AGM plates production process with emphasis in pasting and curing

F. Costa[a,b], T. Vaz[b], M. Casquilho[a], F.Coelho[a]

[a] Instituto Superior Técnico, Avenida Rovisco Pais; 1,1049-001; Lisboa; Portugal
[b] Exide Technologies, L[da]; Avenida Dr. Carlos Leal; 2600-619; Castanheira do Ribatejo; Portugal

ABSTRACT

The plates curing process is an important stage in the production of lead acid batteries, affecting their capacity and lifecycle.

As its main objective, this work aimed at the optimization and approval of the so-called dedicated negative curing in order to decrease the residual lead content in the negative plates of AGM batteries. For that end, the parameters of the curing program that control the Tudor curing chambers, where the process occurs, were optimized. It was found that increasing the temperature set-point to 60ºC resulted in an increase of residual lead oxidation. The (optimized) dedicated negative curing was approved because there was a 70% (relative, as below) reduction of residual lead in the plates and an increase of 6% in the curing chambers capacity.

Accessorily, in the positive curing, the parameters previous to the process that influence the final characteristics of the plates were analysed.

The new curing chamber where new curing programs were created was also approved. The residual lead results of the new chamber were similar (also not above spec) to those of the Tudor chambers. As regards the moisture content of the plates, the results improved by 24%, as the new chamber has an independent extractor that improves the drying.

The mapping of the negative and positive curing process was done by inspection of some plates during the process. Some SEM images and analyses to the plate's contents by X ray diffraction are included. Several conclusions are presented in relation to the evolution of 3BS crystals growth and of residual lead. Two plate were compared, with high 3BS and 4BS content.

Keywords: AGM batteries, curing, curing chambers, optimization, oxidation, residual lead

1. INTRODUCTION

AGM technology became popular in the early 1980s as a sealed lead acid battery for military aircraft, vehicles and UPS to reduce weight and improve reliability. The acid is absorbed by a very fine fiberglass mat, making the battery spill-proof. This enables shipment without hazardous material restrictions. The plates can be made flat to resemble a standard flooded lead acid pack in a rectangular case; they can also be wound into a cylindrical cell.

AGM has very low internal resistance, is capable to deliver high currents on demand and offers a relatively long service life, even when deep-cycled. AGM is maintenance free (recombination), provides good electrical reliability and is lighter than the flooded lead acid type. It stands up well to low temperatures and has a low self-discharge (Battery University 2015).

The manufacture of the lead acid batteries, in this case AGM batteries, is a complex process with many critical stages. One of these stages is the curing process because is the main responsible for the achievement of good characteristics of a plate. In this process, the skeleton of the paste plates is constructed resulting in the formation and growth of sulphates crystals (3BS and or 4BS). The crystals, which give a strong connection of the particles among themselves (cohesion), increase the surface area, since they increase the porosity of the paste. The higher the porosity of the paste, more easily the electrolyte spreads and, therefore, better is the performance of the battery. The residual lead, which was not oxidized in the preparation of the paste, is rusty now. The grid is also oxidized to form a corrosion layer on its surface that will allow the link grid-paste, improving the adhesion.

The Figure 1 shows the three phases of curing: formation and growth of the crystals, oxidation of the residual lead and formation of the corrosion layer (Pavlov 2011).

After the curing, the cured plate is still mechanically weak. This is because most of the particles are linked by the parts hydrated or by water film formed between them. Through the drying, the moisture content can be reduced to values below 1%, and so improve mechanically the plates (cohesion and adhesion). The drying proceeds in two stages (Figure 2): during the first stage, water filling the capillaries is less tightly bound to the particles and evaporates first, large void pores are formed; during the second drying stage, the wedge water evaporates as a result of the precipitation of the lead hydroxides contained in the wedge liquid between the particles and interconnect them into a continuous porous mass (Pavlov 2011).

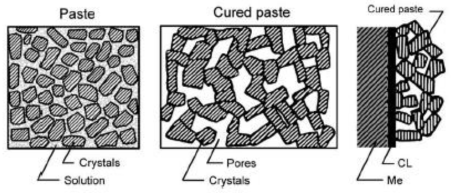

Figure 1- Phases of the curing process.

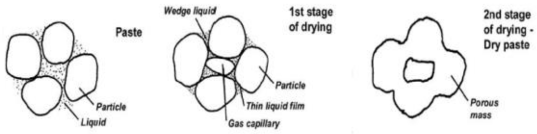

Figure 2- Drying stages.

2. EXPERIMENTAL

2.1. Problem Description

The problem for which held this dissertation was the fact that the plates produced by the new pasting line, Conpast, have a residual lead high content after curing. The Figure 3 displays the data related to the content of residual lead after curing of plates, produced by Cotten Belt Line, spoken by Gravity plates, and Conpast Line, said Concast plates[1].

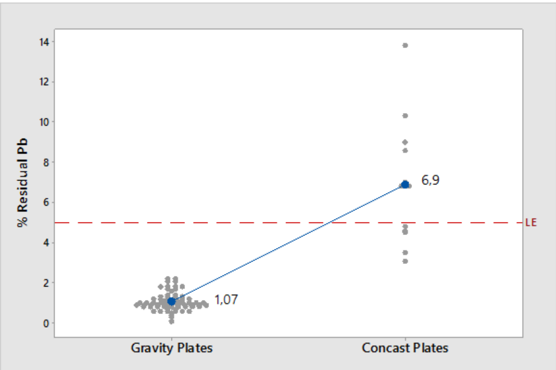

Figure 3- Individual value plot with the comparison of the quantity of free lead between negative gravity plates and negative Concast plates.

Gravity plates have an average of 1.1% (mass) residual lead, while the Concast 1 type plates feature 6.9%. The average residual lead of Concast plates is above the upper limit of specification (5%), which translates into a reduction in the availability of production plates. The aim of this research is the improvement of the curing process, in order to decrease the amount of residual lead in the Concast negative plates.

These are the main causes that explain the occurrence of a bad curing and the present study intended to solve the high residual lead problem in plates: (i) curing time, which may not be enough, (ii) the temperature too low, which could involve changing the profile (Set-point), (iii) incorrect curing profile, (iv) and (v) humidity homogeneous reaction NOK ("not OK") due to the disposal of plates that, given the new pasting technology, is the cause that has more impact on the curing for the Concast plates.

2.2. Curing Chambers

The curing proceeds in curing chambers with controlled air temperature and humidity. The air enters at the top of the chambers cross into a heat exchanger. Then enters inside the chamber through a perforated wall, and flows to another perforated wall, positioned in the middle of the chamber, leaving to the atmosphere. The dampers controls the input and output of the air. To control the humidity level, the chamber has 6 nozzles that inject water into the air. The temperature of the air is controlled by a heat exchange valve.

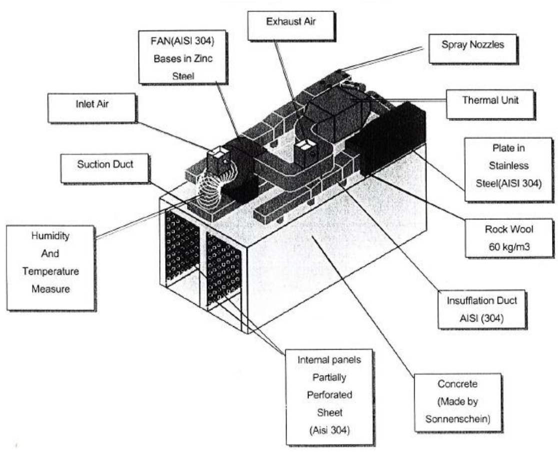

Figure 4- Curing chamber constitution.

The curing programs (software using PID controller) involve three stages: loading, curing and drying. These stages are composed of several steps, where set-points for temperature and humidity are established, as well as the duration of each step.

The loading is the phase when the chambers are full with racks, taking up to 10 h (maximum). During this phase, the relative humidity set-point is in 100% to not activate the reaction (oxidation is an exothermic reaction), starting the reaction of all plates at the same time. The valve of the exchanger is then always switched off.

In curing, the ejectors work in the same way during the filling phase, to control the relative humidity. For the air temperature, the controller

[1] To differentiate the negative plates of each other, the plates are named according the grid technology: Gravity or Concast (continuous casting)

regulates the opening and closing of the valve of the exchanger. This phase takes 21 hours to complete.

During drying, the ejectors are always turned off and the humidity is removed by the opening of butterflies. The temperature is controlled by opening and closing of the valve of the exchanger. This step takes 17-19 hours, if the chambers are T1 or T2 (larger), respectively.

2.3. Pasting Lines and Dedicated Curing

The pasting line has a lot of influence in curing process: the moisture content of the plates and the way that the plates are stack influences the oxidation of the lead. The moisture content is an important factor in curing because works like a catalyst in the oxidation reaction (Pavlov 2011). If the moisture content is too high, the pores in the paste are completely filled with water, preventing the diffusion of oxygen on the surface of free lead. When the paste has less moisture content, all the pores are not filled and a film of water on the surface of lead free is formed, where oxygen diffuses. The initial moisture content of the plates also cannot be too low, since oxidation of lead is an exothermic reaction. Increasing the temperature causes the water evaporation and may get to the point where the water content is so low that will stop the reaction, even if there is free lead to oxidize (Wagner 2009).

On the Castanheira plant case, there are two technologies for the pasting line: the Cotton Belt technology where the plates are horizontally staked and the Conpast line (continuous pasting of negative plates) technology where are vertically stacked. Due to the pressure of the plates on top of each other, the air have less access in Concast plates (negative plates) during curing.

In the past, the curing was performed with mixed plates (negative and positive).

The Figure 5 shows the mixed curing that was used for the negative and positive plates.

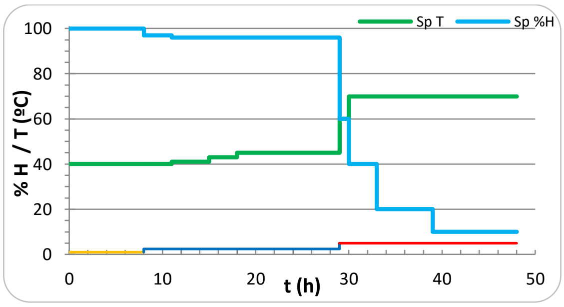

Figure 5- Mixed Curing program. Legend: yellow-loading, dark blue- curing and red- drying.

To increase the rate of oxidation, it should be promoted a more reactive environment and for that it is necessary to raise the temperature of the air. However, this is not possible for the positive plates, due to the formation of crystals 4BS. Therefore, in order to improve oxidation, it was chosen to separate positive of negative plates in curing, pass to a dedicated curing. To this end, it was necessary to change the curing program for the negative plates.

In the curing phase, it was decided to increase the process time from 21 to 23 hours, rather than raise the temperature higher enough that could cause a reaction too sudden, stopping the oxidation. There were also changes in the relative humidity and air temperature steps. The set-point temperature has been changed to 50° C, in the early hours, with high relative humidity, 95%, to provoke the reaction because the plates comes still hot from the paste line, keeping the reaction to occur. However, as the cure of the plate's proceeds, the moisture content starts to decrease, causing a decrease in the speed of the reaction. At this point, it is necessary to increase the temperature of the air for the reaction to continues with a high rate. For this purpose, it was increased the set-point to 60ºC and slightly decreased the relative humidity of the Chamber, making several steps until it reaches that temperature, so that the change is not abrupt.

The time of the drying phase was reduced 4 hours, although 2 hours was added in curing step, so in total the time of this phase was reduced 2 hours in the process. The need of reducing the number of hours of drying was due to the delay in the curing chambers loading, affecting its availability due the change to a dedicated process.

In total, the program lasts for 38 hours and the necessary time to load the chambers was not counted.

The Figure 6 shows the dedicated program for the negative plates.

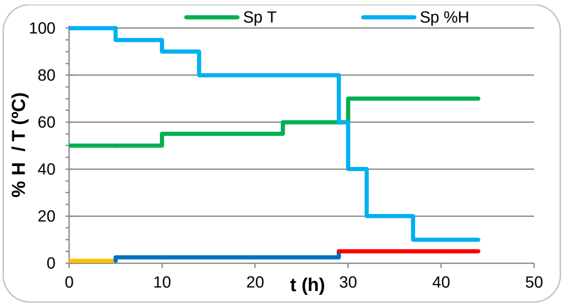

Figure 6- Dedicated negative curing program.

In Figure 7 are the Concast plates results during the mixed curing change to dedicated. In the I-MR control chart, the passage to dedicated curing caused the reduction of the residual lead content average form 6.12% to 3.21%, although the process is still unstable with values outside of specification. Therefore, the dedicated program needs to be optimised.

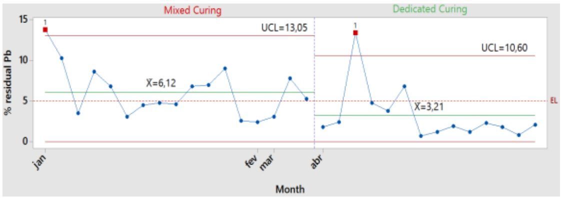

Figure 7- I-MR Chart showing the impact of the change to a dedicated curing in the Concast plates.

2.4. Optimization of the negative curing program

For each test, a fluke and thermocouples are used to measure temperatures of the plates along the process. The data of temperature and humidity will be taken from the probes placed on camera, with the information stored by the software used in the monitoring of this process. In all tests, the probe was placed in the centre of the card stack, where the conditions are more unfavourable.

Each program will be listed according to the changes made, as follows: (i) Program1, original negative dedicated curing program; (ii) Program 1A, negative curing program with the first changes; (iii) Program 1B, negative curing program optimized; and (iv) Program 2A, positive curing program. To identify the test plates, the negative plates are classify depending on the technology that the grids were produced: by gravity or Concast.

The Figure 8 shows the first trial using the Program 1 with different moisture content, 8.5% and 9.5%.

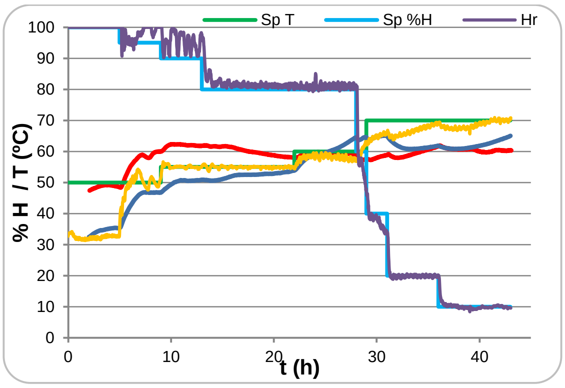

Figure 8-Test with Concast plates with different moisture content's using the Program 1. Legend: red- plates temperature with %H=8.5, dark blue- plates temperature with %h=9.5 and yellow- air temperature, purple- % humidity.

For the trial with moisture content of 9.5%, it turns out that the plates temperature is less than the air temperature, just being higher in the last hours of the curing stage. Knowing that the oxidation reaction is exothermic one can conclude that it was in these last few hours that the oxidation had the greatest impact on the plates.

The moisture reduction in the plates, before the entry in the Chamber, will provoke a more vigorous oxidation reaction, starting sooner and at a higher temperature.

In the drying phase, that begins when occurs a rapid reduction in the temperature of the plates and the air, because the camera to remove moisture, in order to comply with the set-point, open the butterflies causing the escape of heat (which goes along the drying, whenever you have to reduce the moisture in the air).

The Concast plates trial results are in Table 1.

Table 1- Trial results to the type 1 Concast.

Trial	% Residual Pb	% Moisture
Plate with %H=9.5	4.8	0.2
Plate with %H=8.5	1.2	0.8

Although the residual lead stays within the specification limit (less than 5%), is still high. The plate moisture, after Curing, is within limit, less than 1.5%, so the reduction of the number of hours it is possible. The moisture result is fairly low, and may be still possible to reduce the drying time.

While the initial moisture of the plates was decreased to values below 9.5% (theoretical value for which the plate must contain initially a maximum oxidation rate) it turns out that is achievable to reach low residual Pb values with an initial moisture of 8.5%The next step will be to promote an "atmosphere" more reactive that allows oxidation to occur at a higher rate. For this, the last temperature step point (60ºC) of the cure stage was extended.

In the Figure 9 shows the modifications made in Program1.

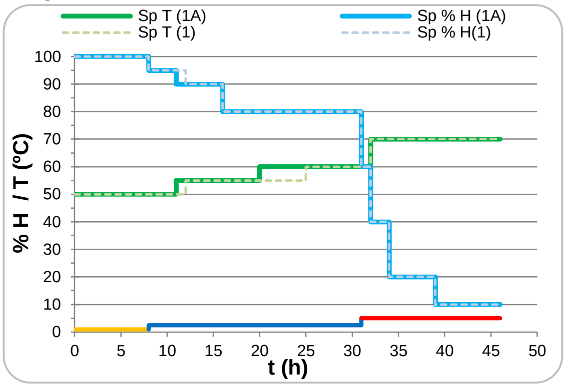

Figure 9- Firsts changes in Program 1: Program 1 (dashed lines) and Program 1A (solid lines)

The Figure 10 shows the Program 1A trial for the Concast plates.

With the change of the Program, the plates react with a greater intensity, as can be seen by the temperature peak, at around 70ºC, at the 20th hour of curing step (25 in total). However, this may harm the oxidation because the reaction peak is close to the drying phase, then when entering in this phase, the reaction may not be complete. So the plates will begin quickly to lose moisture, consequently, will stop the oxidation.

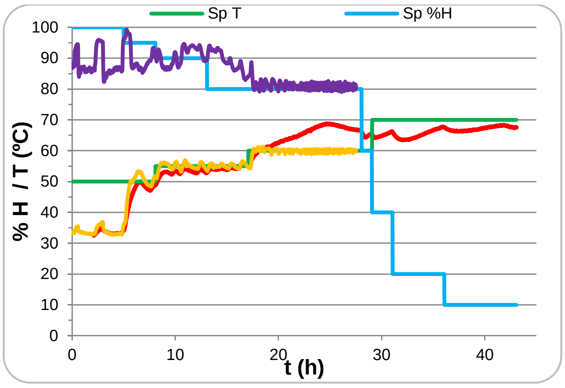

Figure 10- Program 1A trial with Concast plates. Legend: red-plates temperature, yellow- air temperature, purple- % humidity

The trial results are in Table 2.

Table 2- Concast plates results after 24 hours of the end of curing.

% Residual Pb	% Moisture
0.7	0.3

The results shows a significant improvement by decreasing about 4% of residual lead content, compared with the previous programme, with 9.5% humidity.

The program 1A was changed into a program 1B. In the curing phase, the third and fourth step was prolonged for one more hour, so that the reaction occurs sooner (decreasing the previous steps). During this step, it was decided to anticipate the drying first step, in order to take advantage of the butterflies closer by increasing the temperature of the chamber, entering in the drying step with increased thermal load. This step is performed to combat the effect of the drying reduction time. In the Table 3 presents the curing steps of the Program 1B.

Table 3- Curing steps of the Program 1B.

Step	Time (h)	Moisture Content (%)	Temperature (ºC)
1	3	95	50
2	3	90	55
3	5	80	55
4	12	80	60
5	1	60	60

In the drying phase, was reduced 5 hours, in order to increase the availability of cameras. The Figure 11 presents the modifications, as well as the test performed.

Analysing the chart, it appears that the reaction peak occurs at around the 15th hour of curing (20th hours of process in total), the reaction of program test starts about 5 hours sooner.

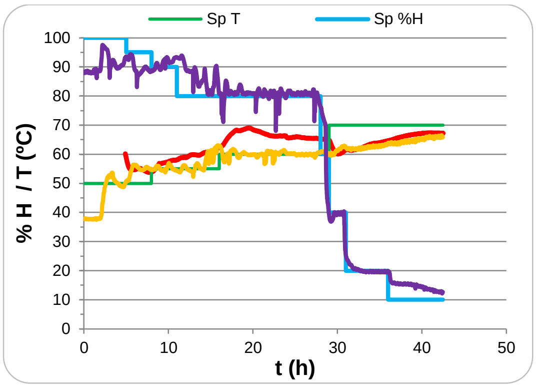

Figure 11-Concaste trial with Program 1B.Legend: red-plates temperature, yellow- air temperature, purple- % humidity

The trial results are in Table 4.

Table 4- Concast plate results for the Program 1B

% Residual Pb	% Moisture
0.9	0.46

Although the results show a residual lead content slightly higher compared with the 1st program, it is necessary to take account that the analysis made to the results of the program 1B was done shortly after the end of the process, while the 1st program was executed a day later. These results show that, using the program 1B, the Concast plates can be used almost immediately (the plates only have to rest in order to stabilize, more specifically, to decrease their temperature. This plates do not need the extra resting time to react the remainder lead) in the Assembly of battery (increased availability).

In Figure 12 shows the temperature profiles of the trials of the several applied programs.

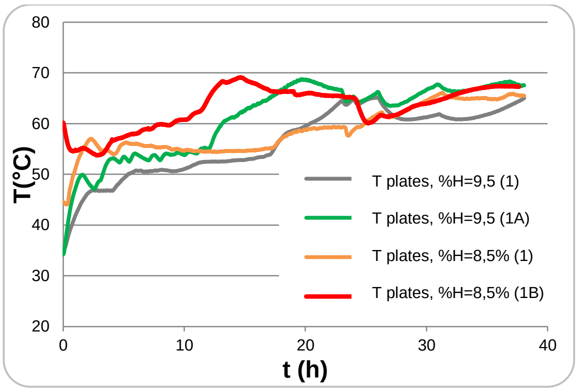

Figure 12-Temperatures profiles of all the trials.

By observing the temperature profiles of the plates, it can be concluded that the programs 1A and 1B favor more the oxidation than the program 1. In the program 1 A, the reaction starts late, in the final hours of cure, and may have the risk to continue during drying. During drying, the moisture is removed from the plates which can lead to the stop of oxidation and therefore the plates can contain pure lead by reacting. On the other hand, if the reaction occur during drying, that could take the plates to huge temperatures and may burn fibers and cause cracks. The program 1B has no longer that risk, since the reaction (high temperature) occurs earlier and with greater intensity for longer. The final proposal of optimization is, as well, the program 1B.

The Figure 13 displays the comparison test between the Concast plates and the Gravity plates using the optimized program (1B). The same evolution between the two types of plates was verified, so it can be concluded that program 1 B also promotes the reaction to the Gravity plates.

The Figure 14 shows the comparison between the dedicated optimized curing program (1B) and the mixed curing. In the figure, the red curves and Brown refer to the temperature of the plates, in dedicated curing (optimized) and in mixed curing, respectively. There was a great improvement in the separation of positive and negative curing and its optimization, as can be seen in the figure.

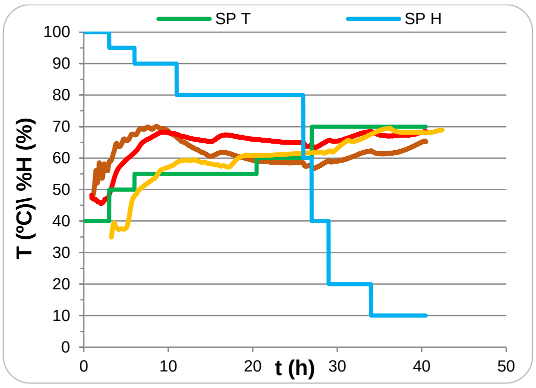

Figure 13- Comparison between the Concast plates and Gravity plates, using the Program 1B.

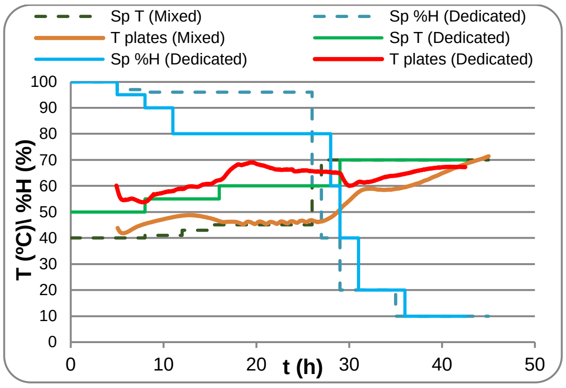

Figure 14- Comparison between the dedicated curing and mixed curing.

2.4. Negative Curing Mapping

In order to see what is really going on during the curing process, it was performed a mapping of the curing for the negative plates, with the main objective to observe the evolution of residual lead of Concast plates. To this, it were retreated oxide and paste samples, and plates during the curing. In order to stop instantaneously the oxidation of the plates it was used liquid nitrogen and then placed in an oven at -18 ºC. These samples were analyzed by X-Rays, SEM (Scanning Electron Microscope) and by a balance of moisture. In Table 5 are the samples identification. In Figure 15 presents the micro photos of the samples from N_0 to N_{10} taken by the SEM.

Table 5- Samples used in the curing mapping

Nº	Amostras negativas
O_N	Óxido negativo
P_N	Pasta negativa
N_0	Placa após o forno
N_1	Placa no início do sazonamento
N_2	Placa retirada na 1ª hora
N_3	Placa retirada na 4ª hora
N_4	Placa retirada na 5ª hora
N_5	Placa retirada na 10ª hora
N_6	Placa retirada na 13ª hora
N_7	Placa retirada na 16ª hora
N_8	Placa retirada na 19ª hora
N_9	Placa no final da cura
N_{10}	Placa no final da secagem

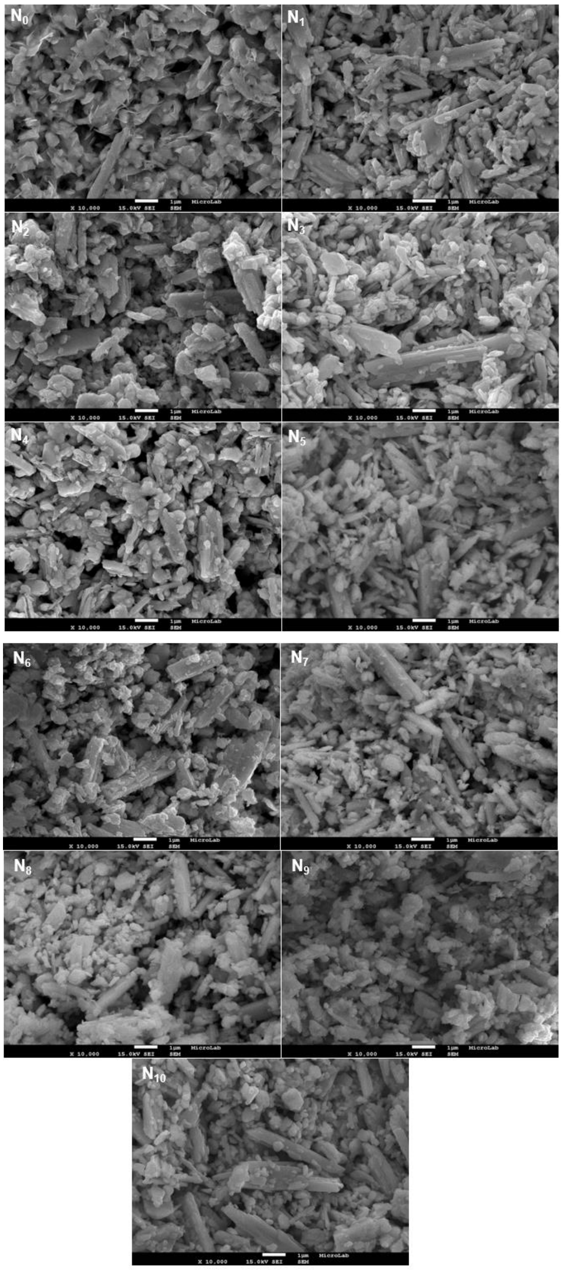

Figure 15- SEM micro photos from the sample N_0 to N_{10}.

Analyzing the images, it can be seen an evolution in the crystals dimensions along the curing, especially in the early hours. One can note also the somewhat flattened in the sample N0 (after the oven) that compared with the next sample, in the beginning of curing, N1, Shows less crystal dimension.

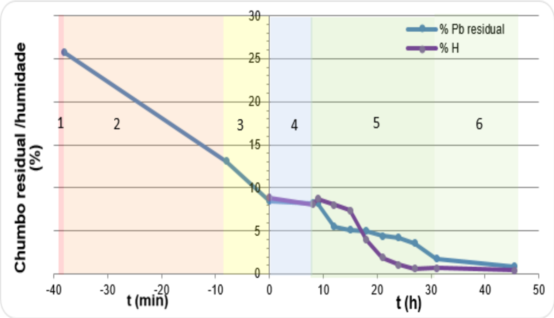

Figure 16- Residual Lead and moisture content evolution, during the curing process.

In Figure 16, it was found that approximately 13% of lead is oxidized during the paste manufacturing, 5% during the pasting and 8% in curing. According to the literature (Pavlov 2011), the amount of residual lead before (oxide) and after the paste production must be in the range 15-25% and 10-15%, respectively. Therefore, the process residual lead values meet the literature (in this test).

The oxidation was more intense in the fourth hour, due to the fact that the plates were still hot because of the oven from the pasting line, and between the 16th and the end of the cure, since the temperature set-point is higher. It turns out that the decrease of moisture accompanies the decrease of residual lead, because as the reaction occurs, the temperature will increase causing the water evaporation.

2.4. Dedicated Curing approval

After optimizing and reducing the number of hours (drying) of the curing process, it was necessary to verify statistically if in fact there has been an improvement in the characteristics of negative plates Concast.

The Figure 17 is an individual values control chart (I-MR chart) for the % residual lead in Concast plates, before and after changing to dedicated curing and after optimization. The changing to the dedicated curing caused the decrease (relative) of 48% on residual lead average. After optimization, the average reached a value of 1.83% residual lead, decreasing 43% of the average before the optimization. Therefore, the change for the curing dedicated and optimized programs caused a reduction of 70% in residual lead. On the other hand, it turns out that the process is not yet stable, since there are four points out of control.

The Figure 18 displays the control chart for the % moisture control for Gravity plates, using data from the years of 2014 and 2015 after optimization, in other words using data with the same conditions (in this case in the Summer). It was confirmed that the drying time reduction is possible for the negative plates, after the improvement, since there was a 37% reducing in the average, although it contains a value outside of the specification. This improvement is due to the increase in temperature and to pre-dry held during the cure, allowing the plates into the drying with higher temperatures. From this chart, it could also be concluded that the Concast plates will have similar results to Gravity plates for the moisture content, since the curing program is the same. However, it is imperative to check if this reduction is possible during the winter, for both types of plates.

In terms of capacity (plates per day), was increased by 4% with the change to dedicated curing (2 hours reduction in drying) and, finally, 6% with the optimization (reduction of another half hour on drying).

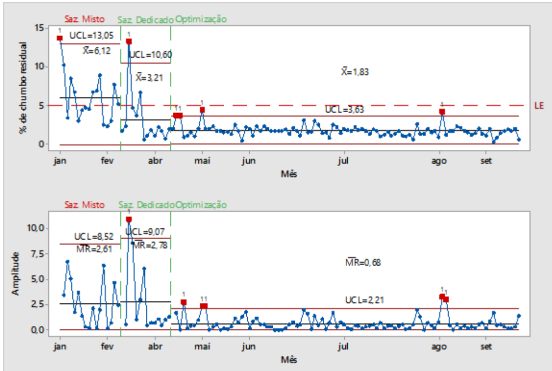

Figure 17- I-MR chart of % residual lead for Concast plates.

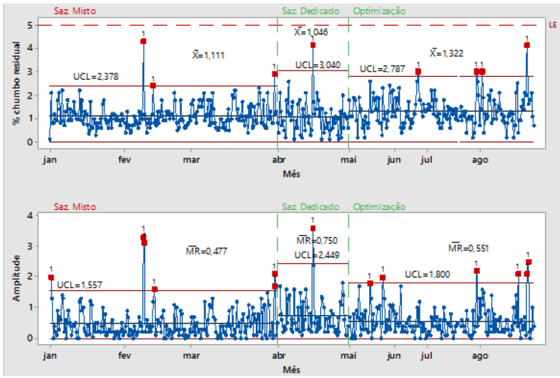

Figure 18- I-MR chart of % residual lead for Gravity plates.

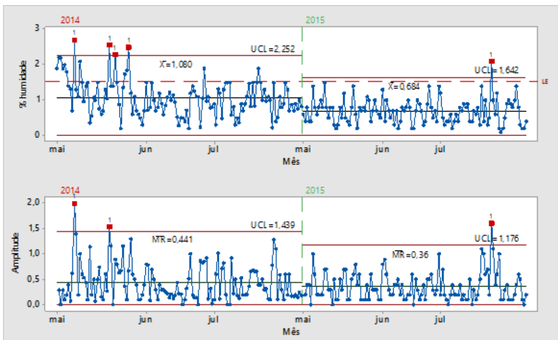

Figure 19- I-MR chart of % moisture content for Gravity plates.

2.5. C_1 curing chamber approval

Contrary to T1 and T2 chambers, this new chamber has no separating wall in the center. The air from a fan circulates from right to left, being expelled on the top by an extractor. During drying, the air moves with help of two mobile systems, wall and flap. To dry the pallets that are placed at the bottom of the Chamber, the flap is switched off and the wall moves, and the reverse happens to dry the pallets placed on top. The air outlet is controlled by the program. Cooling and heating are conducted similarly to T1 and T2 in the chambers. The program consists of 6 steps for curing and drying phases, being the loading in a program step aside. In each step several parameters can be controlled: ramp-up, STOP, air temperature; % Relative air Humidity, % of exhaust and % of ventilation. The ramp-up is a period time to achieve the temperature and the relative humidity of the air in the various steps. This parameter is important in order to avoid too sudden changes of steps. The STOP parameter indicates the time taken for each step. The % exhaust controls the entry and exit of air and is applied to the extractor cycle time (2 minutes). The % ventilation controls the speed of the air flowing into the Chamber.

The Figure 20Figure 20 and Figure 21 displays the negative and positive programs, respectively, based on the T_1 e T_2 curing programs.

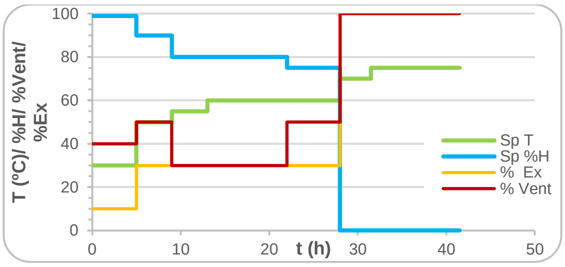

Figure 20- Negative program for the chamber C_1.

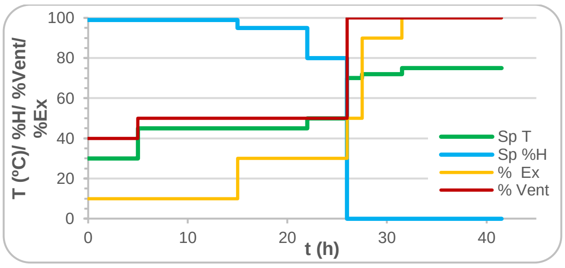

Figure 21- Positive program for the chamber C_1.

Both Figure 22 and Figure 23 shows the trials for the negative and positive plates.In the drying phase, it is intended that the butterflies open to remove the moisture. The effectiveness of this system lies on the fact that the exhaust is independent of the fan because there is a proper system (extractor) that, unlike cameras T1 and T2, prevents the air temperature or being disturbed. (During drying, there is no decrease in temperature always butterflies open to remove the humidity of the Chamber.)

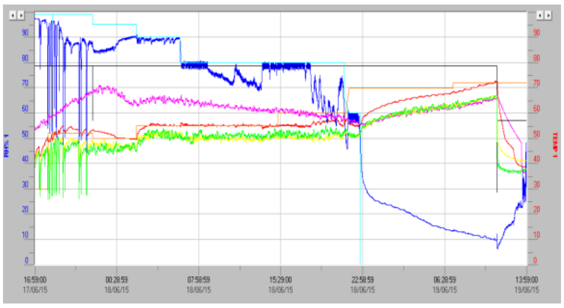

Figure 22- Negative Trial.

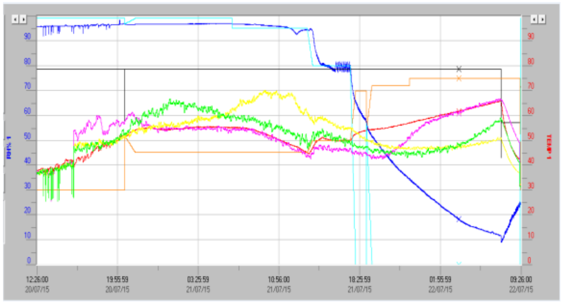

Figure 23- Positive Trial.

In the Table 6 are the trials results.

Table 6- Trials results for the negative and positive plates.

Type	% Pb res.	% Humidade	%3BS	%4BS
Negative	1.8	0.4		
Positive	0.6	1.5	25.3	8.7

Like in the negative curing, in positive curing mapping, Figure 24, there is an evolution of the size of the crystals. However, that formed crystals in positive plates have larger dimensions than the ones formed in the negative plates.

The Figure 25 displays the evolution of the residual lead and moisture content of the positive plates, during curing. Compared with the manufacturing process of negative paste, the residual lead after manufacture of positive paste is quite higher, about 8%. The decrease of residual lead in pasting is approximately 5%. As expected, the positive plates are more reactive than negative, and it is observed, in the early hours (up to 7th hour of healing) of curing, a much sharper decline of residual lead, about 6% (compared to 3%).

The Figure 26 shows a comparison between a high-plate with 3BS, P10 sample, and another with high content in 4BS, P4BS sample. The obtained images illustrate that the 4BS crystals are much larger than the crystals 3BS, explaining that it is more difficult to form the 4BS, in the process of formation (because these crystal needs more time to form).

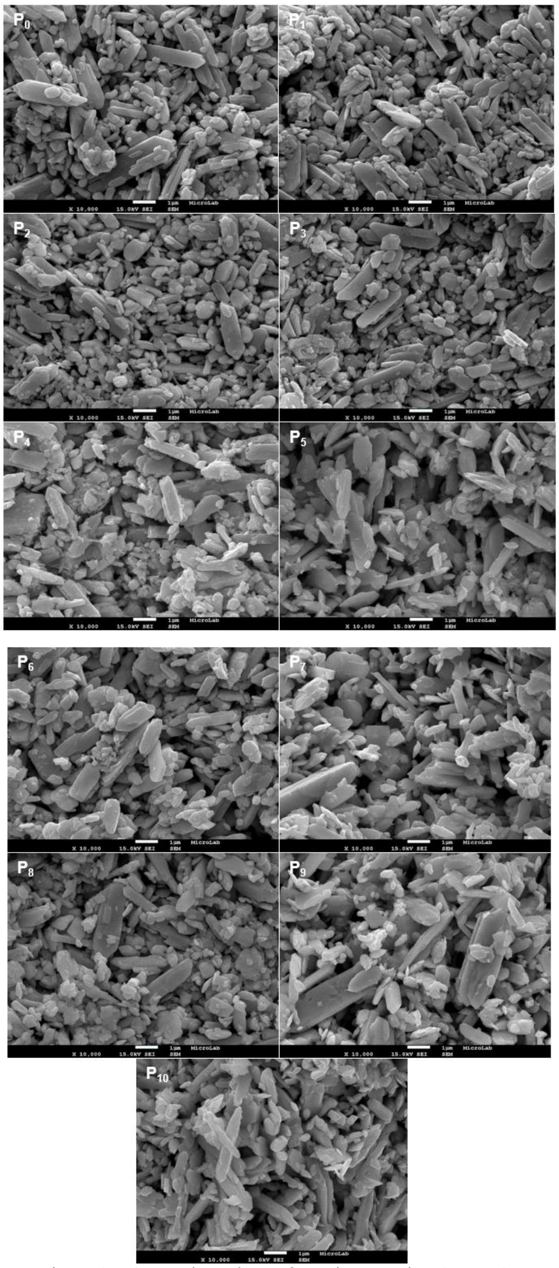

Figure 24- SEM micro photos from the sample P0 to P10

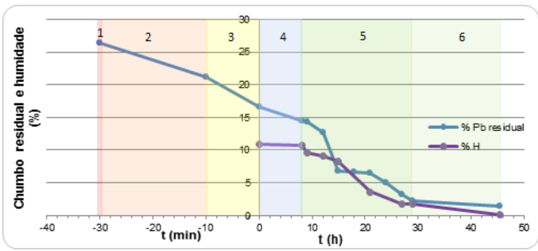

Figure 25- Residual Lead and moisture content evolution, during the curing process.

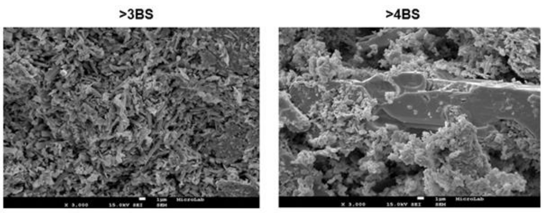

Figure 26- SEM micro photos that compare onde plate with 3BS and another with 4BS.

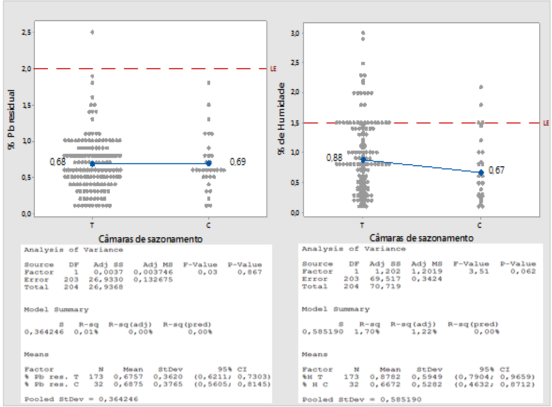

Figure 27-Chambers comparison (T and C) of Residual Lead and moisture content

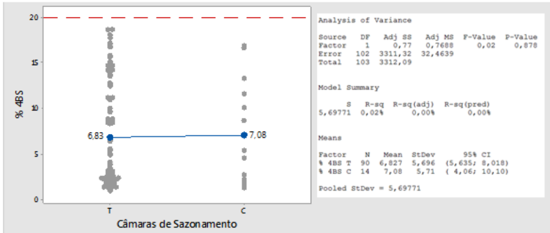

Figure 28- Chambers comparison (T and C) of 4BS.

Through the two-sample test was found statistically that the Chamber C1 results differ from T_1 an T_2 chambers, because the p-value is greater than 0.05: 0.867 to the variable% residual lead, 0.062% to moisture and 0.878 to % 4BS. Regarding the confidence intervals, it was verified that the estimate of the average value is more precise in the chambers T_1 and T_2 than the new chamber. It should be noted also that the population is larger in the case of T_1 and T_2 chambers. It appears that the results of the residual lead content on the plates for the Chamber C_1 have similar results compared to the T_1 and T_2 cameras. Although the results of the humidity of the plates, using the Chamber C_1, contain a point out of specification, the average (0.67%) is 24% lower compared to the T_1 and T_2 chambers (0.88%). In relation to the % 4BS, the C1 Chamber presents an average (7.08%) 3.53% higher than T_1 and T_2 cameras (6.83%). It is concluded that the Chamber C_1 is approved, with similar values in % residual lead and % 4BS, showing better results in the drying.

Conclusions and future perspectives

The results allows to conclude that the residual lead in a mixed curing was disadvantageous to the new Concast plates, since, due to the way they were arranged vertically, the oxidation rate was low, causing them a high lead content by reacting. These plates cause a drop in production capacity, since it is necessary, out of an "atmosphere" as created in a curing chamers, expect to react until the residual lead content is within specification (less than 5%), and can take additionally between 24 and 48 hours.

For the negative curing program optimization, it was verified that with the 1A Program, with the aim of promoting a more reactive "atmosphere", the negative plates reached temperatures of 70° C, being the Program 1 incapable. The Program 1A reached the lowest value of residual lead of 0.7%. Although the results are the best, this program required slight changes, since the peak of the reaction is quite close to the drying step because, if the reaction continues, the drying can cause loss of moisture too quick. This fast reduction can cause the possibility of formation of cracks on the plates, and a stop of oxidation. As it turned out, in program 1B the reaction occurs, in fact, 5 hours sooner after the changes. With the dedicated curing, the plates reach 20ºC more than the mixed curing, proving that the reaction is higher.

The statistical analysis confirmed that the negative curing optimized reduced the percentage of residual lead on Concast, being the average 70% lower than the average of the mixed curing and 43% lower than the dedicated curing before optimization. In relation to the final moisture content of the plates, it turns out that there was any sign out of specification, which indicates that the reduction of the number of hours in the drying not prejudice the characteristics of plates. Therefore, the dedicated curing improves not only the characteristics of the plates, but also increases 6% capacity of the cameras.

Concerning to the new chamber C_1, the created programs show good results, observing the same tendencies in the evolution of the air and plates temperature than the T_1 end T_2 chambers, during the cure. During drying, the chamber C_1 works better than T_1 and T_2 chambers, due to the existence of an independent exhaust system, being by this the moisture removed, not losing heat load during this phase. The statistical results confirmed that the moisture content average after plate drying in C_1 is 24% lower than the average of the T_1 T_2 chambers. The chamber C_1 and curing programs, positive and negative, were approved.

In the process mapping, it was noted by the SEM images a A more pronounced development in the size of the 3BS crystals in the first 8 hours, both in the negative as positive curing, larger crystals in positive curing. It turns out that for the negative curing, the higher oxidation stages are: (i) in the fourth hour, the plates are still hot because of the oven in the pasting line; and (ii) between the 16th and the final time of cure, because that is when the "atmosphere" more reactive is created. For the positive curing, the most critical phase occurs in the first 10 hours of cure, because that is where the temperature is higher, due to the high reactivity of the plates. It is at this stage that there is the highest probability of formation of tetrabasic sulphates (4BS). The growing of these crystals were confirmed of being harmful for the formation process, by comparison between a plate with high content in tribasic (3BS) sulphates and other plate with high content in tetrabasic sulphates (4BS). This comparison shows clearly the different in the dimensions of these two crystals, being the 4BS a much larger crystals.

For future prospects of this work, it is necessary to check if the drying reduction hours is not harmful on the winter. A prototype exhaust system was installed, similar to the C_1 chamber, in one of the T_2 chambers, being necessary to perform tests to determine how to use it properly. Adhesion of the past in the grid of the Concast plates is less than Gravity plates. It is necessary to improve the adhesion: (i) maybe installing a system on the Conpast line to make the grid more rough (as, for example, by abrasion), (ii) optimize the curing in order to get better adherence (this requires studying On the possibility of increasing the step of curing for more than 30 hours, reducing the drying time, and (iii) use an additive with oxidizing properties.

REFERENCES

http://batteryuniversity.com/learn/article/absorbent_glass_mat_agm (acedido em 18 de 10 de 2015).

Pavlov, Detchko. *Lead-Acid Batteries Science and Technology.* 1ª. Elsevier, 2011.

Wagner, R. "Secondary Batteries- Lead Acid Systems: Curing and Formation." In *Encyclopedia of Electrochemical Power Sources*, 662 à 677. Elsevier, 2009.