The Effect of Varying Mixing and Baking Temperatures on the Quality of Pilot Scale Anodes – A Factorial Design Analysis

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Abstract

Identifying optimum anode baking and mixing temperatures are important when producing high quality anodes. The effect of varying mixing and baking temperatures were investigated in terms of the resulting anode density, specific electrical resistivity (SER), air permeability, coefficient of thermal expansion (CTE) and air and CO_2 reactivity. Six pilot scale anodes were prepared at Hydro Aluminium AS using a single source petroleum coke and < 2 mm coke fractions. A coal tar pitch was used with a Mettler softening point of 119.1 °C. The aggregate was mixed at 150 °C or 210 °C, and baked at 1150 °E, 1260 °E or 1350 °E. A 2^2 full-factorial design analysis was performed in order to determine the response of the analyzed properties to the applied mixing and baking temperature. Density, SER and air permeability were found to be highly dependent on the mixing temperature. Density and SER was also slightly affected by the baking temperatures. CTE was found independent of both the baking and mixing temperature. Air reactivity was found to be mainly dependent on the baking temperature, while CO_2 reactivity was dependent on both mixing and baking temperature. The use of the factorial design as a statistics tool is strong when investigating the effects and covariance of various production parameters.

Keywords: Carbon anodes; effect of mixing temperature; effect of baking temperature; anode performance; factorial design.

1. Introduction

Aluminum is produced according to the reaction described in Equation 1 [1].

$$2Al_2O_3 + 3C = 4Al + 3CO_2 \tag{1}$$

Carbon anodes serve as the carbon source on the left-hand side of the equation. The carbon anodes are produced from calcined petroleum coke, and coal tar pitch serve as the binder. The aluminum industry always strive to improve the production of carbon anodes in order to improve cell stability and lifetime of the anodes. As the anodes are consumed, they need to be changed every 22-28 days. Anode change is part of the routine work in a potroom, and causes temporary instability in each individual cell. Hence, good anode quality is crucial to maintain stable operation and optimize lifetime of the anodes [1]. High density, low electrical resistivity, low impurity level, low permeability and low air and CO_2 reactivity are all parameters that characterize a high quality anode. Optimization of carbon anodes rely on many different production parameters such as mixing temperature, baking temperature, coke and pitch quality, aggregate composition etc. The optimum baking and mixing temperatures are dependent on the coke and pitch qualities used [2].

The Mettler softening point of the pitch is commonly used as a standard guideline for selection of the proper mixing temperature between coke, pitch and butts. Most commonly, the mixing temperature is set approximately 50 °C above the Mettler softening point [3]. However, studies using the sessile drop technique show that an even higher temperature may be needed in order to optimize the wetting angle between the coke and the pitch, and that the wetting angle between coke and pitch is dependent on both the pitch itself and the coke substrate [4, 5]. Wilkening [2, 6] has suggested using mixing temperatures as high as 350 °C in order to improve anode density, SER and strength.

During the heating part of the baking process, the pitch binder is carbonized to pitch-coke with release of 20-40 wt% of volatiles [7]. Porosity is introduced to the anodes during the baking process due to the carbonization and the volatilization processes. This porosity is inevitable but can be reduced by good baking furnace design with good temperature control, low ΔT throughout the furnace and by using a slow heating rate [8, 9]. A target baking temperature also needs to be found, as overbaking can cause desulfurization and hence increased microporosity of the anode [9]. Jentoftsen et al. [10] suggested that underbaked anodes caused lower anodic current efficiency in the potroom.

1.1. Factorial Design as a Statistical Tool

Factorial design is a statistical tool that allows investigation of the effect of many factors simultaneously, provided that these factors are independent [11]. The 2^2 full factorial design is the simplest of its kind. The 2^2 nomenclature denotes two factors varied at two levels [12]. In the present experimental design, the two factors varied are mixing temperature and baking temperature. The two levels are a high and low value. For the mixing temperature, the high level is 210 °C and the low level is 150 °C. Baking temperature was varied on three levels (1150 °E, 1260 °E and 1350 °E, where °E denotes equivalent temperature – a measure of calcination level commonly used by Hydro to describe the baking level of an anode. More on the technique is described elsewhere [13, 14]). The statistical analysis was performed as three 2^2 full factorial designs, by treating the baking temperature in pairs, with three low and high levels i.e.: 1150 °E (underbaking) vs. 1260 °E (target baking), 1260 °E (target baking) vs. 1350 °E (overbaking) and 1150 °E (underbaking) vs. 1350 °E (overbaking). In factorial design analysis, it is common to use the term "main factor" [11] on the factors that are varied, hence mixing temperature (A) and baking temperature (B) are the two main factors. The low values are denoted -1 and the high values are denoted +1. Table 1 shows the three 2^2 factorial design setups that are investigated in this work.

Table 1. The three 2^2 factorial design setup with main factors A (mixing temperature) and B (baking temperature), and -1 indicating low levels and +1 indicating high levels.

Prod. param.		Main factor		Prod. param.		Main factor		Prod. param.		Main factor	
T_{Mix}	T_{Baking}	A	B	T_{Mix}	T_{Baking}	A	B	T_{Mix}	T_{Baking}	A	B
°C	°E			°C	°E			°C	°E		
150	1150	-1	-1	150	1260	-1	-1	150	1150	-1	-1
210	1150	1	-1	210	1260	1	-1	210	1150	1	-1
150	1260	-1	1	150	1350	-1	1	150	1350	-1	1
210	1260	1	1	210	1350	1	1	210	1350	1	1

The effects on anode quality when varying the main factors are investigated through physical properties testing including density, specific electrical resistivity, air permeability, coefficient of thermal expansion, air and CO_2 reactivity. Each physical property is termed a "response" of the main factor [11], where density = y_1, SER = y_2, permeability = y_3, CTE = y_4, CO_2 reactivity = y_5 and air reactivity = y_6. The effect of each main factor is calculated according to Equation 1.

$$\text{Effect} = \frac{\sum y_+}{n_+} - \frac{\sum y_-}{n_-} \tag{1}$$

Equation 1 simply states that the effect of a main factor A or B is the average of the high responses subtracted by the average of the low responses. n is the total number of data collected at each level [11].

The interaction effect, AB, between the main factors A and B is calculated by averaging the positive AB responses and subtracting the average negative AB responses [11]. In this factorial design setup, the positive AB responses is from line one and four in Table 1 (since -1*-1=+1 and +1*+1=+1). The interaction effect helps determine if one factor or the other, or a combination of the two affects the responses of the experimental setup.

2. Experimental

2.1. Pilot Anode Materials

A pilot anode line (Ø = 130 mm, h = 180 mm) of six different anodes was prepared by Hydro Aluminium AS in Årdalstangen. A single source industrial sponge coke of anisotropic character was mixed with an industrial grade coal tar pitch. The coal tar pitch had a Mettler softening point of 119.1 °C and a QI level of 7.8 %. The particle size of the coke aggregate was 0-2 mm and this small-scale aggregate was chosen in order to ensure homogeneity between samples in small-scale laboratory experiments. The coke aggregate recipe was kept constant between the pilot anodes, while mixing and baking temperatures were varied. A vibroformer was used and the anode paste was transferred directly from the mixer to the vibroformer with minimum time delay in between and a short temperature equilibration time.

2.2. Physical Analysis of the Anodes

The anodes were characterized using industry ISO methods as summarized in Table 2. These test methods are considered as standard methods at Hydro. Only one test was performed for each sample. The reproducibility within a lab and between labs are indicated in Table 2. These numbers are given in the ISO standards. No data on the reproducibility is available for the CO_2 reactivity and air reactivity since these are in-house methods developed by Hydro. However, it is to be expected that the reproducibility of these tests are high. This implies that it is relevant to perform a statistical factorial design analysis on the basis of the present figures (shown in Tables 3-5) and that the variance seen between the physical properties between the six samples are a result of the production parameters.

Table 2. ISO standard methods used when characterizing the pilot anodes.

Physical property	ISO standard	r*	R**
Density	12985-1:2000	0.004	0.008
SER	11713:2000	1.2	1.5
Air perm.	In-house method at Hydro comparable to 15906:2007	0.03	0.13
CTE	14420:2005 (temp.range extended to 300-700 °C)	0.1	0.17
R_{CO2}	In-house method at Hydro comparable to 12988-1	N/A	N/A
R_{Air}	In-house method at Hydro comparable to 12989-1	N/A	N/A

*Reproducibility within-lab

**Reproducibility between-labs

3. Results and Discussion

Tables 3-5 show the anode production parameters with corresponding raw data physical properties for the three factorial design setups demonstrated in Table 1. The 2^2 factorial design setup is indicated with main factors A (mixing temperature) and B (baking temperature), and standard notation -1 indicating low levels and +1 indicating high levels.

Table 3. Underbaking vs. target baking. Anode production parameters and corresponding physical properties (y_n) of these anodes.

Prod. param.		Main factor		y_1	y_2	y_3	y_4	y_5	y_6
T_{Mix} °C	T_{Baking} °E	A	B	Density g/cm^3	SER µΩm	Perm. nPm	CTE µm/mK	R_{CO2} mg/cm^{2}h	R_{Air} mg/cm^{2}h
150	1150	-1	-1	1.502	73.4	6.88	4.1	14.7	46.3
210	1150	1	-1	1.584	60.3	1.27	4.12	13	47.9
150	1260	-1	1	1.526	65.1	5.31	3.93	17.5	41.5
210	1260	1	1	1.576	59.7	1.4	4.07	15	48.1

Table 4. Target baking vs. overbaking. Anode production parameters and corresponding physical properties (y_n) of these anodes.

Prod. param.		Main factor		y_1	y_2	y_3	y_4	y_5	y_6
T_{Mix} °C	T_{Baking} °E	A	B	Density g/cm^3	SER µΩm	Perm. nPm	CTE µm/mK	R_{CO2} mg/cm^{2}h	R_{Air} mg/cm^{2}h
150	1260	-1	-1	1.526	65.1	5.31	3.93	17.5	41.5
210	1260	1	-1	1.576	59.7	1.4	4.07	15	48.1
150	1350	-1	1	1.554	60.4	3.18	4	18.5	29.8
210	1350	1	1	1.598	57.4	1.66	4.03	16.5	26.9

Table 5. Underbaking vs. overbaking. Anode production parameters and corresponding physical properties (y_n) of these anodes.

Prod. param.		Main factor		y_1	y_2	y_3	y_4	y_5	y_6
T_{Mix} °C	T_{Baking} °E	A	B	Density g/cm^3	SER µΩm	Perm. nPm	CTE µm/mK	R_{CO2} mg/cm^{2}h	R_{Air} mg/cm^{2}h
150	1150	-1	-1	1.502	73.4	6.88	4.1	14.7	46.3
210	1150	1	-1	1.584	60.3	1.27	4.12	13	47.9
150	1350	-1	1	1.554	60.4	3.18	4	18.5	29.8
210	1350	1	1	1.598	57.4	1.66	4.03	16.5	26.9

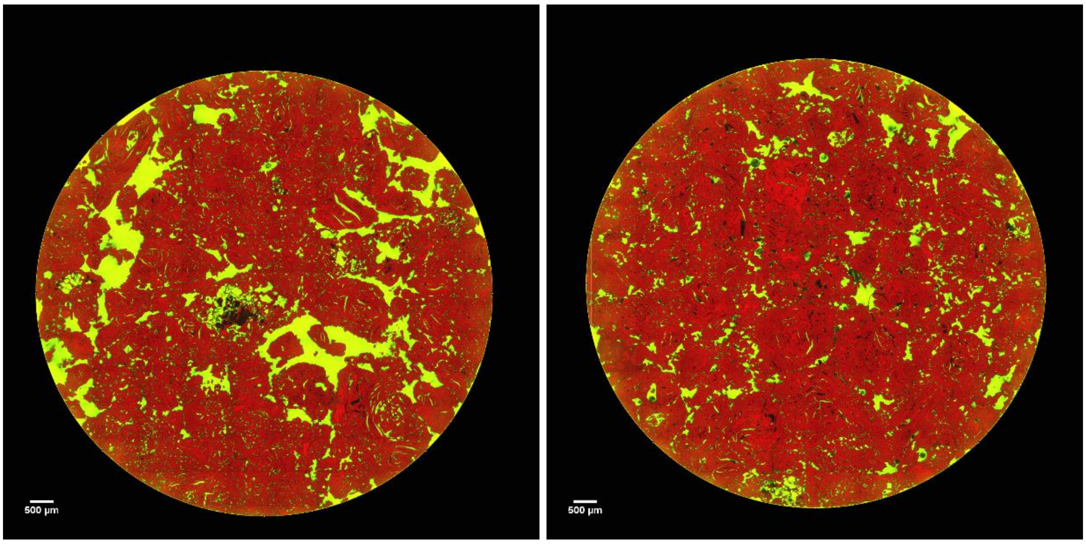

Figure 1. Optical microscopy image of anode samples mounted in fluorescent epoxy. Pores filled with epoxy appear yellow and carbon matrix appear red. The image to the left shows the anode with low mixing temperature and target baking temperature. The image to the right shows the anode with high mixing temperature and target baking temperature.

Figure 1 shows the visual effect of mixing temperature on the porosity in the anodes. This difference in porosity affects air permeability and SER directly, as shown in Table 4 and Figure 2. Figure 2 shows the effect of mixing temperature and baking temperature on the physical parameters density, specific el. resistivity and air permeability. Figure 3 shows the effect of mixing temperature and baking temperature on the coefficient of thermal expansion, CO_2 reactivity and air reactivity. The left column shows underbaking vs. target baking, the middle column shows target baking vs. overbaking and the right column shows underbaking vs. overbaking.

A steep slope between low and high level of mixing temperature indicates a high effect of mixing temperature on the physical properties. Density, air permeability and CO_2 reactivity show a steep slope between low and high mixing temperature. Density increases and air permeability decreases with higher mixing temperature. Specific el. resistivity also decreases somewhat with higher mixing temperature. Both the decrease in air permeability and SER are related to the increase in density. A higher mixing temperature is clearly beneficial in terms of density, air permeability and SER.

A large difference between the two graphs indicate a large effect of baking temperature on the physical property. In Figure 2, the difference in physical properties between high and low baking temperatures is not significant, except when comparing underbaking and overbaking. This is true especially at the low mixing temperature level indicating that low mixing and low baking temperatures give a particularly poor quality anode, as expected, with low density, high SER and high air permeability.

In Figure 3, a fairly large difference is observed between the graphs of CO_2 and air reactivity, indicating a high influence of baking temperature on these physical properties. CO_2 reactivity increases with higher baking temperature and intuitively this could be argued to be due to some release of sulfur from the coke structure during baking as described in literature [9]. Sulfur is a known inhibitor to CO_2 reactivity as it forms inactive metal-sulfur complexes with metal catalysts [15]. However, the coke used in this work is a low sulfur coke (< 1 %, found by XRF, ISO 12980:2000) and low sulfur coke has shown low "puffing" effect and little release of sulfur at the temperatures operated with during the baking process [15]. Additionally, in Figure 2, an increase in density is observed at increasing baking temperature, also for the anodes that are so-called overbaked (at 1350 °C). This also implies that little sulfur is released during the baking, since desulfurization would cause increased microporosity in the coke structure and lower final density of the anode. CO_2 reactivity decreases with higher mixing temperature, indicating a covariance between CO_2 reactivity and anode density.

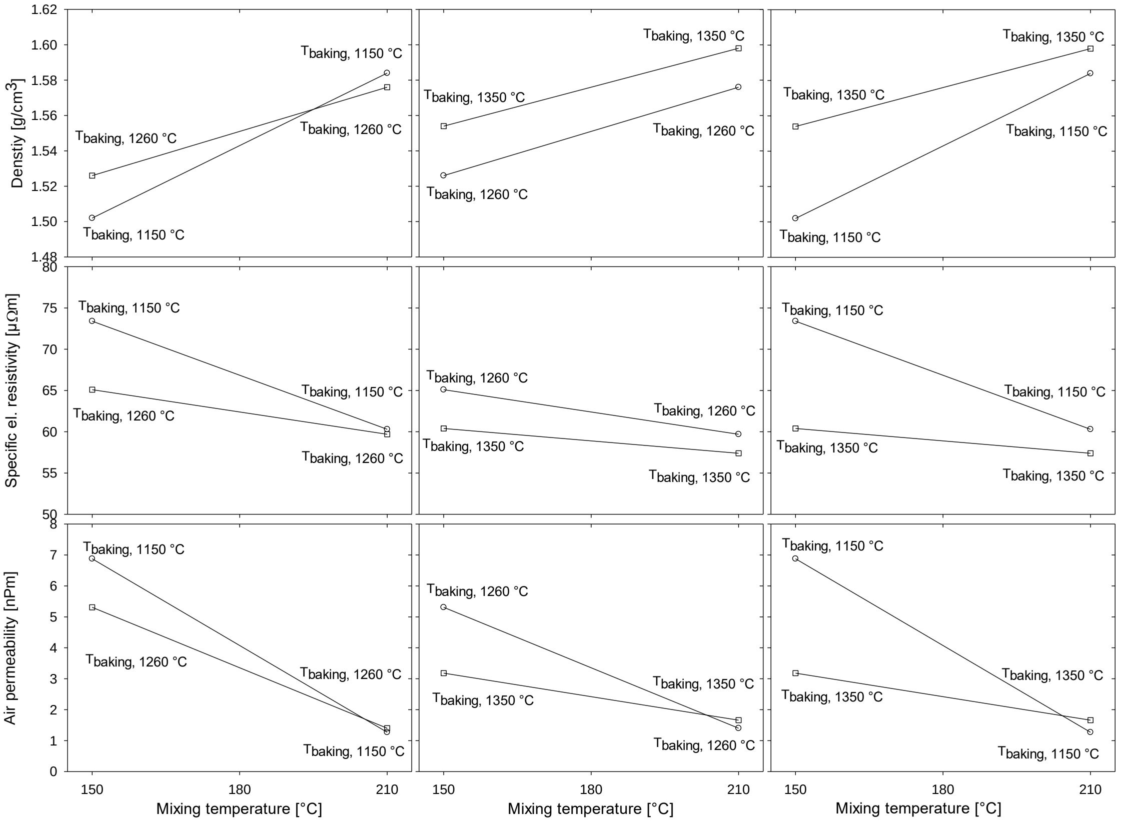

Figure 2. Interaction of mixing temperature vs. baking temperature on the physical parameters density, specific el. resistivity and air permeability.

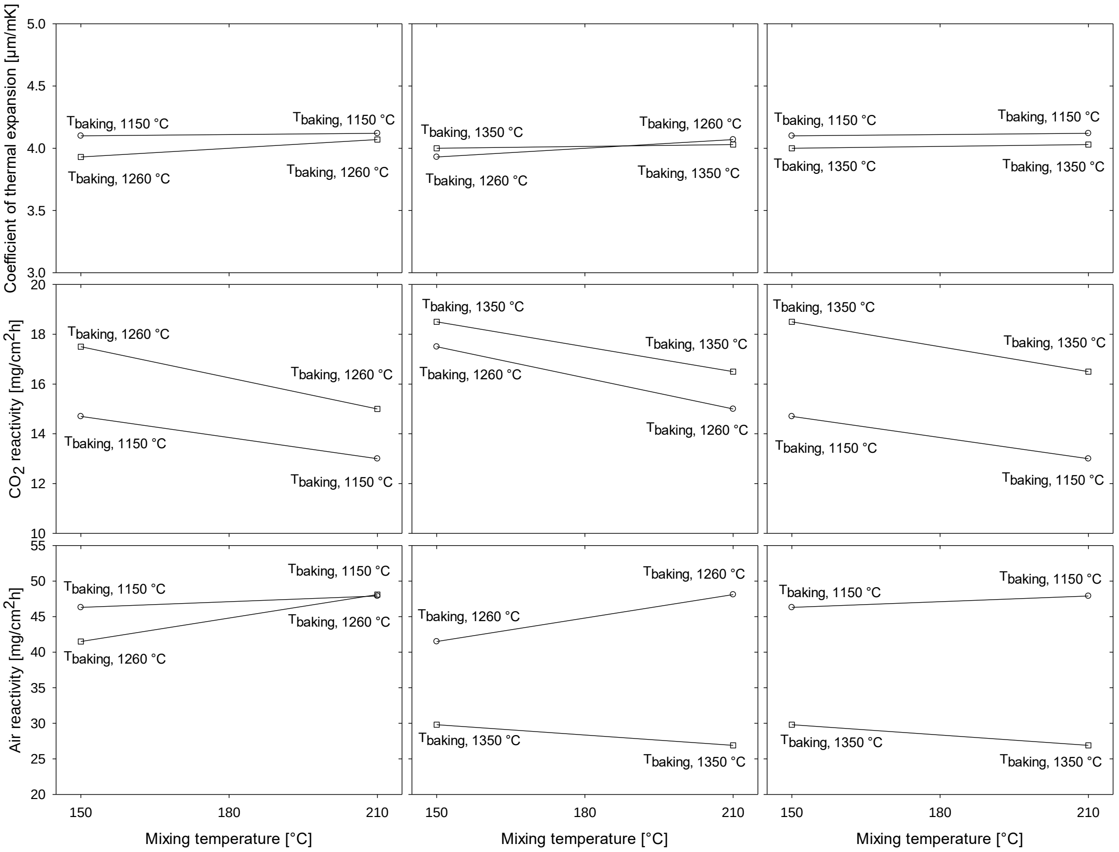

Figure 3. Interaction of mixing temperature vs. baking temperature on the physical properties coefficient of thermal expansion, CO_2 reactivity and air reactivity.

The effect of main factors A and B, namely mixing temperature and baking temperature can be calculated using Equation 1. Tables 6-8 show the calculated effects of main factors A and B and the interaction effect AB for the three factorial design setups demonstrated in Table 1. When investigating Tables 6-8, it is clear that mixing temperature is a factor that determines the output density to a much larger degree than the baking temperature. Also, the interaction effect is rather small between mixing and baking temperature. However, for SER, both mixing and baking temperature is affecting the output property. The interaction effect is also rather high. Mixing temperature is important in controlling the density, as seen visually in Figure 1. A higher baking temperature is beneficial for the SER supporting the argument that little sulfur is released from the coke structure. Air permeability is also strongly affected by mixing temperature, and a higher mixing temperature decreases the permeability.

No significant difference is seen between the high and low baking and mixing temperatures for coefficient of thermal expansion. CTE is clearly not affected by either mixing or baking temperature suggesting that CTE is a raw material property, mainly the coke.

Both mixing and baking temperature is affecting the CO_2 reactivity. However, the interaction effect is rather low. A higher mixing temperature lowers the CO_2 reactivity, while a higher baking temperature increases the CO_2 reactivity. As observed in Figure 1, the lower mixing temperature gives larger and more pores compared to when using a higher mixing temperature. A large open porosity will increase CO_2 reactivity due to an increased exposed surface area. Additionally, at the same binder level, the higher mixing temperature will spread the binder better and thinner between and within coke particles. This usually leads to higher coke yield of the binder coke and gives better protection against CO_2 attack of exposed surfaces inside the anode.

Air reactivity is strongly affected by baking temperature, as shown in Figure 3 and Tables 7 and 8, however, for the underbaking vs. target baking case, the mixing temperature also appear to affect the air reactivity. Air reactivity decreases with higher baking temperature suggesting that some metal complexes are released from the coke structure upon heating. Vanadium is a known metal airburn catalyst as it destabilize the metal structure of the surrounding carbons [16]. Since the mixing temperature is not affecting the air reactivity significantly, this indicates that other factors such as metal impurity concentration is more important than porosity and exposed surface area.

Pareto charts [11] created of the absolute values of the effects of A and B, and interaction effects AB are shown in Figure 4. The Pareto chart helps visualize which effects are most important for each physical property underlining the discussion above.

Table 6. Underbaking vs. target baking. Effects of main factors A and B, and interaction effect AB on the various physical parameters.

	y_1	y_2	y_3	y_4	y_5	y_6
	Density g/cm^3	SER μΩm	Perm. nPm	CTE μm/mK	R_{CO2} mg/cm^{2}h	R_{Air} mg/cm^{2}h
Effect of A	0.066	-9.25	-4.76	0.08	-2.1	4.1
Effect of B	0.008	-4.45	-0.72	-0.11	2.4	-2.3
Interaction effect AB	-0.016	3.85	0.85	0.06	-0.4	2.5

Table 7. Target baking vs. overbaking. Effects of main factors A and B, and interaction effect AB on the various physical parameters.

	y_1	y_2	y_3	y_4	y_5	y_6
	Density g/cm^3	SER μΩm	Perm. nPm	CTE μm/mK	R_{CO2} mg/cm^{2}h	R_{Air} mg/cm^{2}h
Effect of A	0.047	-4.2	-2.715	0.085	-2.25	1.85
Effect of B	0.025	-3.5	-0.935	0.015	1.25	-16.45
Interaction effect AB	-0.003	1.2	1.195	-0.055	0.25	-4.75

Table 8. Underbaking vs. overbaking. Effects of main factors A and B, and interaction effect AB on the various physical parameters.

	y_1	y_2	y_3	y_4	y_5	y_6
	Density g/cm^3	SER μΩm	Perm. nPm	CTE μm/mK	R_{CO2} mg/cm^{2}h	R_{Air} mg/cm^{2}h
Effect of A	0.063	-8.05	-3.565	0.025	-1.85	-0.65
Effect of B	0.033	-7.95	-1.655	-0.095	3.65	-18.75
Interaction effect AB	-0.019	5.05	2.045	0.005	-0.15	-2.25

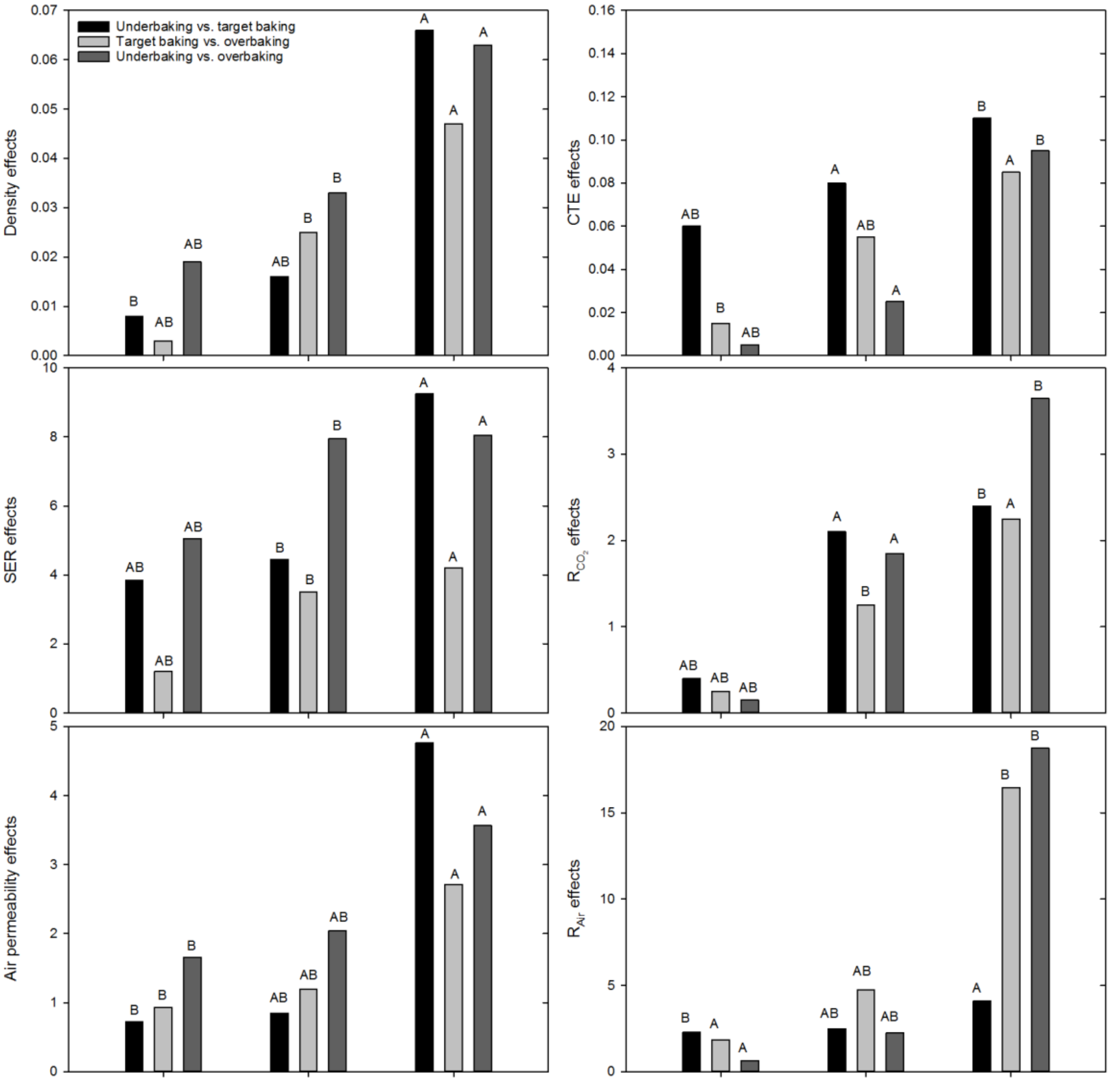

Figure 4. Pareto chart showing effects A, B and interaction effect AB for all three cases.

4. Conclusion

By factorial design analysis, it has been shown that density and air permeability was highly affected by the mixing temperature – a higher mixing temperature increased the density and decreased the air permeability. A higher baking temperature was beneficial to the density, but the effect was smaller than that observed for mixing temperature. Air permeability was not affected by baking temperature to a large extent and the interaction effect between baking and mixing temperature was also low. Specific electrical resistivity was affected by both baking and mixing temperature and the interaction effect between the mixing and baking temperatures was fairly high. This is directly mirroring the increased density observed both when increasing the mixing and baking temperature. Coefficient of thermal expansion was not affected by either mixing or baking temperatures, suggesting that the coke quality determines this property. CO_2 reactivity was affected by both mixing and baking temperatures; however, the interaction effect was low. Increased open porosity has a negative effect on CO_2 reactivity as it gives increased reaction sites for CO_2 in the carbon matrix. Air reactivity was highly affected by baking temperature.

Factorial design helps visualize which production parameter affects the physical properties, and if any interaction between the production parameters can be seen. Factorial design can and should be used further by industry to help optimize anode production parameters; however, good planning of the experiments is crucial for experiments to be successful.

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