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Diagnosing Changes in Baked Anode Properties using a Multivariate Data-driven Approach

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Abstract

The baked anode quality control scheme used in most carbon plants consists of lab testing of anode core samples and monitoring weekly averaged properties. Both the low anode sampling rate and the averaging hide a significant amount of variability in the anode populations. Additional consideration depending on the sampling procedure needs to be taken into account while analyzing the core sample properties. In previous work, a multivariate latent variable PLS model was developed for predicting individual anode properties at the end of the baking cycle. All the data available at the Alcoa Deschambault smelter were used to build the model. This work investigates how to use this model to learn from data and, in particular, to help diagnose the root cause of variations in the electrical resistivity and L_C. Changes in raw material suppliers and non-uniform temperature distribution within the baking furnace were found to contribute to the drifts.

Introduction

The standard procedure for monitoring baked anode properties is based on weekly averages of core sample properties obtained by laboratory measurements. Since less than 1% of the anodes produced are core sampled, the results are most likely not representative of the whole population manufactured during a given time period. Furthermore, it takes from two to four weeks to obtain lab measurements, and the common practice of averaging them based on a given sampling period (e.g. weekly) often hides the measured variability [1]. The detection of abnormal situation is therefore only possible if long term trends or large deviations in anode quality occur. The carbon plants sampling strategy can also have a significant impact of the interpretability and use of the anode property data [2].

The low frequency sampling problem cannot be overcome easily due to the resources needed to test a greater number of samples, but the way current data is analyzed can be improved by using multivariate statistical analysis. These methods allow for efficient analysis of the large datasets collected at carbon plants (process and lab data) and enable the user to monitor the whole process using a single model. Previous results [3] described the methodology for predicting the anode physical properties on an anode per anode basis. An overview of the possibility to use this model for troubleshooting was also presented. The prediction results for weekly averaged properties were also presented earlier at a TMS conference [4]. This paper focuses on the offline analysis of some anode quality deviation observed at the Alcoa Deschambault smelter (ADQ). It will also be demonstrated that using weekly averages can mask high anode variability even on a long time period.

The predictive ability of the model was recently presented in JOM [3]. An observation was made about the declining quality of the prediction for the electrical resistivity (ER) over time. The degrading quality can be seen in Figure 1, where the increased variability of ER is not well predicted by the model (in 2011 and 2012), meaning that something unseen in the training dataset was going on. This paper will focus on investigating the source of this increased variability. Note that all the data shown in this paper have been scaled to protect sensitive information.

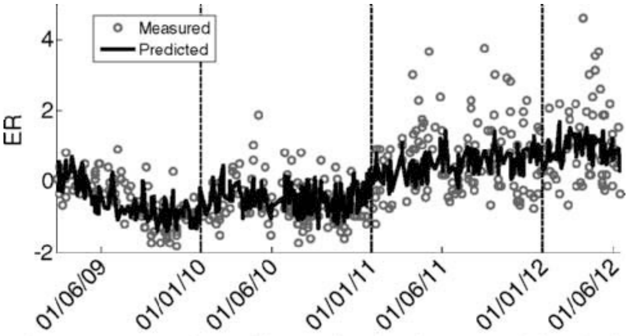

Figure 1. Comparison of the predicted and measured electrical resistivity (adapted from [3])

ADQ anode sampling procedure

The sampling procedure established at ADQ consists of sampling cores from two anodes baked at specific pit position in each section of the baking furnace. Each section contains 108 anodes. Unfortunately, not all core samples can be analyzed due to different reasons. The two positions that are cored are selected to correspond to the hottest and coldest region in the baking furnace pit. Figure 2 presents a schematic of a furnace section and the two sampling position. The hot anode is sampled on the top row of the inside pit and the cold anode is cored from the bottom row in the middle pit. It is well documented that the temperature distribution and heat-up rate are not uniform throughout a baking furnace section and pits [5].

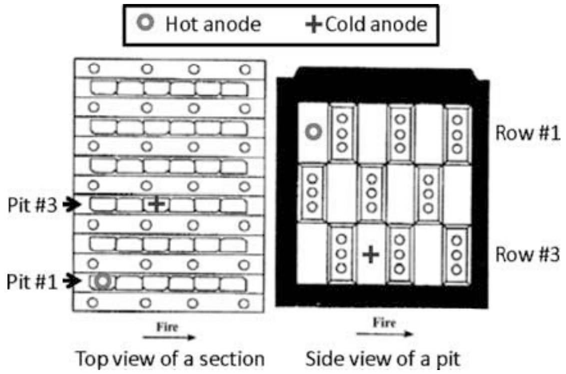

Figure 2. Schematics of a baking furnace section with cored anode position indicated

This sampling strategy was selected in order to monitor the properties of the anodes baked at the two ends of the temperature distribution. This creates two populations of samples that might not be representative of the whole anode produced. Unfortunately, the monitoring procedure does not take into account the two populations by averaging on a weekly basis all the measured properties. One of the best example of this situation is that of the crystallite length (L_C), because the difference in final anode baking temperature causes a difference in crystallinity [6]. Figure 3 shows the L_C values measured from the coldest and hottest anodes as well the weekly averages.

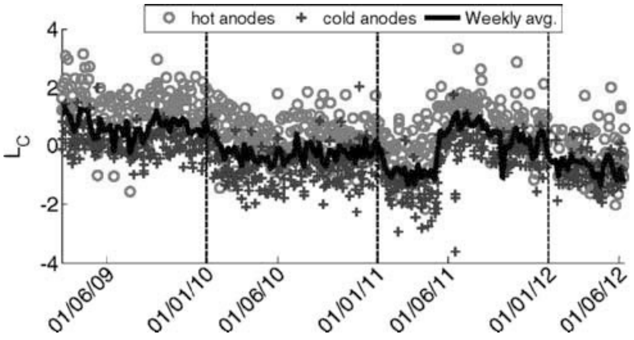

Figure 3. Time series of L_C measured at the coldest and hottest sampling positions within the baking furnace and their weekly averages.

It is obvious in that figure that the averages at each position are different from each other and that the overall weekly averages hide the spread of L_C values. Since the sampled anodes represent the two extremes of the baking process, the assumption that the population mean corresponds to the overall sample average is used, but this has not been verified. Using the averages of the two sampling position can however mask the variability of the anode population especially if this occurs at only one sampling position. The electrical resistivity (ER) is a good example of this situation and is presented in Figure 4.

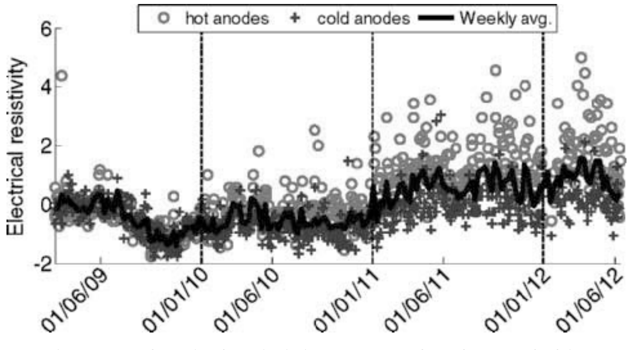

Figure 4. Electrical resistivity measured at the two baking positions and their weekly averages

In this case, there is a major change in the variability of the resistivity in only one of the two sampled position. At the beginning of the analysis period (2009), there was no difference in the two populations. But all of a sudden at the end of 2010 the variance of ER for anodes baked in the hottest position increased sharply. This situation is completely masked by the weekly averages used to monitor the anode properties.

Analysis of variance of electrical resistivity

The standard deviation of the ER measurements shown in Figure 5 for each week, confirms a two to four folds increase in standard deviation in 2011 and 2012. Since only the weekly measurements were used for process monitoring, this situation went unnoticed for a certain amount of time before it was detected and is investigated here.

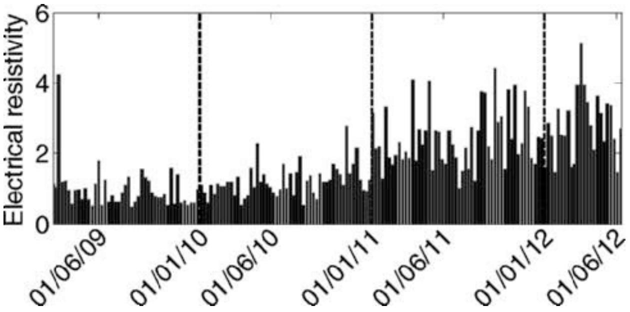

Figure 5. Standard distribution of weekly averages for the electrical resistivity

The results shown in Figure 4 for individual anodes indicate that baking position within the furnace is an important contributor to the variance of ER. It is also possible to notice that the hot anodes produced in 2011 have a systematically higher ER and variance than the cold anodes. Obviously, something changed at the beginning of 2011 to make the anode more sensitive to the baking operation conditions. Except for a few month in 2012, the baking furnace operation conditions were kept constant and no major changes where introduced except the fire cycle time. In the winter 2012 (from mid-January to the end of May) the final baking temperature was lowered for the hot anode position, but the normal conditions were restored in June. The increase in resistivity variance began while the baking furnace operation was constant. Also, when the final baking temperature was lowered, the difference between the hot and cold final anode temperature was smaller but the variance of the hot anode did not diminish. No reasonable explanation could be found in the furnace operation so the multivariate model was used to help investigate the process variables correlated with the increase in ER variance.

The analysis is performed on the same data that was used in [3]. They include the properties of raw materials (i.e. coke, pitch and butts), green mill and baking furnace operating conditions as well as anode sample laboratory analysis. For detailed explanation of the model the interested readers can also refer to [7]. To start this investigation, a contribution plot is used. Contribution plots are commonly used tools in latent variable PLS modeling to highlight the change in process variables that are the most closely associated with a change in anode properties. The two groups of anode used for this analysis are shown in Figure 6.

Figure 7 presents the contribution of each variable to the change in electrical resistivity between anodes produced in 2010 (average of group 1) and those manufactured in 2011-2012 (average of group 2).

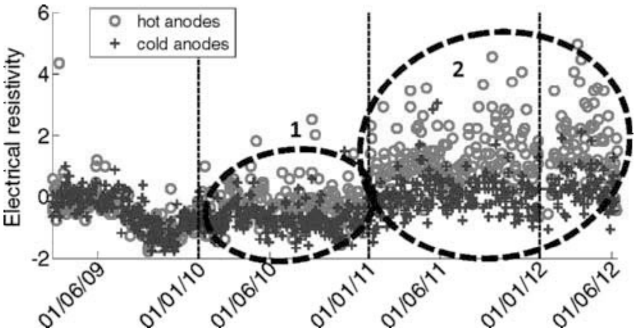

Figure 6. Measured electrical resistivity for individual anodes baked in the coldest and hottest position with the baking furnace

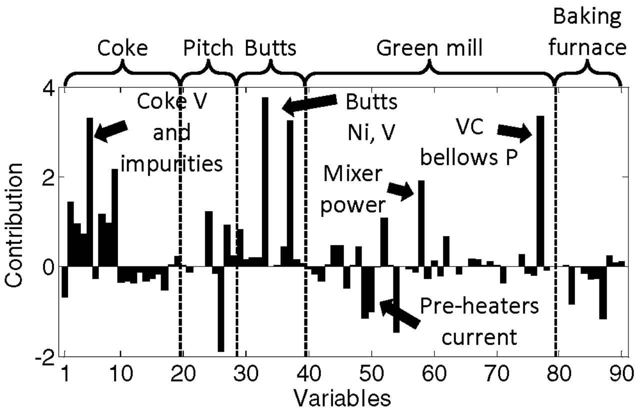

Figure 7. Contribution to change in ER from group 1 to group 2 in Figure 6

For the raw materials, the coke impurities and especially the vanadium content increased. There is no literature on the effect of coke impurities on ER. But there was a change in suppliers at the beginning of 2011 that could be associated with this situation. The different coke and pitch blends used for the past three years are listed in Table I.

Table I. Raw material blends used at ADQ in the past three years

Blend	Starting date	Coke 1	Coke 2	Coke 3	Coke 4	Pitch
1	2009-01-26	A	B	C	-	1
2	2009-04-06	A	B	D	-	1
3	2009-07-27	A	B	D	-	2
4	2009-12-28	C	D	-	-	2
5	2010-07-05	C	E	-	-	2
6	2011-01-17	C	F	-	-	2
7	2011-05-16	C	G	-	-	2
8	2011-10-03	C	G	A	-	2
9	2011-11-28	C	G	A	H	2
10	2012-04-02	C	F	D	-	2

It can be seen that a small increase in variability started in 2010 with the introduction of coke C used in combination with a new type of pitch (#2). The situation got worse with the introduction of coke F but continued even after the coke F was replace by coke G. This leads us to hypothesize that a particular combination of cokes (C plus F or G) and a new pitch may be more sensitive to baking conditions and could contribute to explaining the increase in ER variability (i.e. synergistic effect). The very few coke physical and mechanical properties routinely measured do not allow the confirmation of this assumption. Additional properties, such as the coke electrical resistivity, would help better characterize coke blends and their impact on the manufacture of baked anodes.

Some green mill operating conditions are also important in Figure 7, such as a decrease in the dry aggregate pre-heaters electrical current draw and an increase in mixer power. These changes were not very sharp but occurred slowly over time. Again, this could reflect significant changes in the properties of coke/pitch blends. There was also a step change in the vibro compactor bellows pressure but it occurred in the middle of 2011 and not at the beginning of the variance increase. Even if we cannot identify specific variables, evidences point towards a contribution of raw materials since the variability increase occurred while most of the other process variables were constant. Unfortunately, there are not enough raw material measurements to confirm this diagnostic.

The operating conditions of the baking furnace are now investigated as a potential cause of ER variability. The setpoints of the operating conditions on the fluewall temperature profile and the anode temperature profile were kept constant from 2009 to the end of 2011. So it does not explain the increase in ER variability. At the beginning of 2012, the final anode temperature setpoint and flue wall temperature trajectories were lower for the outer pits (i.e. flues 1, 2, 6 and 7 in Figure 8). The flue wall temperature profiles were left unchanged for the middle pits.

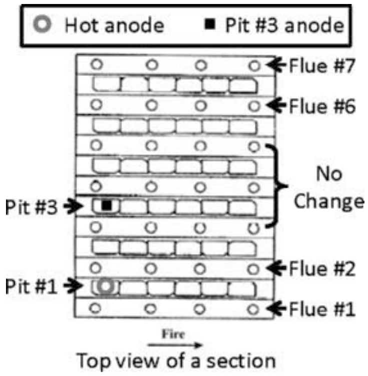

Figure 8. Position of cored anode relative to the change in flue wall temperature profile

For routine operation of the furnace, two anode temperatures are measured on the surface of the anode in the packing coke: the hot cored anode and the first anode on the top row of the pit #3 (i.e. the pit where the cold anode is cored). The effect of this change in process operating conditions lowered the final temperature of the hot anode (in pit #1) but it didn't affect the pit #3 anode and the cold anode final temperature. This situation is demonstrated in Figure 9, where the final anode temperature for the hot anode and for the pit #3 anode is shown.

It is well known that L_C is a good indicator of the anode baking history and is strongly influenced by the final anode temperature [5]. The Lc for individual anodes is investigated in Figure 10 to look for clues associated with changes in baking conditions.

Even with a lower final anode temperature on most hot cored anode there was no effect on the high ER variability. A two to four folds variability increase from the 2009-2010 baseline can still be seen in Figure 5.

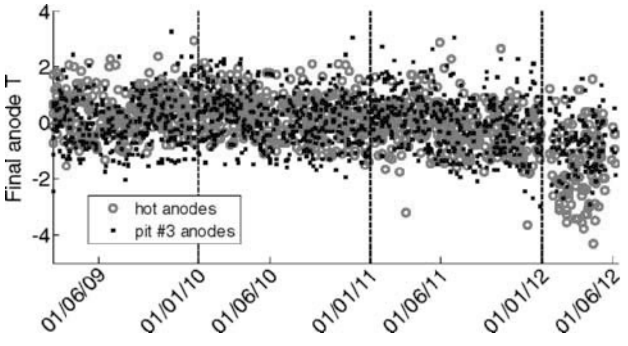

Figure 9. Measured maximum anode temperature for the hot anodes and the pit #3 anodes

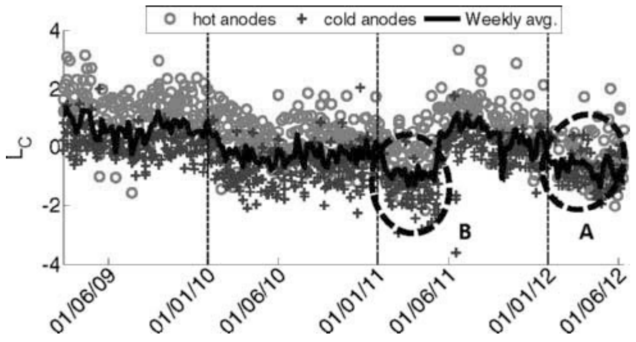

Figure 10. Individual anodes and weekly averages for L_C

In this figure, the individual anodes are also marked by their pit position. The hottest anodes have a systematically higher L_C than the cold anode. This behavior is expected due to the temperature distribution in the furnace. When the final baking temperature was lowered in 2012, the temperature difference between both anode positions was lowered. That is the hot anode final temperature was lower, but not the cold anode. The anodes marked as group A in Figure 10 have a lower hot/cold L_C differences.

A recent pit survey performed in one of the furnace sections confirms the final anode temperature distribution. As can be seen in the Figure 11, the anodes on the top row have a higher final temperature than the anodes on the bottom row.

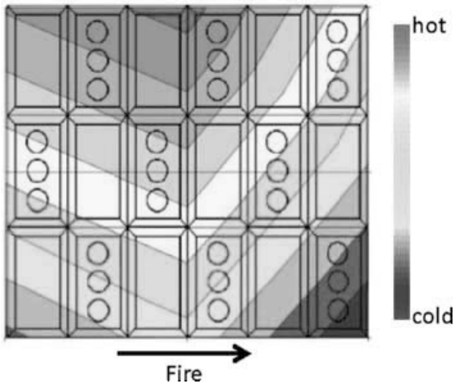

Figure 11. Final anode temperature distribution in one pit during a recent pit survey (Courtesy of Alcoa)

The decrease in anode temperature influenced the L_C but not the ER. This suggests that the increase in the ER variability could be due to other parameters than the final baking temperature alone. A hypothesis is that the heat-up rate during the volatile degassing is not the same throughout each row of the baking furnace and this could cause the hottest anode to endure more thermal stress. This could lead to a higher number of crack formation and increased measured electrical resistivity in the hot anodes (i.e. top rows). Since the heat-up rate is not measured in normal operation, the hypothesis can only be verified during a pit survey. The results are presented on a scaled axis in Figure 12. In the figure, the heat-up rates are plotted every half hour for anode temperatures between 100°C and 500°C.

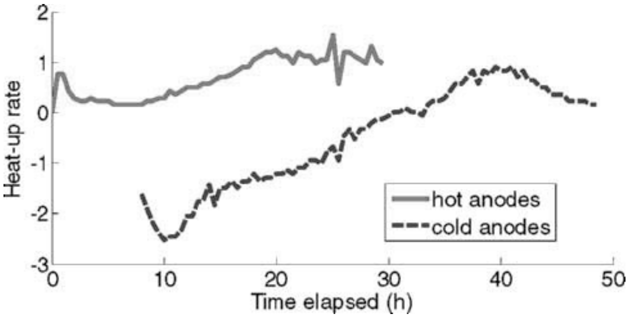

Figure 12. Heat-up rates during degassing of volatiles between 100°C and 500°C for hot and cold anodes (Courtesy of Alcoa)

This figure demonstrates that the heat-up rate during degassing is more severe for the hot anode than the cold anode (i.e. bottom row anodes). Severe heat-up rate can cause volatile pressure build-up in the anodes during the degassing phase and create cracks. As described by Fischer et al. [5], higher heat-up gradients increase the propagation of cracks in the anodes and this causes the standard deviation of the electrical resistivity measurements to increase. The combinations of coke C, F and G and pitch #2 may have been more sensitive to very different heat-up rates.

This analysis demonstrates the importance of not relying only on weekly averages for monitoring the quality of baked anodes. The averages can mask important information like increased variability and differences in the sampling population. There are also some multivariate monitoring tools available to facilitate the investigation. The green mill parameters are well instrumented, but important measurements are probably missing for the raw material characterization and the baking furnace operating conditions.

Analysis of the L_C deviation

Another interesting situation can be observed in Figure 10. There was a sharp decrease in the averaged L_C during winter 2011 (Jan. – May). These anodes are indicated by ellipse B. The high L_C values (hot anodes) have not changed much, but the L_C values of cold anodes have decreased. This situation is investigated using a contribution plot from the anodes in ellipse B to the model average. Results are shown in Figure 13.

For this situation, the variables correlated to the decrease in L_C are the coke real density and the pitch QI. The coke real density and coke L_C are positively correlated [8]. Although the coke L_C is not known the lower coke real density could have an impact on the lower anode L_C. Finally, the high pitch QI has an effect on the coking of the binder pitch by inhibiting the coalescence of mesophase and affecting the crystallite growth [9,10]. The weekly

QI values are presented in Figure 14 where the period with high QI is indicated by the ellipse corresponding to the low L_C period (group B) in Figure 10. This is likely the most obvious cause for this low L_C period. The use of the multivariate model in this case led to rapid identification of the most likely cause for the studied situation.

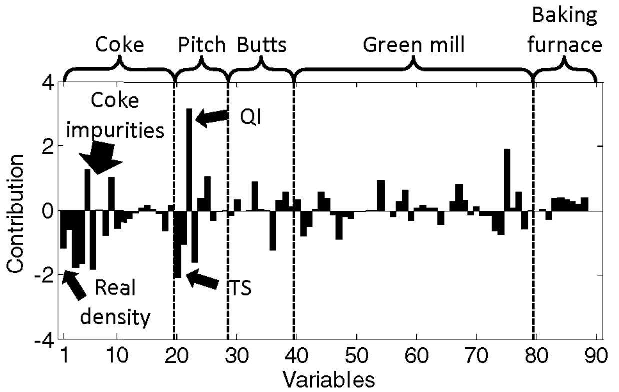

Figure 13. Contribution plot for the lower L_C deviation observed in ellipse B

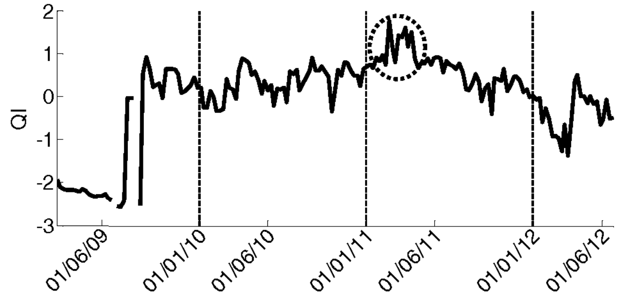

Figure 14. Historical pitch QI levels

Conclusion

The main objective of this paper was to investigate the causes of the increased of electrical resistivity variability. At the same time some shortcoming of the standard anode quality monitoring procedure were highlighted. No precise diagnostic could be made, but empirical evidence point towards certain combinations of cokes and pitch being more sensitive to the distribution of baking conditions in the furnace. Also the increase in measured resistivity is due to cracks formation during baking and these are cause by the heat-up rate during the degassing of pitch volatiles. This hypothesis cannot be verified by routine operation data and further investigation is needed.

While investigating the effect of the sampling location on the L_C, a period with low values of crystallite size was observed. Using the latent variable model, a period of high pitch QI was rapidly identified as the most likely cause.

Finally, the multivariate statistical analysis could be improved by having better data on the raw material properties and the baking furnace operating conditions.

Acknowledgments

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