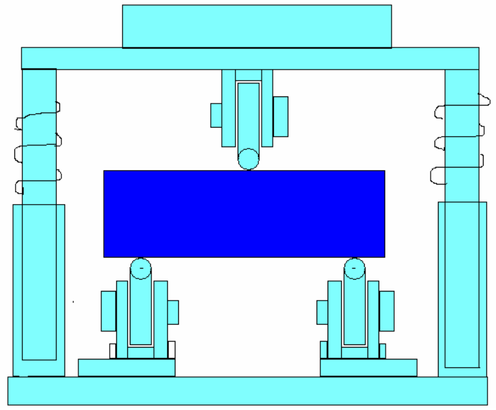

Figure 8: Flexural strength trial

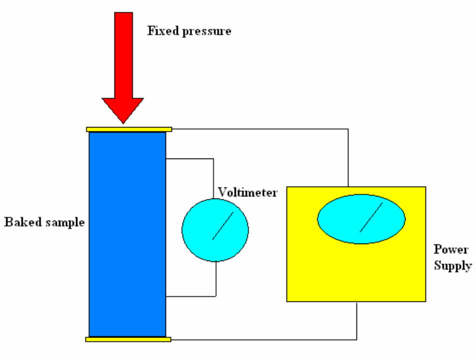

Figure 9: Assembly to measure resistivity

Information about thermo mechanical stresses generated in the electrode with different types of paste can be obtained from mathematical modelling. In figure 10, the mechanical stresses generated in an electrode made of a paste with a low Young's Modulus are expressed in kg/cm^2. The model predicts that a moderate flexural strength of 3 MPa is enough to withstand the stress with sufficient margin of safety for this kind paste.

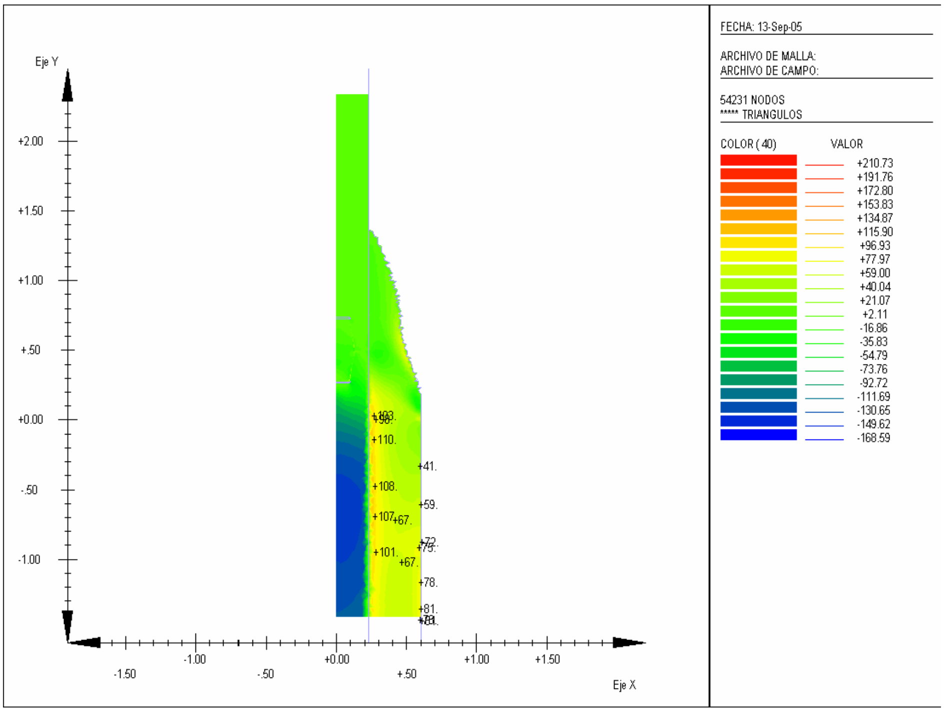

Figure 10: Data from the mathematical model of the electrodes

Taking into account the model of the electrode, it is desirable a low value of Young's Modulus in order to obtain less brittle and more flexible electrodes. The optimal range is between 2 and 4 GPa. A minimum value of 100 microohms×m, after baking at 900 ºC, for the electrical resistivity it is necessary to assure the flow of electrical current.

2.2 2.Segregation index

Samples baked in vertical positions can show differences in density between the top and the bottom part. This difference, expressed in percentage, is the segregation index. Good segregation indexes are those below 5%.

2.2 3. Shrinkage during baking

Between 500 and 900ºC the paste still has possibility of shrinkage, basically depending of the type and amount of pitch. This shrinkage is a main factor in the stresses between the paste and the graphite core on the baking zone of the paste. It can be especially important on the nipple area. A dilatometer can be used to measure shrinkage of the paste. Values around 0.5% of shrinkage are acceptable.

3. SAMPLES FROM THE ELECTRODE BREAKAGES

When a breakage occurs, it is a good practice to study the furnace parameters, like current intensity, column position, and slippage of the electrode and so on. To obtain further information, is useful to take samples from different areas of the electrode, as is shown in figure 11

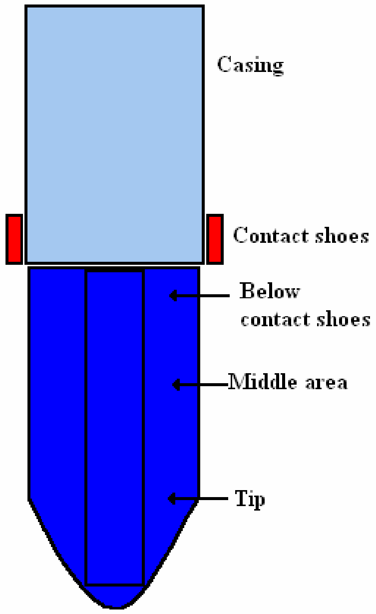

Figure 11: Sampling zones on the electrodes

The normal situation in the electrode is an increase in density and mechanical properties and a decrease in the electrical resistivity and porosity going from contact shoes to the tip. XRD signal increases because the paste becomes graphitized when the temperatures are higher. Common values of these parameters can be seen in figure 12.

The graphitization process of the electrode can be followed using the X Ray Diffraction (XRD) technique. When the paste is near the tip of the electrode, it suffers big changes until it become graphitized. In addition to this, it is possible to detect CSi formation in samples from middle area and from the tip. This CSi is picked

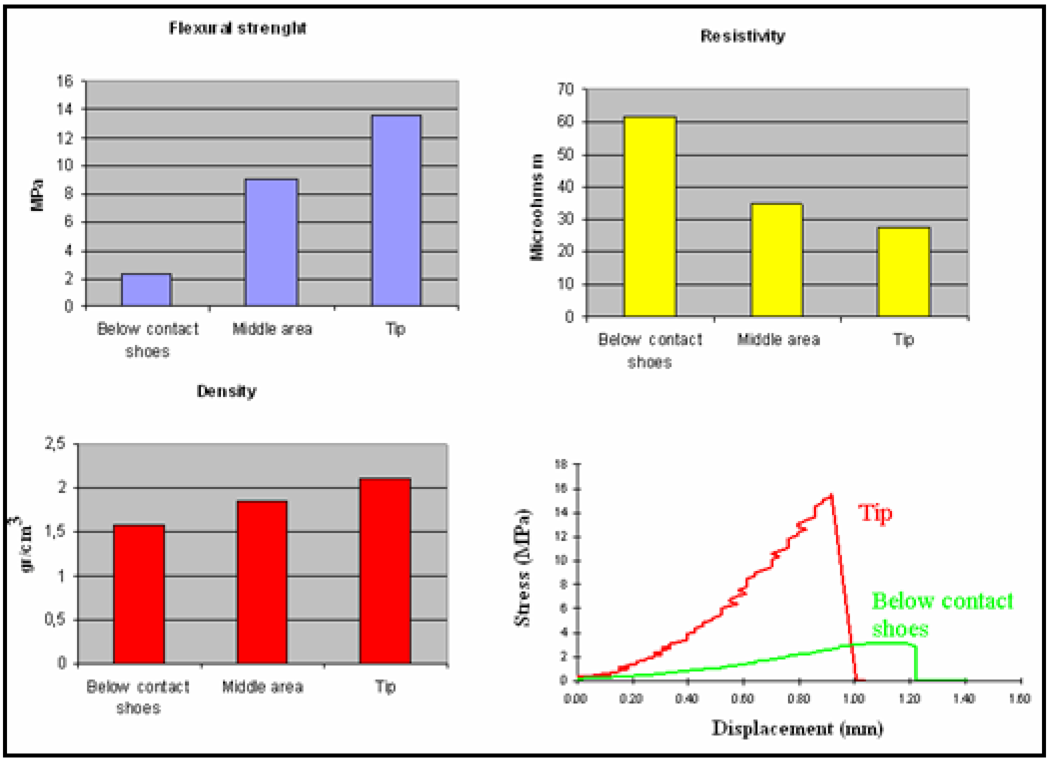

Figure 12: Normal values of different areas of the electrode

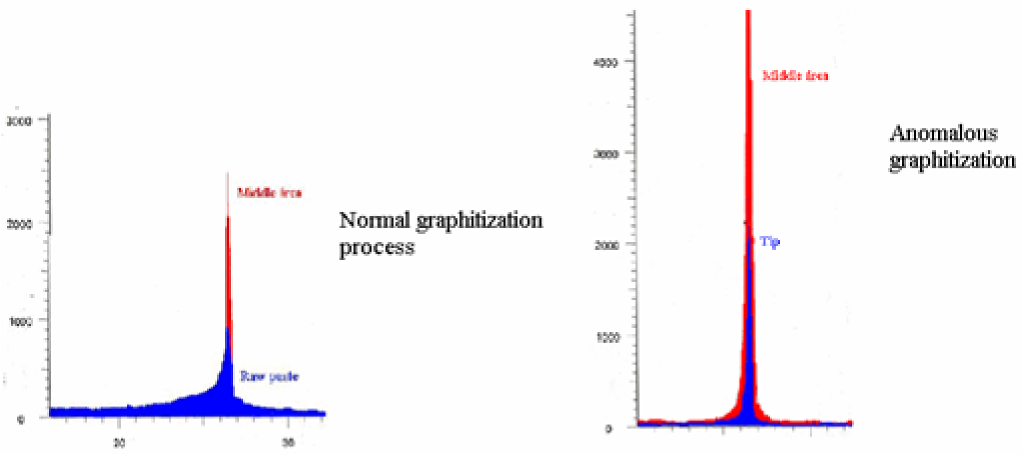

Figure 13: Normal and anomalous graphitization process

out from the process during normal furnace operation by reaction between C and SiO. The CSi sometimes increases the mechanical properties of the electrodes very much in silicon furnaces. This type of reinforced composite made of carbon and CSi have never been observed in electrodes used in ferroalloys furnaces.

In a normal graphitization process, the carbon paste must graphitize gradually from below contact shoes to the tip. It is possible to measure that, because the XRD signal of the samples suffers a gradual increase till the tip as the structure of the carbon is more ordered.

An earlier graphitization, sometimes observed in samples taken from contact shoes area of a broken electrode, it is always an indication of overheating or arcing on this area. That must be avoided because the overheating causes loosening of the carbon material and a diminution in the mechanical properties of the electrode. This is the case shown in figure 13 in which an earlier graphitization process on contact shoes area caused a breakage. As is shown on the picture of the anomalous graphitization, the XRD signal in middle area is excessively high, even more intense than in the tip. This implies that the electrode reached more than 2000ºC on that area, when the temperature should have been around 1500ºC, according to the mathematical model.

4. CONCLUSIONS

The paste consistency is an important parameter for the right electrode operation. Ferroatlantica I+D developed a battery of tests which permit to determine the characteristics of the paste before using it into the furnace to avoid problems. With the same battery of tests it can also be predicted if the paste will operate well in the electrodes and particularly in the ELSA electrode for silicon metal. These tests are carried out at the laboratory of the plant and more from the point of view of the paste consumer than from the point of view of the paste producer. A periodic analysis of the paste, from the usual suppliers or previous to a change of suppliers, avoids a lot of problems in the electrode operation

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