

CB10 - Introduction of a Vertical Shaft Kiln Coke at Ma'aden Green Mill

Ghanem Al-Osaimi¹, Manoj Kumar Mishra² and Majed Saad Al-Zahrani³

1. Manager-Carbon Technical

2. Senior Engineer-Process Engineering

3. Engineer, Chemical (PDP)

Ma'aden Aluminium Company, Ras Al Khair, Saudi Arabia

Corresponding author: osaimig@maaden.com.sa

Abstract

Due to the floating nature of calcined petroleum coke (CPC) in the marketplace globally in terms of supply and quality, it is always discussed to introduce vertical shaft kiln (VSK) CPC for anode manufacturing and to perform several studies based on trials to apprehend the anode quality as an impact to outline the finest or optimum recipe. This study gives CPC behavior and overall performance contrast of CPC produced with different kinds of calcining technologies (Vertical Shaft and Rotary Kiln) from a process performance, system limitation and product quality perspective. It describes the effect of different blending ratios of coke in the recipe and its effect on the quality to meet product excellence. In alignment with the subject, design of experiment (DOE) has been conducted to study newly introduced calcined petroleum coke performance/behavior within Ma'aden Aluminum (MA) green anode plant. green petroleum coke (GPC) batch selected under this study was calcined through a vertical shaft kiln technology against regular coke used at Ma'aden Aluminium, calcined through rotary kiln technology. Under subject study, CPC behavior with green anode plant, process and equipment will be monitored and observation will be made as response amongst raw material, equipment, operation practice and process parameters.

Keywords: Calcined petroleum coke (CPC), Green petroleum coke (GPC), Vertical shaft, blending, Optimization, Rotary kiln.

1. Introduction

To explore CPC supply for green anode manufacturing at Ma'aden Aluminium, we underwent performance evaluation of CPC calcined through the vertical shaft kiln, where most supplies are from China. At Ma'aden Aluminium we aimed to evaluate the performance of the CPC to maximize green apparent density (GAD) in parallel with baked apparent density (BAD), air permeability (AP), and specific electrical resistivity (SER). The study will also evaluate other baked anode properties made by CPC as supportive performance evaluation for example carboxy reactivity residue, air reactivity residue, compressive strength etc.

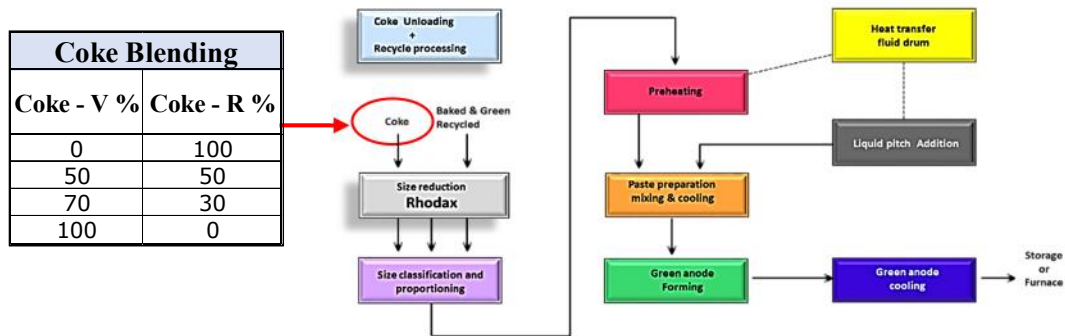
2. Raw Material Selection and Design of Experiment

Ma'aden Aluminum typically uses technology recommended CPC specifications, like other smelters. For the specific trials involving vertical shaft calcined CPC, the first task was to measure and compare the specifications of the CPC to be used in the test. The coke selected for testing was within Ma'aden specification (Table 1). Based on experience and understanding, the green anode formulation is a key factor that determines the behavior and performance of CPC within green anode plant (GAP), as well as properties of the baked anode. The CPC is added to the dry aggregate recipe in a specific mixing ratio as a variable input. Figure 1 summaries the process and DOE model that was followed during the trial.

Table 1. CP coke analysis.

Parameters	VBD	RD	SER coke	-50 mm	+4 mm	-0.25 mm	Sulfur	Vanadium	Nickel	Iron	Silicon	Sodium	Calcium	Phosphorus	lead
UOM	g/cc	g/cc	$\mu\Omega\text{-m}$	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
CPC- Vertical	0.92	2.05	510	100	35	9	2.8	296	176	225	231	51	115	8.5	19
CPC- Rotary	0.88	2.062	-	100	36.89	4.02	2.66	326	199	181	193	60	64	7	-

Process and DOE model overview



Dependent variable response- 1. GAD, 2. BAD, 3. AP, 4. SER.

Figure 1. Process overview with DOE model.

3. Design of Experiment Implementation and Data Collection

To conduct the experiment, it was decided to use each selected blending in a batchwise manner with controlled operation and process parameters and each batch must be tracked with all green and baked anode process parameters having identified storage location at every stage of processing. The following describes the activities and observations made at each stage of the trial.

3.1 Grain Size Distribution (GSD) – CPC

Under this trial, after having selection for coke blending ratio, it was necessary to have coke GSD analysis which can be correlated later with anode properties. GSD is considered one of the key factors in anode manufacturing and it needs to be maintained within control limits. Based on the DOE strategy, Figure 2 represents the actual blending GSD that entered the system. It can be observed from the graph that the increase in percentage of the vertical shaft coke leads to larger particles as compared to rotary kiln coke. Because of the weight load and the compaction in the lower section of a shaft, a degree of agglomeration of the coke grains takes place, increasing the grain size of the CPC produced by vertical shaft kiln [1]. Vertical shaft calcining improves the grain size of CPC produced due to the agglomeration effect and results in lower porosity and higher VBD [1]. GSD comparison of the coke entering green anode plant system shows small variation compared to the CPC supplied as it is very difficult to avoid segregation within the coke storage and handling system which also makes it difficult to maintain the constant GSD throughout the blending. Figure 2 shows the blended CP coke GSD for each blend change.

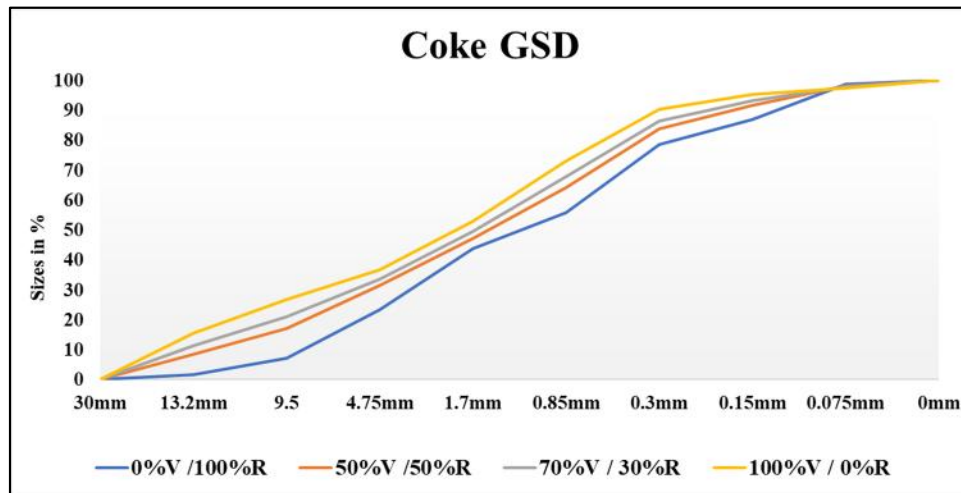


Figure 2. GSD graph of coke entering GAP.

3.2 Grain Size Distribution (GSD) - Dry Aggregate

It is most important to achieve optimum GSD within the anode recipe in anode manufacturing, as it is considered as one of the critical parameters and control for anode properties. It was important at Ma'aden Aluminum to understand the vertical shaft CPC behavior in terms of particle crushing at the crushing system. While performing the study, maximum effort is made to keep the recipe as close for each batch so that deviation caused by such can be eliminated or minimized. After selection of the respective recipe for each CPC blend trial, the system was allowed to operate for a certain duration till the material reaches the anode forming section. Based on observation carried out after anode forming, pitch content (%) with other mixing and forming parameters were set to achieve optimum and stable conditions during production. Table 2 summarizes the anode recipe that was adopted during the study.

Table 2. Green Anode recipe for each blend.

Blending		Recipe		
Coke - V %	Coke - R %	Baked Recycle (butt + scrap BA) %	Green recycle %	Pitch %
0	100	24	6	13.1
50	50	24	6	12.4
70	30	24	6	12.1
100	0	24	6	11.9

After recipe optimization and achieving production stabilization, dry aggregate sampling was conducted to determine recipe GSD. After analyzing GSD result, an increase in coarser particles was observed with an increase in blending % of vertical shaft coke, i.e., dry aggregate GSD was on the coarser side with 100% vertical shaft coke whereas the optimum side with 100% rotary kiln coke. Explained observation can be easily seen with the graphs plotted against the optimum GSD curve for each trial blending. Dry aggregate GSD trends (Figures 3 - 7) explain the variation within the GSD against each blending ratio and it clearly shows the GSD change phenomenon with the change in coke blending in the recipe. The variation in particle size after final crushing in the cone crusher may be attributed to variations in the process coke, i.e., variations in mechanical characteristics such as hardness and density, which can have an impact on crushing performance and result in operational limitations. At this moment of trial, it is difficult to identify the contribution of each factor which requires further study. Furthermore, at Ma'aden it also needs to be understood that only 2 fractions are defined for anode recipe with Rhodax (producing a

recipe based on two size fractions only leading to a drastic flow sheet simplification) [2], which are Grain (> 0.3 mm) & Sand (<0.3 mm) having ultrafine (UF, <0.032 mm) as compared to traditional green anode plant where more fractions are used in the recipe which allows more control over crushed size and proportioning of desired sizing in the recipe. Figures 3-7 show dry aggregate GSD with different coke blending.

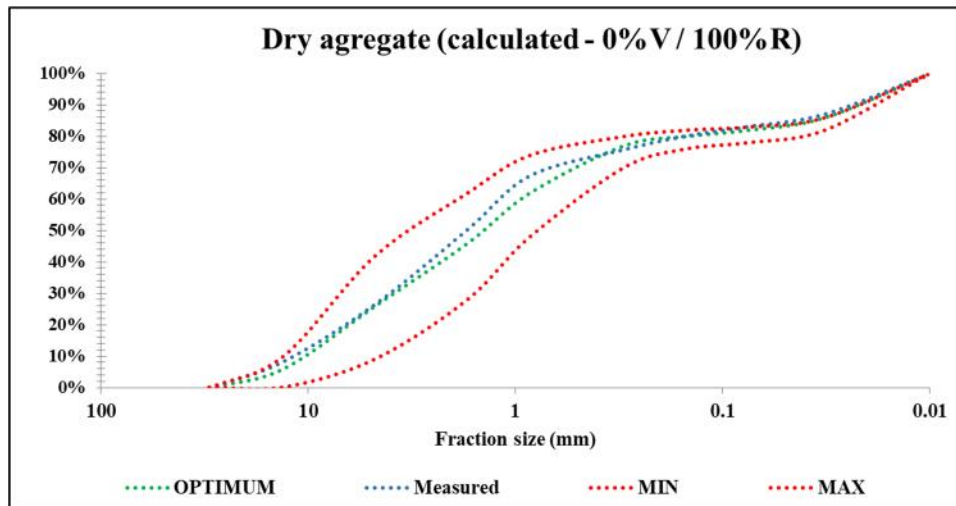


Figure 3. Dry aggregate GSD (CP coke blending 0 %V: 100 %R).

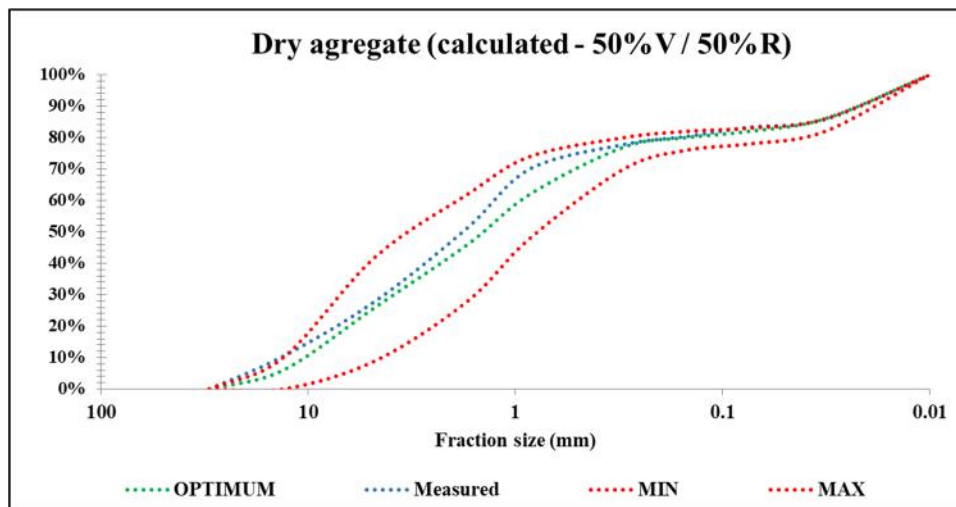


Figure 4. Dry aggregate GSD (CP coke blending 50% V: 50% R).

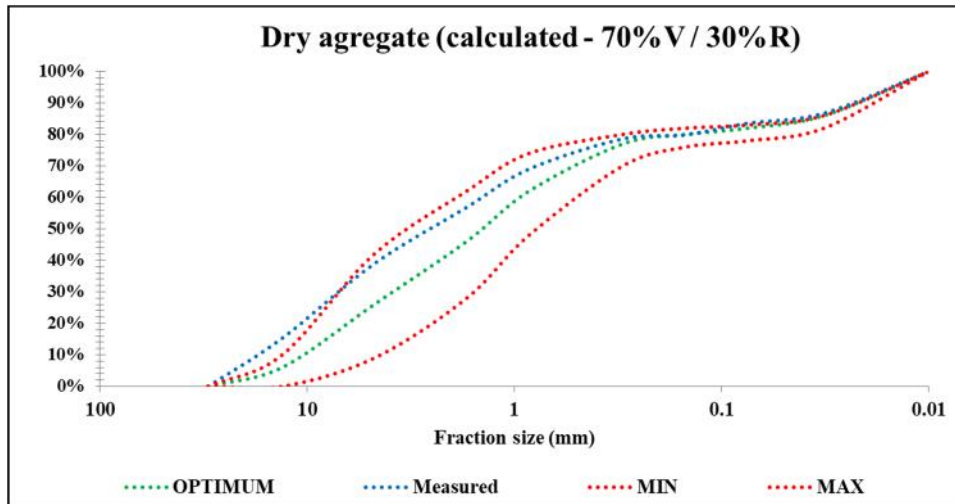


Figure 5. Dry aggregate GSD (CP coke blending 70% V:30% R).

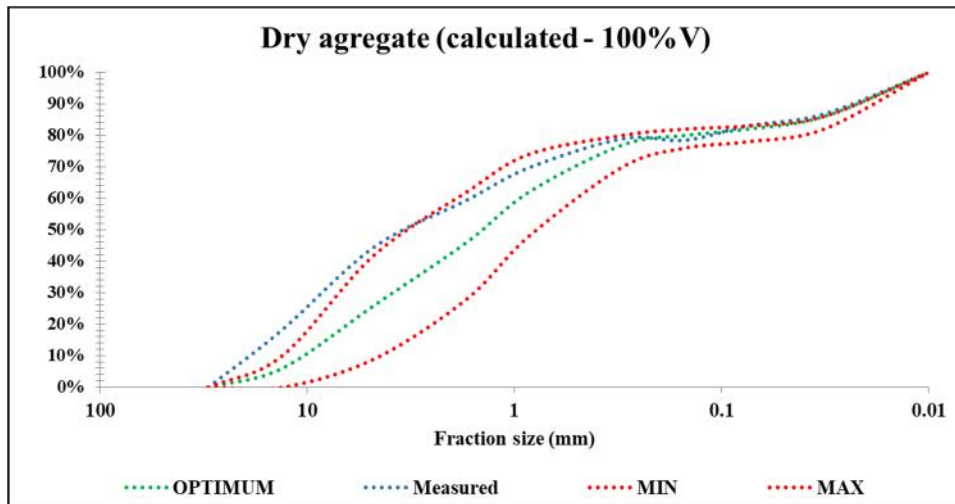


Figure 6. Dry aggregate GSD (CP coke blending 100 %V: 0 %R).

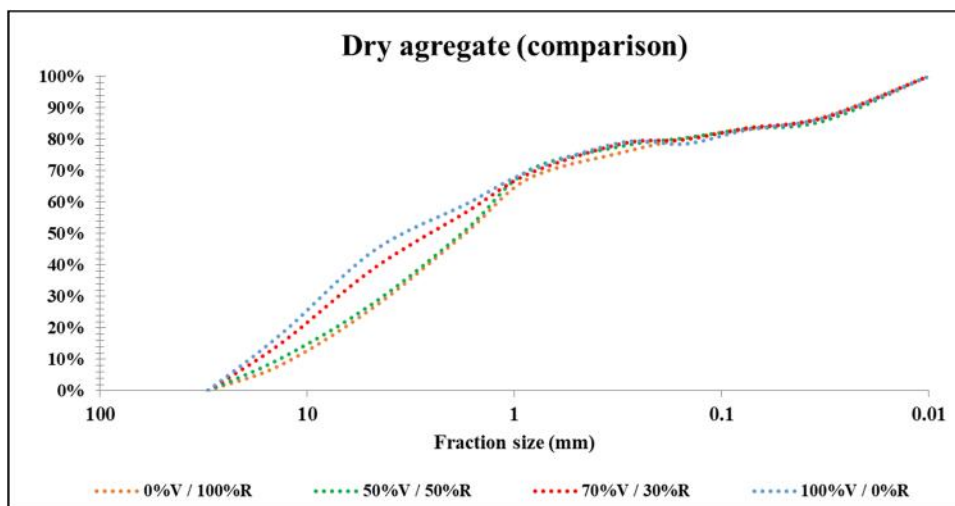


Figure 7. Dry aggregate GSD comparison for different coke blending.

3.3 Green Anode Quality

Each process parameter for the green anode formation was closely monitored during the trial. Table 3 represents the green anode properties of each coke blend. The highest green apparent density (GAD) was achieved by having a controlled process followed by pitch optimization with 100 % regular coke in the recipe. One of the surprising points that was observed was that both coke had VBD close to each other, but when they were used in recipe 100 %, they showed a higher difference in GAD with change in GAD standard deviation.

Table 3. GA property against recipe and blending.

Blending		Recipe		Green anode property				
Coke-V %	Coke-R %	Recycle (butt + scrap BA)%	Pitch %	GAD (kg/dm ³)	Height (mm)	Dry density (kg/dm ³)	Weight (kg)	GAD stdv.
0	100	24	13.10	1.651	681	1.440	1086	0.006
70	30	24	12.40	1.651	680	1.455	1085	0.007
50	50	24	12.10	1.648	679	1.450	1087	0.006
100	0	24	11.90	1.645	682	1.448	1084	0.009

3.4 Final Anode Temperature during Baking Process

Each green anodes trial batch with different coke blending ratio was tracked at anode baking furnace (ABF) and loading was completed on an identified furnace. The complete baking process was monitored for trial batches, from preheating to cooling to maintain baking parameters within strict compliance. All the preheat temperature and under pressure were controlled within the target curves and pitch burn was also inspected at regular intervals. Across all the three anode thermocouples, the final baking temperature was in the range of 1095 Deg C +/- 5 Deg C.

3.5 Data Analysis and Interpretation

On a routine basis we analyse 1% of baked anode at our smelters. During our experiment, we considered collecting more samples to better our understanding of anode quality. Approximately 5% of the anode samples from each trial batch were collected. 15-18 samples were chosen from each trial batch, representing anodes from all three anode layers in a pit, including the outside pits. The sampled batch was then stored in a designated location within the storage area. Later, the anode casting was conducted in alignment with the anode change schedule to provide a controlled supply of cast anodes for the reduction process. All the baked core analysis was performed at Ma'aden smelter laboratory to collect anode quality information for each batch of anode produced through different blending. Anode quality data has been statistically analyzed using ANOVA (Statistical analysis of variance). ANOVA tests the hypothesis that the means of two or more populations are equal. ANOVA assesses the importance of one or more factors by comparing the response variable means at the different factor levels. The null hypothesis states that all population means (factor level means) are equal while the alternative hypothesis states that at least one is different. Table 4 shows trial baked anode properties whereas Figures 8-10 shows ANOVA outcome for AP, SER and AD, for coke blending, respectively.

Table 4. BA property with blending change.

Parameters	0% V - 100% R	50% V - 50% R	70% V - 30% R	100% V - 0% R
Apparent Density (kg/dm ³)	1.589	1.599	1.577	1.55
Electrical Resistance (μΩ.m)	51.1	54.5	54.3	59.7
Air permeability (nPm)	0.66	0.90	1.29	1.97
CO2 reactivity Residue - (%)	93.7	92.9	90.2	89.5
Air reactivity Residue - (%)	74.9	74.8	71.1	71.7
L _c (Å)	31.6	31.9	31.4	31.5
Compressive Strength - (MPa)	47.5	43.7	41.7	39.4

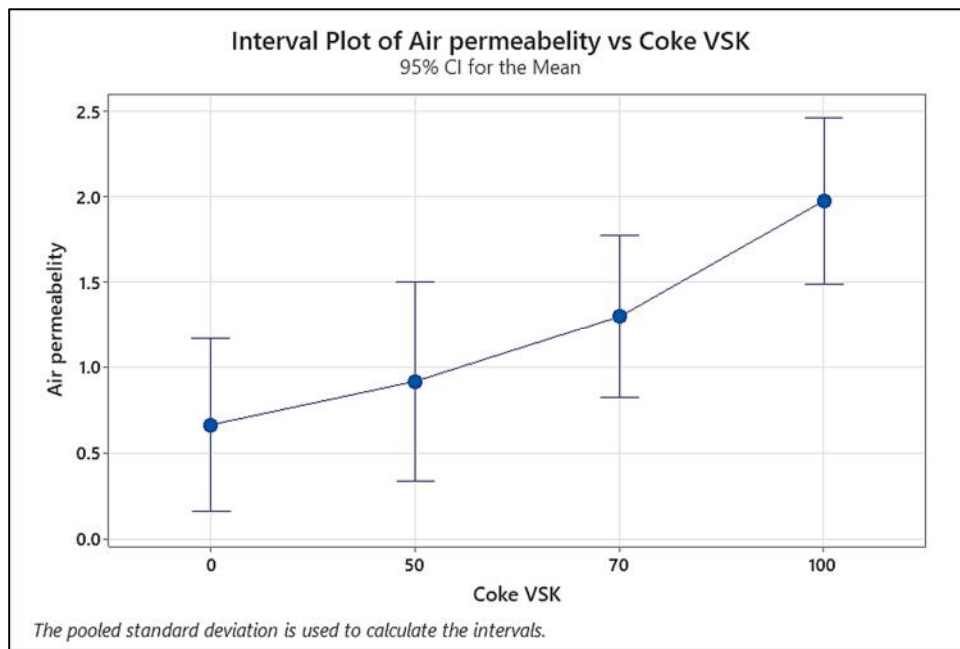


Figure 8. One-way ANOVA: Air permeability versus VSK blend.

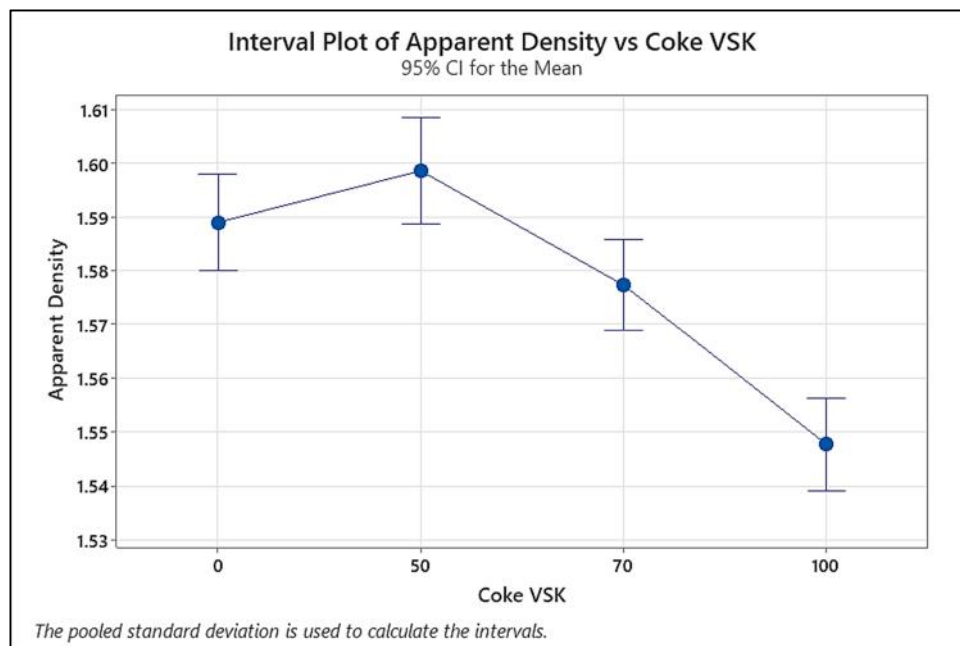


Figure 9. One-way ANOVA: Apparent Density versus VSK blend.

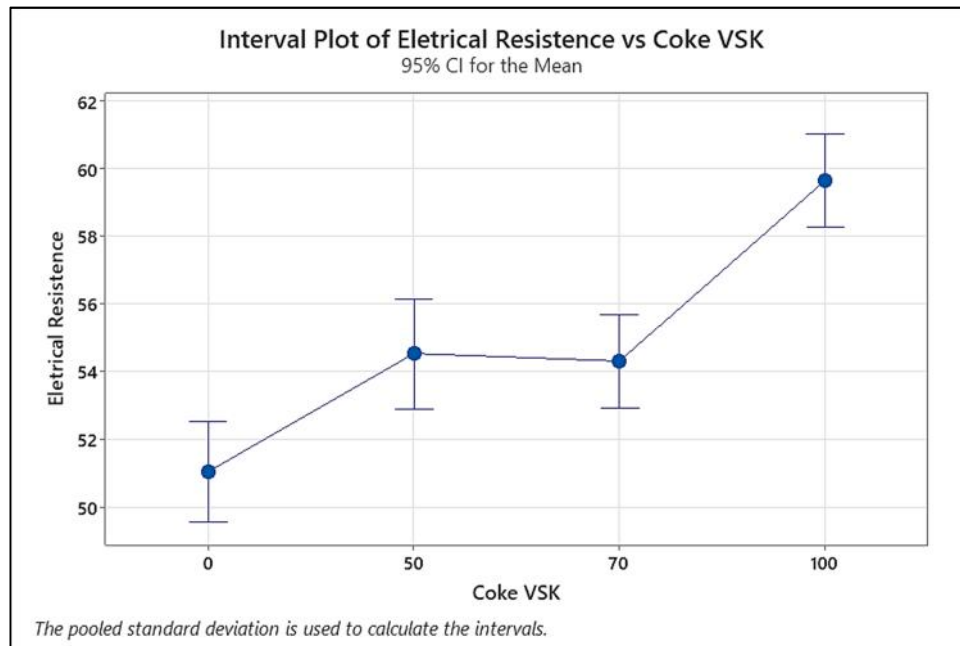


Figure 10. One-way ANOVA: Electrical Resistance versus VSK blend.

4. Design of Experiment (DOE) Summary

To determine whether any of the differences between the means are statistically significant, we compared the p-value to our significance level to assess the null hypothesis. A p-value is the probability of obtaining an effect at least as extreme as the one in the sample data, assuming the truth of the null hypothesis. The significance level (denoted by alpha or α) is the maximum acceptable level of risk for rejecting the null hypothesis when the null hypothesis is true. Usually, a significance level (denoted as α or alpha) of 0.05 works well. A significance level of 0.05 indicates a 5 % risk of concluding that a difference exists when there is no actual difference. Assuming an equal means null hypothesis and a significance threshold of 0.05, all p-values in this study are less than the critical value of p-value = 0.05 or $F_{obs} > F_{crit}$, causing us to reject the null hypothesis.

When all test batches are compared, this implies that the alternative hypothesis is correct, and the test batch cannot repeat statistically equivalent mean or anticipated outputs when the mixing ratio is changed on the upper side. Ma'aden's upper limit for AP is surpassed with a combination of 70 % and 100 %, which is undesirable. Additionally, reducing the amount of vertical coke in the formulation by 50 % improved results without any equipment or process changes. Table 5 shows the mean variance for baked anode properties and the mean difference between each blending.

5. Observations

During the trial, sample batches did not contain over-pitched or over-baked anodes since pitch optimization was undertaken with controlled baking parameters. Variation in anode properties is linked to the green apparent density and anode paste homogeneity. The factors contributing to density variation include CPC properties, interaction with plant equipment, anode recipe, dry aggregate GSD. The distribution of the specific electrical resistance in an anode shows the level of homogeneity [3]. This was observed during our trial as:

Table 5. Baked properties with ANOVA comparison for each blending.

Test Rank	Parameter	Blend % (VSK)	Mean	Stdv.	Mean differs from test rank based on alpha (p) value		
1	Air permeability (nPm)	0	0.7	0.2	3	4	-
2		50	0.9	0.6	-	-	-
3		70	1.3	0.9	1	-	-
4		100	2.0	1.6	1	-	-
1	Apparent Density (kg/dm ³)	0	1.589	0.0163	4	-	-
2		50	1.599	0.0176	4	3	-
3		70	1.577	0.0186	4	2	-
4		100	1.55	0.0193	3	1	2
1	Electrical resistance (μΩ.m)	0	51.1	1.7	2	3	4
2		50	54.5	1.9	1	4	-
3		70	54.3	2.3	1	4	-
4		100	59.7	4.5	1	2	3

Based on the trial findings and observations, the following are a few proposed points for future studies that have showed improvements:

1. Reduction in max size of vertical shaft coke as raw material to 30 mm instead of 50 mm respecting all other fraction within Ma'aden specification. This trial also can be taken into consideration to avoid larger vertical shaft coke in system and to achieve more medium and intermediate fraction.
2. Reduction of cone crusher (Rhodax) output crushing size by maintaining the optimum gap of 18 - 19 mm. The recirculation of particle size greater than 25 mm instead of 30 mm for crushing will be the next step as a trial which can minimize deviation within GSD. Such changes will have an impact on crusher output rate, which may slow plant throughput, so an optimum rate needs to be established.

6. Conclusions

It has been observed from above statistical analysis that the introduction of vertical shaft calcined coke on higher ratio with rotary calcined coke during the trial was not able to reproduce the baked anode properties in the range of optimum accepted level as well as in the range of running average. With the current system, every change in coke blending ratio (vertical shaft coke) impacts the baked anode properties, a higher vertical shaft coke % in the recipe further deteriorates the anode property. This study shows that due to the nature of the two different cokes properties and considering green anode plant equipment (technology) which have limited control over fractioning in a recipe, a lower percentage of vertical shaft coke can be used in a recipe, as 30 % on the safer side with limiting to max 50 % having few adjustments on process and recipe parameter. A few more tests can be done with major changes to the system to see the effect of increased vertical shaft coke on the anode quality. It is also important to consider that blending capability limits can be eliminated either by reducing shipment size or by having additional silo capacity installed.

7. References

1. Oscar Mascarenhas et al., Petroleum coke shaft calcining technology - salient features of construction and production techniques, *Proceedings of 33rd International ICSOBA Conference*, Dubai, United Arab Emirates, 29 November - 1 December 2015, *Travaux* 44, 409-419.

2. Christophe Bouché et al., CB07 - The First Rhodax Green Anode Plant in China, *Proceedings of the 39th International ICSOBA Conference*, 22 - 24 November 2021, Virtual, *TRAVAUX* 50, 591-603.
3. Yasar Kocafe, Duygu Kocafe, Dipankar Bhattacharyay, Quality control via electrical resistivity measurement of industrial anodes, *Light Metals* 2015, 1097-1102.