CB14 - Superior Sensitivity of Blaine Method Compared to Sieving Analysis of Ultrafines

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Abstract

One of the most critical components of the aluminium reduction technology is the carbon anode. For the manufacturing of prebaked anodes several process steps have to be optimally combined to obtain high quality anodes including an optimal recipe. In the carbon paste plant the petroleum coke and the butts are sieved, crushed, weighed, and preheated. The required fines fraction is produced by milling the petroleum coke. Experience shows that the consistency of the fines fineness is crucial to ensure good carbon anode quality. The Blaine value corresponds to the external specific surface area characterizing the fines fineness. It is indirectly determined by measuring the air permeability of the fines powder bed. This paper describes the Blaine method as a rapid, reliable and accurate test as a key process parameter in the carbon paste plant. In fact, the data of Aluminum of Greece show that the Blaine method has a sensitivity being 3 times superior as compared to the sieving analysis of the ultrafines < 32 µm.

Keywords: Paste plant, carbon anodes, fines fineness, Blaine value, ultrafines, process control

1. Introduction

The production of aluminium is carried out in electrochemical cells. The Hall-Héroult process consists of the electrolysis of alumina (Al_2O_3) dissolved in a bath of molten cryolite (mostly Na_3AlF_6) at approximately 960 °C, high amperage, and low voltage [1]. The current is passed through immersed carbon anodes and flows to a layer of molten aluminium formed at the carbon cathode surface. Steel bars imbedded in the cathode blocks carry the electricity to the next cell.

The electrochemical reaction of the aluminium production is the following:

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

The carbon anodes used in the aluminium industry are consumed during the electrolysis as shown in Equation (1). The primary raw materials of an anode are calcined petroleum coke (CPC) as the dry aggregate and coal tar pitch (CTP) as binder. Anode recycled material, i.e. anode butts, remaining after the electrolysis together with green and baked scraps are also added in the recipe. Typically, prebaked anodes are made of approximately 60 % CPC, 15 % CTP and 25 % recycled material. The anode manufacturing process flow starts with the paste production. First, the dry aggregate is prepared, preheated and mixed with pitch. The paste is then compacted, and green anodes are formed by vibrocompacting or pressing. Finally the anodes are baked and rodded embedding the steel stubs into the anode [2].

Thus, the dry aggregate is composed of different fractions of CPC and butts previously sieved and crushed according to a defined recipe line, optimized for the highest possible apparent density. The butts particles compose the coarse fraction while the medium and fine fractions usually consist of CPC particles [3]. The fineness of the fines and its percentage in the dry aggregate are known to be decisive for the pitch demand of the paste.

2. Aluminium of Greece Reduction and Anode Plant Facilities

The smelter of Aluminium of Greece (AoG) was constructed with technology from Pechiney and started up in 1966 with an initial Al production capacity of 72,000 tons per annum (tpa). Today, three potlines are in operation with a total production capacity of 184,000 tpa. The green anode plant was constructed in 1966 also based on technology from Pechiney. The targets of the production and dosage of fines in the dry aggregate were adapted towards less but finer fines in the recipe, aiming to minimize the risks of anode block thermal shock cracking.

A detailed testing of the anode properties has shown that the variabilities of key-properties were below the benchmark, including the specific electrical resistance and flexural strength. The green anode blocks weight range was above 3 %.

Therefore, a complete technical assessment of the entire chain of the anode production from the raw materials storage to the rodding shop was performed to identify the root causes of the above mentioned anode deficiencies. In this paper, the status quo of the fines preparation and of the pitching in the green paste is addressed. Eventually the potential adaptations of the grain fractions preparation and of the ball mill circuit are considered aiming to squeeze the variability of the green anode production.

2.1 Green Anode Production and Variability

With a throughput of 17 t/h and a scrap rate of 4 %, the green anode plant at AoG has a nominal capacity to produce 101,000 tpa of green anodes. Several studies have shown that recipe parameters and in particular the granulometry influence different aspects of the anode quality [4].

The Figure 1 shows, in blue, the evolution of the daily mean green anode density (GAD) from October 2022 to March 2023. It also illustrates the evolution of the pitch content over the same period. The pitch content varied from 13.2 % up to 14.1 %. The GAD oscillates from 1.67 kg/dm^3 down to 1.62 kg/dm^3. The benchmark of GAD range is about 3 times lower and this with no noticeable drift to guarantee a constant anode block weight and height.

The excessive variations in GAD observed in Figure 1 are induced by several factors such as the raw materials properties. Certainly, the absence of blending facilities leads to GAD variations so that about half of the observed variability can be attributed to the different CPCs. The other half is related to the dry aggregate preparation and especially the fines characteristics, i.e. by the fines percentage in the recipe and its fineness, as well as to the pitch content in the green anodes. These variations in the GAD induce variations on the baked anode density disturbing the pot operations.

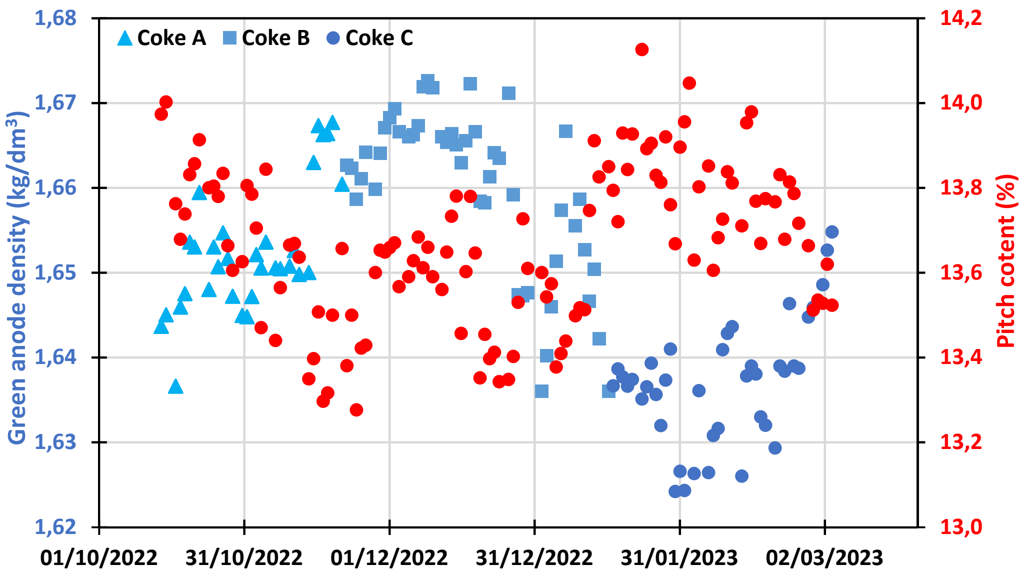


Figure 1. Daily mean of green anode density (blue) and pitch content (red) evolution from October 2022 to March 2023.

The average and ranges of GAD, pitch content and rejected green anode blocks are summarised in Table 1.

Table 1. Green anodes production parameter at AoG.

Process Parameters	**Average**	**Range**
Green Anode Density (kg/dm^3)	1.65	0.07
Pitch Content (%)	13.7	0.9
Rejected Green Paste & Blocks (%)	4	3

The green anodes are rejected when cracks or grain segregation are visible on the anode surface for instance. The green scrap rate, consisting mainly in green paste, was (4.0±1.5) % during the studied period from October 2022 to March 2023. Appropriate pitching and good temperature control are the keys for reducing the green rejects.

2.2 Dry Aggregate and Fines Preparation

The dry aggregate is composed by different fractions of CPC and butts previously sieved and crushed according to a defined recipe line, optimized for the highest possible density. The butts particles compose the coarse fraction while the medium and fine fractions consist of CPC particles [5].

The Figure 2 shows the simplified flow diagram of AoG's paste plant.

At AoG, different fractions are routed to the ball mill feed. As shown in Figure 2, the overflows of coke coarse, i.e., (6 – 1.25) mm, and medium, i.e., (1.25 – 0) mm, fractions are fed into the ball mill. Optimally, the ball mill feed should be crushed and screened to a consistent sizing to avoid variation in the ball mill product [6].

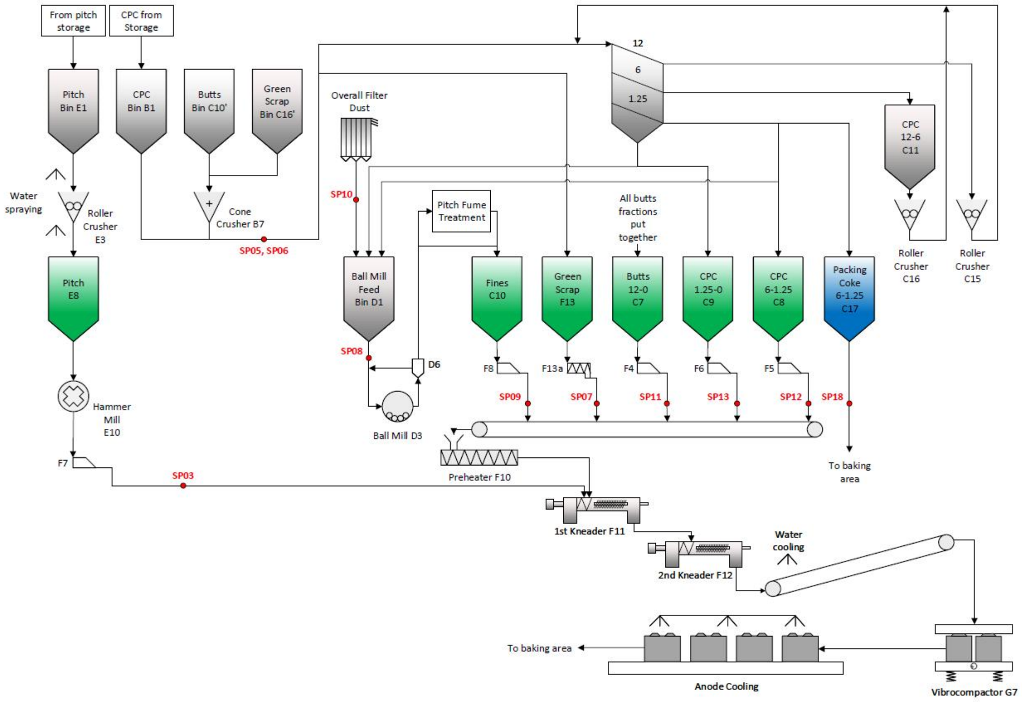


Figure 2. Paste plant flow diagram of AoG.

The ball mill is a large rotating tube containing steel balls crushing the grains to fines (cf. Figure 3). A static air-classifier combined with a cyclone and a filter separate and collect the fines particles while the larger particles are recycled to the ball mill circuit.

Figure 3. Ball mill and static classifier at AoG.

3. Testing the Fines Fineness

3.1 The Sieving Method

AoG controls the fines fineness by measuring the quantity of particles < 32 microns (µm) measured by air forced sieving in the Pan 200 Mesh (75 µm) material obtained by a mechanical sieving machine. Eventually this is reported as the fines < 32 µm present in the total dry aggregate fed to the downstream paste production. The repeatability of this methodology is 0.5 % abs., i.e., 4 % rel. in the case of AoG dry aggregate.

The fines percentage and the target of fines < 32 µm in the dry aggregate recipe is given in Table 2. The philosophy behind these setpoints definitions is to operate with an elevated fineness and relatively low fines percentage in the dry aggregate recipe. The fines content in the dry aggregate was defined to be 25.5 % and the target for the quantity of particles < 32 µm in the recipe was set at 14 %. Despite the relatively low fines content, the target of the fines < 32 µm is rather conventional, underlining the rather high level of fineness of the fines expected from the ball mill circuit.

Table 2. Fines and ultrafines (< 32 µm) content targets in AoG's dry aggregate recipe.

Target settings	**Content (%)**
Fines content in the dry aggregate	25.5
Ultrafines (< 32 µm) content in dry aggregate	14

The Figure 4 illustrates the high scatter of the daily values of the air jet sieving analysis on the fines < 32 µm measured in the dry aggregate from October 2022 to March 2023. The defined target of the percentage < 32 µm, i.e., 14 %, cannot be achieved, which makes the process control problematic. This unsteadiness of the fines production process disturbs the green anode production and contributes to the GAD variations.

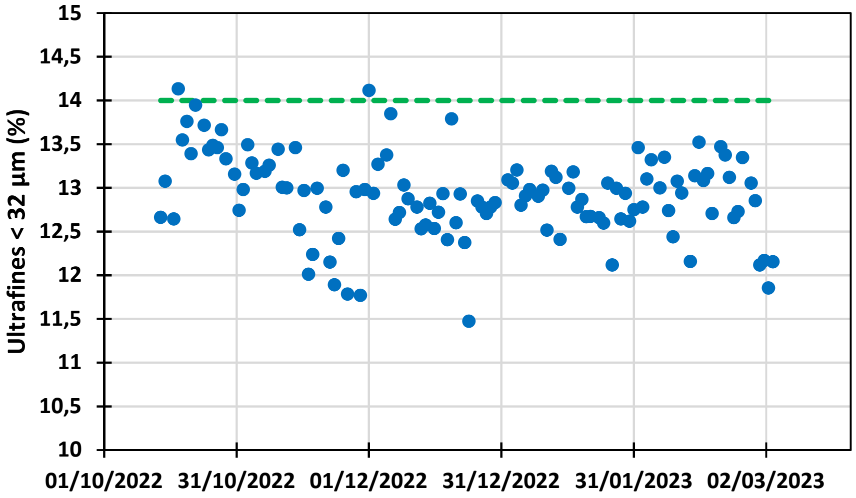


Figure 4. Actual ultrafines (< 32 µm) in the dry aggregate (●) and target (- - -) at AoG.

The sieving methodology is rather cumbersome as it consists in a combination of mechanical sieving with a 75 µm sieve followed by air jet sieving with a 32 µm sieve on the passed 75 µm material. Fines showing the same percentage of fines < 32 µm might have different distribution below this size, especially according to the variability of the fineness of the much finer filter fines. Therefore, a methodology giving valuable information on the surface area of the fines was contemplated at AoG.

The optimum anode formulation is one of the biggest challenges faced by the anode manufacturers, especially with the determination of the appropriate pitch requirement. The fines fineness and content in the dry aggregate recipe substantially influence the anode production and resulting properties. The following sections introduce an alternative method for measuring the fines fineness to improve the process control of the green anode production.

3.2 Testing the Fines Variability: The Blaine Method

In collaboration with R&D Carbon Ltd., a Blaine measuring apparatus was installed at AoG's paste plant to control the fines fineness and assess the ball mill operation. This study relates the implementation of the Blaine value as a key process control parameter in the paste plant of AoG.

The ball mill product and the filter fines are often added together to form the combined fines in the dry aggregate. This fraction contributes to more than 90 % of the total dry aggregate surface area, as shown on Figure 5. It largely impacts the optimum binder requirement of a given dry aggregate during the green anode production as well as the overall anode quality and performance. It is of first importance to ensure stable fineness of any fines of the dry aggregate and to monitor it.

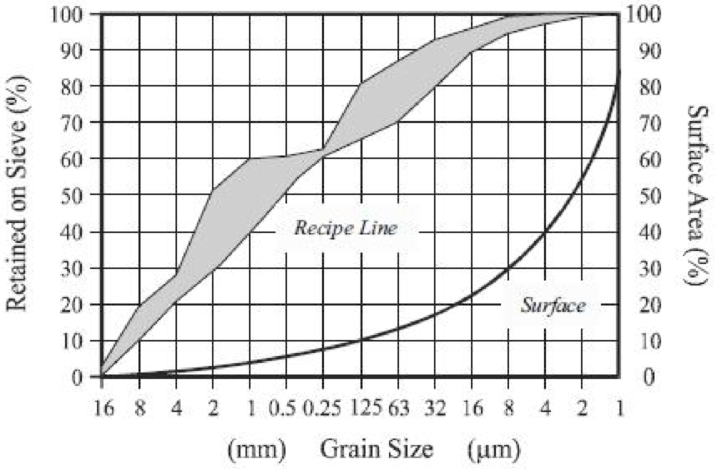


Figure 5. Recipe line size distribution and surface area [7].

3.2.1 Principle of the Blaine Method

This fineness can be measured by the determination of the Blaine number which corresponds to the external surface area of the fines [8]. The fines fineness of a sample is determined by a comparative method. The time required by a certain volume of air to pass through a fines sample and the volume of the sample bed are measured. This time is compared to the time required for a reference material having a certified fineness level. This comparison yields the fines fineness (or Blaine Number), expressed in Blaine units (BL) equivalent to cm^2/g.

The external specific surface, S, is determined using a comparative technique whereby a standard with a known value, S', is used for calibration purposes allowing subsequent measurements of unknown samples to be made [9]. In 1943, Blaine derived the Darcy's law and the Carman-Kozeny equation considering a bed of constant real density, σ, and given porosity, ε, where the seepage velocity, μ, is proportional to a given measuring time, t, so that:

$$\frac{S}{S'} = \frac{\sigma' \cdot \sqrt{\mu'} \cdot (1-\varepsilon') \cdot \sqrt{\varepsilon^3} \cdot \sqrt{t}}{\sigma \cdot \sqrt{\mu} \cdot (1-\varepsilon) \cdot \sqrt{\varepsilon'^3} \sqrt{t'}} \tag{2}$$

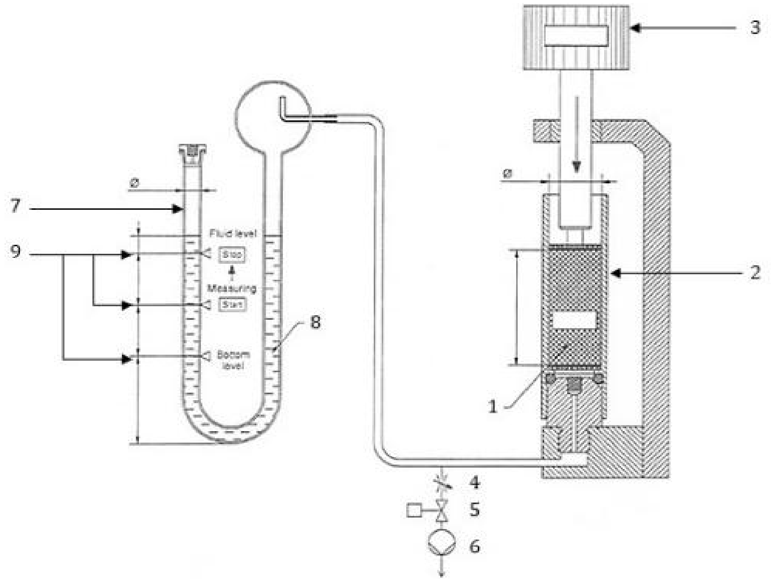
where:

S	Specific surface or Blaine number [cm^2/g]
σ	Real density [kg/dm^3]
μ	Seepage velocity [m/s]
ε	Porosity [-]
t	time required to pass a fixed volume of air through the powder bed [s]

Additionally, to its reliability and speed [10], one important advantage of the Blaine method is to perform the analysis on a representative sample of fines that composes the dry aggregate recipe. With the Blaine method the entire fines fraction of the dry aggregate is measured whereas with the air jet sieving method only the ultrafines are considered.

3.2.2 Description of the Equipment

The Figure 6 illustrates the Blaine value measuring apparatus.



1	Fines sample	2	Sample Holder	3	Frame with load
4	Flow control valve	5	Soleinoid valve	6	Vacuum pump
7	U-Tube	8	Measuring fluid	9	Level detectors

Figure 6. Illustration of the Blaine value measuring apparatus.

The apparatus consists of a powder permeability unit equipped with a membrane vacuum pump. The permeability cell consists of a sample holder into which the fines are filled, and a load piston. The load piston, which is capped with a perforated disc to let the air pass through the entire bed surface, moves at a given speed. This piston applies a given constant load on the sample.

The U-tube manometer, with position sensors as shown in Figure 6 is filled with a non-hygroscopic fluid of low viscosity. The connection to the vacuum pump can be closed by a valve, which then leads to a decrease of the vacuum by air flowing through the test specimen due to its air permeability. Thereby, the time taken by the fluid to flow in between two levels inside the U-tube can be measured.

3.2.3 Description of the Measuring Procedure

The methodology developed by R&D Carbon Ltd. maintains constant pressure and sample quantity regardless of the fines apparent density, the latter dropping substantially for finer fines. The apparatus measures the pressed density of the sample bed and the amount of time taken to equalize the pressures on the U-tube drawing air through the powder bed. The Blaine value is calculated according to the Equation 2.

4. Fines Variability at AoG

4.1 Blaine and Sieving Methods: Testing Results

The Blaine value of the fines composing the dry aggregate was measured at AoG from October 2022 to March 2023. In Figure 7, the results of the Blaine value evolution at AoG's paste plant are presented and compared to the percentage of fines in the dry aggregate with particle size < 32 µm obtained by air jet sieving on the same samples.

The Blaine value varied from 3,200 Blaine up to 5,600 Blaine. The average Blaine value was 4,800 ± 1,000 Blaine. This relative variability of 20 % drastically contrasts with the 7 % relative 2σ of the results obtained with the < 32 µm sieving method.

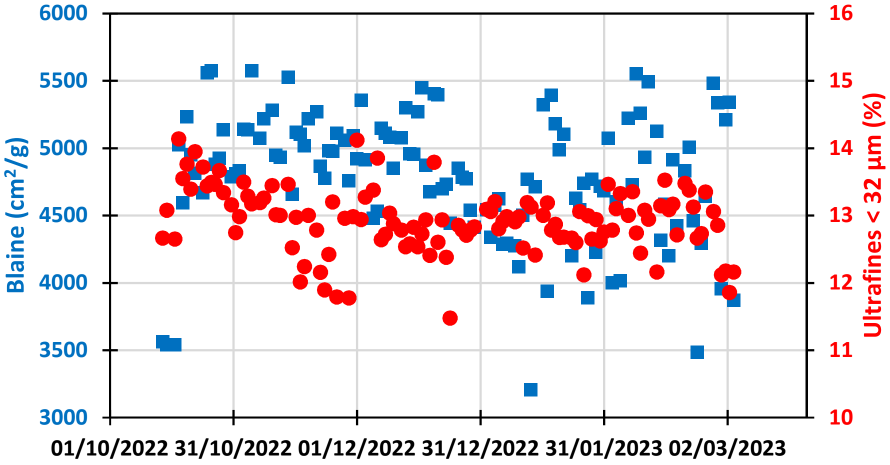


Figure 7. Blaine value (■) and ultrafines (< 32 µm) percentage (●) evolutions at AoG.

By employing the Blaine method to control the process of fines production, the sensibility is enhanced by a factor 3 compared to the sieving method. This allows the process engineers to better control the ball mill operation and anticipate the pitch requirement evolution.

An acceptable level of variation is a standard deviation 2σ less than 10 % of the mean Blaine value. Deviations in fineness are mainly due to variations in the ball mill feed sizing, throughput, and other instabilities in the mill operation. Concerning the variability of the filter fines that are added to the ball mill feed, a one-week campaign of Blaine testing has shown a huge range of values between 4,000 and 14,000 Blaine. With a ratio filter to ball mill fines of 1:10, the variability of the filter fines results in a 1,000 Blaine variability range for the combined fines. This corresponds to 50 % of the measured Blaine range at AoG.

Table 3. Fines and pitching production parameters.

Process Parameters	Average	Range	Rel. Range
Ultrafines particles < 32 µm (%)	12.9	2.0	15 %
Blaine value (cm²/g)	4,800	2,000	42 %
Pitching range at AoG (%)	13.7	0.8	-
Pitching range according to Blaine value (%)	13.7	2.0	-

4.2 Effects of the Blaine Value of the Fines on the Pitch Requirement

The role of the pitch is to bind the dry aggregate particles together by wetting and coating the coke particles and consequently by partially filling the coke porosity. Many factors affect the pitch demand such as the raw materials, the recipe, and processing parameters. As stated in the Figure 5, the pitch requirement is driven by the surface of the dry aggregate, which is dominantly represented by the external surface area. The Blaine method allows quick assessment and identification of the characteristics of the fines fineness. Thus, the Blaine value representing the external surface area of the fines is a very valuable indicator of the pitch requirement, as shown in Figure 8.

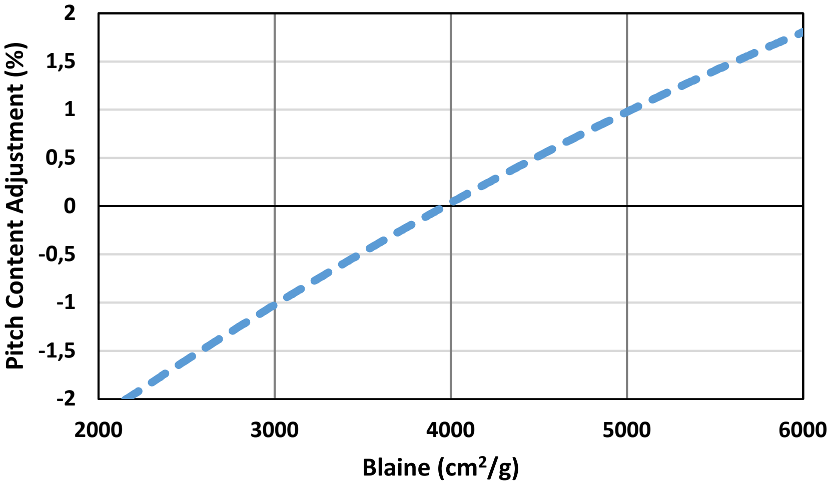


Figure 8. Adjustment of the pitch content as a function of the Blaine value [11].

Fischer et al. have demonstrated that higher fines contents and higher fines fineness result both in increased pitch requirements [12]. These studies have demonstrated that the pitch requirement increases by 1 % for an increase in fines fineness of 1,000 Blaine.

The range of the pitch content at AoG was 0.8 %, this to cope with the different cokes that are processed. Considering the range of variations of the Blaine number, the pitch requirement range should theoretically be 2.0 %. However, this variation in the pitching is not acceptable for the stability of the baking process.

The Figure 9 suggests that under- and overpitching occur at AoG. Anodes made with low Blaine fines are overpitched. Deformation of green block during transportation is observed. During baking, internal cracks are generated and sticking of packing material is noticed. Anodes made with high Blaine fines are underpitched. This results in poor levels of mechanical strength, specific electrical resistance, and air permeability of the baked anodes. In the pots, selective burning of the anode binder matrix leads to fines generation which contaminates the anode cover and the bath. Actions must be taken to squeeze the variability of the fine fineness to the minimum for producing consistent green and optimum baked blocks quality.

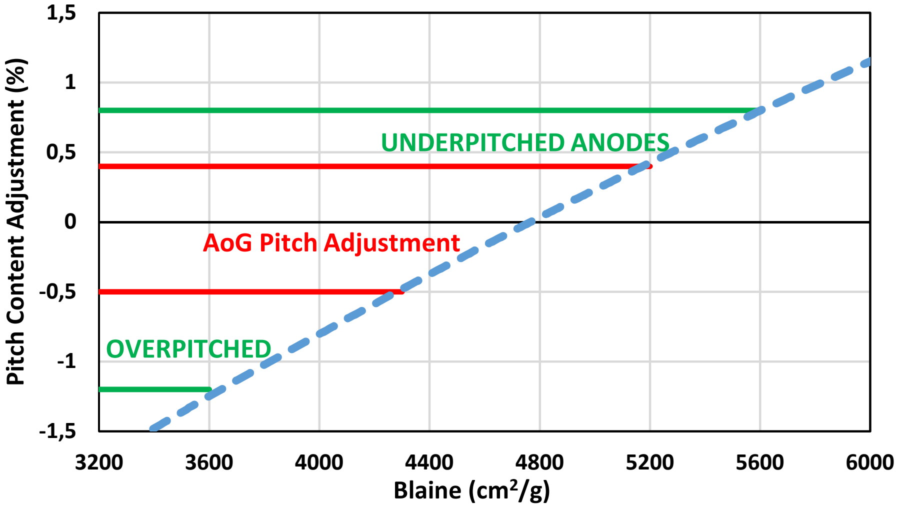


Figure 9. Variation of the *fines* fineness at AoG leads to under- and overpitched anodes.

5. Conclusion and Perspectives

The recipe parameters, particularly the *fines* fineness and *fines* content have a significant impact on the anode characteristics such as the baked anode density or the pitching level, both being highly interactive. Indeed, the higher the *fines* fineness and *fines* content, the higher is the pitch requirement. This is due to the larger external surface area available for binder coating. Therefore, it is crucial to monitor the *fines* fineness for an optimal process control at the paste plant, to ensure constant and high anode quality. The Blaine method is a sensitive, reliable and fast test enabling to follow the ball mill operation and the consistency of the *fines* fineness.

The entire dry aggregate preparation is under review at AoG to precisely identify the opportunities for improving the anode performance in the potlines. The implementation of the Blaine apparatus will improve monitoring the achieved progress towards consistent fineness of *fines* because of the superior sensitivity as compared to the ultrafines air jet sieving method.

6. References

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