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AIR AND CO_2 REACTIVITY OF CARBON ANODE AND ITS CONSTITUENTS: AN ATTEMPT TO UNDERSTAND DUSTING PHENOMENON

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Abstract

Carbon anode, used in the Hall-Héroult process, is subject to both air oxidation and carboxy gasification by CO_2. These reactions are considered as being the main causes of dusting phenomenon in the electrolysis bath. More precisely, it is believed that CO_2 and O_2 preferentially attack the baked pitch (pitch coke) resulting in detachment of coke and butt particles in the form of dust. The present work aims at elucidating this phenomenon by studying the air and CO_2 reactivities of the prebaked carbon anode and also of its constituents. The air and CO_2 reactivities were evaluated using thermo-gravimetric analysis and the standard reactivity test of R&D Carbon, ISO Standard 12981-1. The microstructural features of the samples, *i.e.* real density, crystallite size and specific surface area, were measured. The reactivity of the anode and its constituents was assessed separately and their effect on dusting phenomenon was discussed.

Introduction

The Hall-Héroult process produces aluminum by reducing alumina powder in an electrolysis cell. The cell is made up of carbon anodes, carbon cathode and molten cryolite as electrolyte. The overall electrolysis reaction can be written as Equation 1:

(1)

The carbon anode is composed of calcined petroleum coke, recycled anodes (butts) and coal tar pitch. Due to the high temperature of the anode (about 525 °C at the top and 960 °C at the bottom), the carbon anode reacts with the O_2 in the air and the CO_2 of the electrolysis reaction, according to the Equations 2 and 3 (called also carboxy gasification), respectively. These reactions are considered as being undesirable since the carbon anode is consumed without producing metal. These air and CO_2 reactivities are limited by the mass transport in the anode pores [1-6].

$$\text{C (anode)} + O_2 \quad \rightarrow \quad {}_2\,\text{(g)} \qquad (2a)$$
$$2\ \text{C (anode)} + O_2 \quad \rightarrow \qquad (2b)$$

$$\text{C (anode)} + CO_2 \quad \rightarrow 2\ \text{CO (g)} \qquad (3)$$

It is believed that the selective consumption of pitch coke (baked pitch) may result in the detachment of coke particles from the anode surface, causing a phenomenon called "dusting" [4, 7]. The presence of carbon dust in the electrolysis cell is a major challenge of the process because it could yield to an increase in the bath temperature, to a smaller interpolar distance and also to a lower current efficiency [8]. These authors listed the possible sources of the carbon dust as:

- cathode wear;
- coke detachment due to the selective consumption of the pitch coke;
- carbon from the anode cover materials (containing 2 to 5% of carbon);
- carbon impurities in the secondary alumina.

Although several sources contribute to carbon dusting, the coke detachment from anode is considered to be the major dusting source [8]. The preferential consumption of the baked pitch is attributed to its higher reactivity compared to those of coke and butt particles [9, 10]. The higher reactivity of the baked pitch was explained by the higher quantity of impurities in pitch and its lower graphitization level (lower L_C) [11, 12]. However, the reactivity of baked pitch alone and the other constituents of anode have not been reported and the above mentioned speculations still need to be verified. The present work is focused on the measurement of air and CO_2 reactivities of the anode and its constituents, *i.e.* coke, butt and baked pitch, separately. The objective is therefore to reveal if the baked pitch is more reactive than coke and butt and that it causes dusting phenomenon through its preferential reactivity with air and CO_2.

Experimental procedure

Sample preparation and characterization

The prebaked anodes were prepared according to a typical recipe used in the aluminum manufacturing process, with the exception that the large particles of coke and butt (>4 US Mesh) were not included in the recipe. Particle size as well as the weight percent of coke and butt used in the anode recipe are listed in Table 1. The coke and butt particles were crushed and sieved through seven different USA standard sieve trays (4, 8, 16, 30, 50, 100 and 200 US Mesh sizes; 4760, 2380, 1410, 595, 297, 149, 74 μm) in order to get seven different size fractions of each material. The "Fine" fraction of the recipe was obtained by ball milling of the large particles until a Blaine number of 4000 was reached. This Blaine number, which is determined by Mastersizer 2000 (Malvern Instrument, USA), is an indication of the specific surface based on the particle size distribution.

Pitch (16.8 wt.%) was added to the dry mixture, followed by preheating in an oven at 185 °C, and then mixed for 10 minutes in a domestic Hobart N50 mixer in order to obtain an anode paste. The paste was cooled to 150 °C and placed in a rigid steel cylindrical mold with an internal diameter of 63 mm and compacted in a MTS Servohydraulic Press (MTS headquarters, USA) at 150 °C. The loading force was increased to 70 MPa, using a displacement rate of 10 mm/min, and then maintained at 70 MPa for 1 min [13]. The compacted anodes were then placed in an Inconel© box and covered with coke particles in order to protect them against air burning during the baking process. Baking was performed in a box furnace (Pyradia furnace, Canada), using the following cycle: from room temperature to 150 °C at a heating rate of 60 °C/h, then from 150 to 650 °C at 20

°C/h, followed by an increase up 1100 °C at 50 °C/h. The furnace temperature was then kept at 1100 °C during 20 hours before being switched off, thus allowing the samples to cool down to room temperature.

The other constituents of anode were also baked separately, using the same heating cycles. The coke particles were baked in a quartz mould. To bake the pitch samples, an alumina tube was used as a mould in order to prevent the contamination of liquid pitch with SiO_2. Since the butt particles had remained in the electrolysis cell for 25 days at high temperature, they were used as is, without further baking.

Table 1: Particle size distribution of calcined coke and butt (wt %) used for the preparation of the anode samples.

Particle sizes (US Mesh)	- 4 + 8	- 8 + 16	- 16 + 30	- 30 + 50	- 50 + 100	- 100 + 200	Fines (4000 Blaine Number)
Particle sizes (µm)	- 4760 + 2380	- 2380 + 1410	- 1410 + 595	- 595 + 297	- 297 + 149	- 149 + 74	149>
Coke (wt.%)	13.6	9.7	13.2	7.4	4.9	2.1	25.8
Butt (wt.%)	10.1	6.1	7.3	0.0	0.0	0.0	0.0

The baked samples (anode, coke, pitch and butt) were crushed and sieved through two different USA standard sieve trays (16 and 20 US Mesh; 1.4 and 1.0 mm). These samples were used in the reactivity tests. This size was chosen according to the standard test ISO 12981-1.

Air and CO_2 reactivity tests

In the present study, two types of reactivity tests were used to measure the reactivity; a Thermo-Gravimetric Analysis (TGA) and the standard test ISO 12981-1.

The Thermo-Gravimetric Analysis (TGA)

TG analysis was used to determine the gasification percentage (R_{CO2}) of the anode and its constituents. The mass loss due to air and CO_2 reactions was recorded using a TG analyzer (Netzsch STA 449 F3 Jupiter, Germany). The sample mass loss was measured during a defined interval of time (0 min to 600 min) and under isothermal conditions; 525 °C and 960 °C for the air and CO_2 tests, respectively. The gasification percentage was obtained using the following equation:

$$\frac{i - \quad t}{i} \tag{4}$$

where: m_i denotes the initial mass of the sample and m_t is its instantaneous mass at time t.

An alumina sleeve (crucible with a low height) with an external diameter of 6.45 mm and a height of 1.82 mm was used for all TGA measurements. A small quantity of sample (between 1 and 5 mg, corresponding to the mass of 1 to 3 particles) was deposited into the sleeve and placed on the sensor. The particle size of the samples was chosen between 1.0 and 1.4 mm, a particle size being recommended by the ISO 12981-1 standard. The temperature was then increased from room temperature to the target reaction temperature at a rate of 30 °C/min. During the heating cycle, the sample was kept under an N_2 atmosphere (Praxair, 99.995%, USA, flow rate: 100 ml/min). Once the target temperature was reached, the sample was kept at this temperature for 15 minutes to stabilize the temperature. The flow of the sample protecting gas, N_2, was then decreased and kept at 20 ml/min while the flow of the reactive gas CO_2 (Praxair, 99.9%, USA) or dry Air (79.1% N_2 and 20.9% O_2; Praxair, 99.9%, USA) was turned on and kept at 100 ml/min during the reaction time. At the end of the reactivity test, the reactive gas was switched off and replaced by N_2 while the furnace was let cool to room temperature.

The ISO 12981-1 standard test

The CO_2 reactivity of the materials was determined according to the ISO 12981-1 standard, established by R&D Carbon (Sierre, Switzerland). About 5 g of sample particles, having a size comprised between 1.0 and 1.4 mm, were exposed to a carbon dioxide stream of 50 l/h during 100 min at 1,000 °C. At the end of the reaction, the mass loss was measured and the reactivity (R_{CO2}) was expressed by equation 4, where m_t denotes the final mass of the sample.

Analytical techniques

The level of impurities of the starting samples was determined by X-ray fluorescence spectroscopy (XRF) (Axios max, Panalytical, USA) according to the standard test method ASTM D4326-06. The mean crystallite height (L_C) of the samples was determined by X-ray diffraction (PW 1800, Phillips, Germany), applying the ISO 20203 standard method, which is frequently used in the aluminum industry for the characterization of carbonaceous materials.

The real density of the samples was obtained by Helium-Pycnometer (Micromeritics, AccuPyc II 1340, USA) performed on the pre-milled samples having an average particle size of 30 µm. Pre-milling results in the opening of the closed pores, thus slightly increasing the pycnometer density. When the measured density as a function of particle size reaches a plateau, it would be reasonable to assume that all closed pores were opened. Since the pycnometer density did not change beyond 30 µm, this particle size was chosen to measure the real density. The helium pycnometer was also used to measure the density of the reactivity tests samples (+ 1.0 mm – 1.4 mm). For all measurements, about 15 grams of material was used for each data point and repeated 3 times. The volume fraction of the closed pores was obtained using the difference between the real density and the helium density of the large particles, calculated from the following equation:

$$oo\ \ t\ \ (\ \ )\ \ \frac{e\ a\ \ en\ t\quad \text{Helium}\ en\ t}{e\ a\ \ en\ t}$$

The bulk density of particle bed (Scott density) was measured using a Scott volumeter with a 25 cm^3 cylindrical cell [14].

The specific surface area of the samples was evaluated on 0.4 to 2.0 g of crushed materials using a gas adsorption analyzer (Micromeritics, Tristar II 3020, USA). Samples were degassed for four hours at 250 °C under nitrogen prior to surface measurements. The surface measurements were performed in triplicate using both N_2 at -196 °C and CO_2 at 0 °C. According to several studies [15-19], the total specific surface area of carbon materials (TSA) can be evaluated using nitrogen and carbon dioxide adsorption isotherms, respectively measured at -196 °C and at 0 °C. Molecular cross-sectional areas of N_2 and CO_2 are considered to be respectively 0.162 nm^2 and 0.170 nm^2 [15, 16, 20-24]. The surface area of the micropores is usually measured by

CO_2 adsorption while N_2 adsorption measures the surface area related to meso and macropores. Taking into account the limitations such as gas diffusion due to the analysis temperatures (-196 °C for N_2 and 0 °C for CO_2), the range of relative pressure, and the difference in molecular size, it follows that the determination of the surface area by N_2 is limited to the pore diameters larger than 1.4 nm (mesopores and macropores), while that for CO_2 adsorption is between 0.4 and 1.4 nm (micropores)

Results and Discussion

Characterization of baked anodes and their constituents (coke, pitch and butt)

The chemical compositions of calcined coke, coal tar pitch and butt are presented in Table 2. The as-received coke is a calcined coke with a calcination temperature comprised between 1350 and 1400 °C. Crystallite size (L_C) of the coke and butt before baking, were found to be respectively 25 Å and 31 Å. The Mettler softening point of the coal tar pitch was 109.5 °C whilst the quinoline insoluble (QI) content and the coking value were 16.5 % and 58.8 %, respectively.

Table 2: Chemical composition of calcined coke, coal tar pitch and butt.

Raw materials	Coke	Coal tar pitch (not baked)	Butt
S (%)	2.13 +/-0.06	0.55 +/- 0.02	1.77 +/- 0.05
Na (ppm)	100 +/-7	48 +/- 3	360 +/- 25
Si (ppm)	120 +/- 17	254 +/- 36	100 +/- 14
Ca (ppm)	130 +/- 7	71 +/- 4	170 +/- 9
V (ppm)	360 +/- 18	N/A	150 +/- 8
Fe (ppm)	460 +/- 23	209 +/- 10	570 +/- 29
Ni (ppm)	250 +/- 13	N/A	140 +/- 7

N/A: Not Available

Anode, pitch and coke samples were baked separately, as described earlier. After baking, all samples were crushed in a jaw and a roll crusher. These materials were then sieved and the size fraction between 1.0 and 1.4 mm was used for analyzing their level of impurities, crystallite height (L_C) and specific surface area. The results are given in Table 3. All samples were contaminated by iron during the crushing step. In addition, butt samples showed higher level of sodium, which is related to its contamination by cryolite during the electrolysis process. The crystallite height (L_C) of the anode, coke and pitch samples is similar (about 27.5 Å) while that of butt is higher. This is most likely due to the long stay of butt at high temperature during electrolysis. As can be seen in Table 3, the specific surface area measured by CO_2 is systematically higher than that measured by N_2. However, the gap of two measures for baked pitch is considerably higher, indicating that the surface of micropores is much higher than that of meso and macropores in baked pitch.

Table 3: Sample properties of baked anode, baked coke, baked pitch and butt crushed and sieved between 1.0 and 1.4 mm.

Sample Properties	Baked Anode	Baked Coke	Baked Pitch	Butt
S (%)	1.74 +/ 0.05	2.05 +/- 0.06	0.19 +/- 0.01	1.71 +/- 0.05
Na (ppm)	127 +/- 9	69 +/- 5	126 +/- 9	445 +/- 31
Si (ppm)	260 +/- 36	193 +/- 27	721 +/- 101	80 +/- 11
Ca (ppm)	182 +/- 9	155 +/- 8	120 +/- 6	152 +/- 8
V (ppm)	309 +/- 15	448 +/- 22	4 +/- 0	156 +/- 8
Fe (ppm)	705 +/- 35	664 +/- 33	612 +/- 31	662 +/- 33
Ni (ppm)	186 +/- 9	250 +/- 13	11 +/- 1	127 +/- 6
(V + Ni) / S	284 +/- 37	340 +/- 44	79 +/- 10	165 +/- 22
L_C (nm)	27.5 +/- 0.5	27.1 +/- 0.5	27.8 +/- 0.5	30.9 +/- 0.5
Real density (g/cm^3)	2.055 +/- 0.001	2.103 +/- 0.003	2.020 +/- 0.001	2.117 +/- 0.003
Helium density (g/cm^3)	1.991 +/- 0.004	2.030 +/- 0.005	1.968 +/- 0.004	2.030 +/- 0.003
Closed porosity (%)	3.1 +/- 0.0	3.5 +/- 0.0	2.6 +/- 0.0	4.1 +/- 0.0
Bulk density of particle bed (g/cm^3)	0.79 +/- 0.01	0.71 +/- 0.01	0.69 +/- 0.01	0.82 +/- 0.02
SSA, N_2 with BET equation (m^2/g)	5.8 +/- 0.6	1.3 +/- 0.1	0.1 +/- 0.0	1.5 +/- 0.1
SSA, CO_2 with DR equation (m^2/g)	6.9 +/- 0.3	2.4 +/- 0.3	2.4 +/- 0.1	2.7 +/- 0.4

BET: Brunauer–Emmett–Teller
DR: Dubinin–Radushkevich

Air reactivity test with TGA

In order to establish a relationship between the gasification percentage and the reaction time, an isothermal air reactivity test was used. For that purpose, a specific temperature of 525 °C was chosen, based on the temperature used in the air reactivity standard test available from the R&D Carbon standard 12989-1 [25]. The variation of gasification percentage as a function of reaction time of the four samples is presented in Figure 1. The TG analyses were performed on only 1 to 3 particles, placed on the TGA plate, to ensure that gas composition be the same at the surface of each particle. Each curve is an average of three tests. After 7 hours of reaction, the coke particles were totally consumed (97.5% of gasification) while the gasification percentage of the pitch material was only about 6.5% and those of the anode and the butt particles were respectively 84.2% and 69.5%. These results showed that, in spite of a same level of graphitization, the coke particles are much more reactive than anode and pitch. The gasification percentage of these samples correlates neither with N_2 nor with CO_2 specific surface areas. In addition, although the L_C of butt is slightly higher than that of pitch, its reactivity is lower.

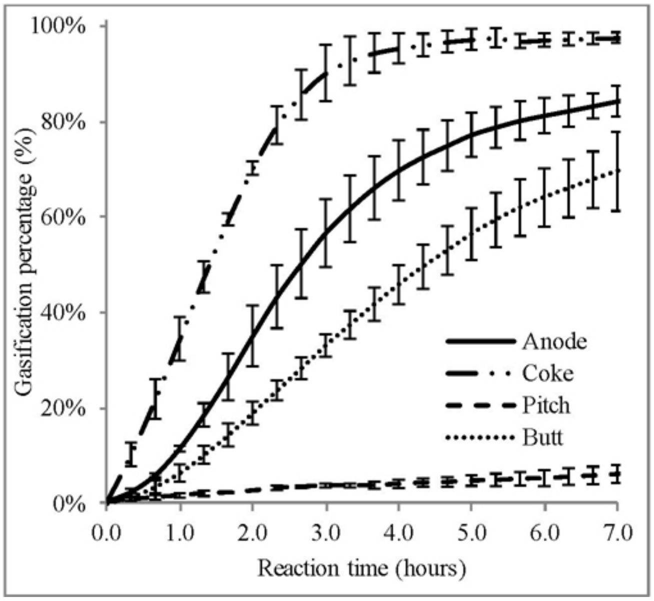

Figure 1: Experimental gasification percentage versus reaction time for anode, coke, pitch and butt; analyses were performed on a TGA under air atmosphere at 525 °C.

Considering the chemical composition of the samples, one can see that the gasification percentage of all samples correlates with the level of vanadium and nickel, the impurities well known to catalyse the carbon-air reaction [26]. Sulfur is also known to inhibit the catalytic effect of the impurities for carbon oxidation [26, 27]. It is therefore logical to assume that the ratio (V+Ni)/S be an important factor for the reactivity of samples. For this purpose, this ratio was calculated and presented in Table 3. Although this ratio is not the only factor determining the reactivity, a very good correlation can be seen between this factor and the gasification percentage. Figure 2 shows the gasification percentage of the samples as a function of (V+Ni)/S ratio after 4 hours of reaction, the time required for the most reactive sample to be totally consumed. The low reactivity of the baked pitch could be explained by its low ratio of (V+Ni)/S. Butt sample shows slightly higher reactivity than that expected by (V+Ni)/S. This could be attributed to the high level of sodium in butt; another impurity with catalytic effect on carbon oxidation reaction which is not included in the equation (V+Ni)/S.

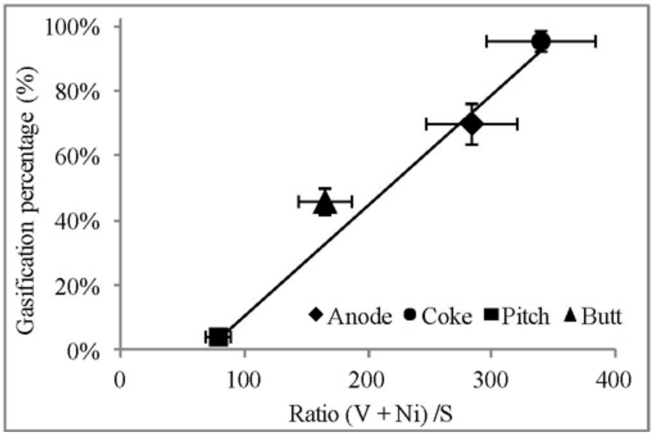

Figure 2: Gasification percentage of samples after 4 hours of reaction under air at 525 °C as a function of (V+Ni)/S.

CO_2 reactivity test with TGA

The CO_2 reactivity of the same samples was evaluated at 960 °C. This specific temperature was based on the ISO standard 12988-1 test, established by R&D Carbon company [28]. Again, only 1 to 3 particles were placed in the TGA plate to ensure that gas composition be the same at the surface of each particle. Each curve is an average of three tests. Figure 3 shows the gasification percentage as a function of the reaction time under CO_2 gas stream. The CO_2 reactivity results are quite similar to those obtained for the air reactivity tests, indicating the lowest reactivity for the baked pitch and the highest for coke, all showing a good correlation with (V+Ni)/S ratio (Figure 4). However, the butt particles were found to be more responsive to the Boudouard reaction than the other samples, showing a significant increase in gasification percentage.

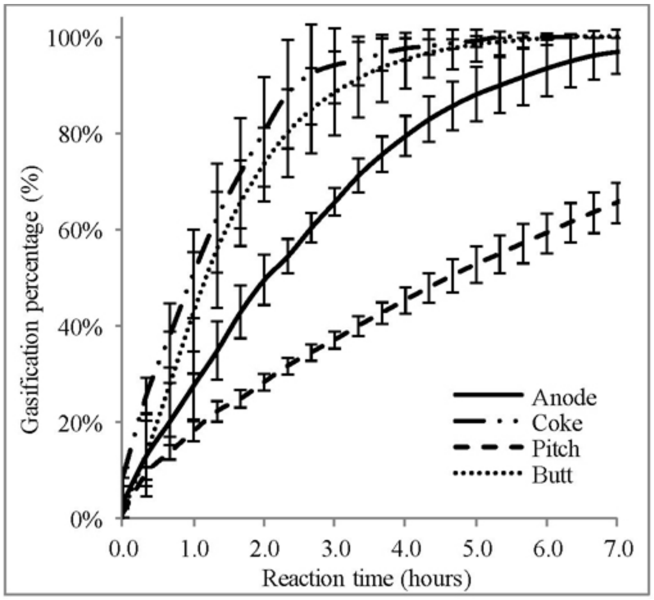

Figure 3: Experimental gasification percentages of the anode, coke, pitch and butt materials as a function of the reaction time at 960 °C and under a CO_2 atmosphere. Analyses were performed on a TGA instrument.

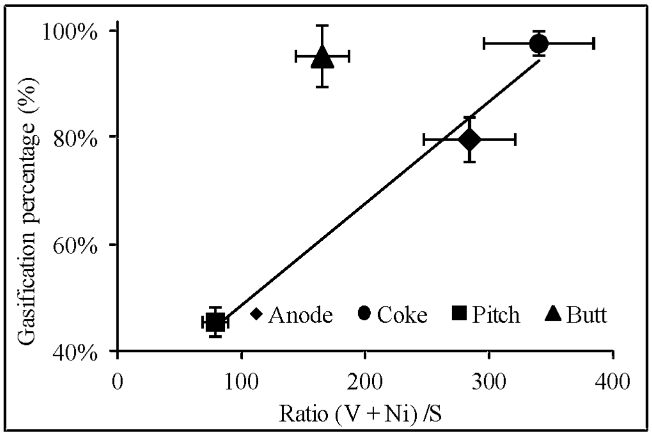

Figure 4: Gasification percentage of samples after 4 hours of reaction under CO_2 at 960 °C as a function of (V+Ni)/S.

In comparison with the results obtained for the air reactivity, the butt shows a CO_2 reactivity very close to that of the coke. Again, the high reactivity of butt samples could be explained by the activation of the sodium at high temperature and its catalytic effect on carbon oxidation with CO_2 [29, 30]. Müftüoglu and Øye [29] reported that the effect of sodium on anode gasification is quite different for CO_2 and air reactions. They showed that the air reactivity of anode increases slightly with sodium content while this increase is very sharp for CO_2 reactivity.

The difference in catalytic activity of sodium is attributed to its catalysis mechanism under air and CO_2. The main catalytic effect of sodium for CO_2 reaction is based on the formation and decomposition of Na_2CO_3. Metallic sodium reacts with CO_2 to form Na_2CO_3 (equation 5). At high temperature, Na_2CO_3 reacts with carbon and sodium is reduced to metallic state (equation 6). The metallic sodium continues to react with CO_2 to form Na_2CO_3 and completes the catalytic cycle.

$$2\ Na + 2\ CO_2 \rightarrow Na_2CO_3 + CO \qquad (5)$$

$$Na_2CO_3 + 2\ C \rightarrow 2\ Na + 3\ CO \qquad (6)$$

The reaction 6 is temperature-sensitive, with an equilibrium constant of $4x10^{-24}$ at 527 °C. The extremely small equilibrium constant suggests that the reaction is almost inexistent during air reaction at 525 °C. This could explain why the effect of sodium is much more pronounced at high reaction temperatures, i.e. during CO_2 reactivity test, than it is at low temperature, i.e. during air reaction test.

Both CO_2 and air reactivity results suggest that the reactivity of baked pitch, when it is baked alone, is significantly lower than that of the other anode constituents. Thus, considering the experimental conditions conducted in this work, it can be concluded that baked pitch could not be preferentially consumed in the anode, therefore, not being responsible for dusting phenomenon, if all constitutes of anode were exposed to the same CO_2 concentration. However, one may argue that the reaction conditions in a real anode are quite different. For instance, the gas composition within the pores could be different from that on the surface of the anode, or the pitch structure could be different when it is baked alone or baked in the presence of solid coke particles.

Obviously the gas concentration could influence the carbon oxidation reaction. For instance, CO is well known to poison the reaction sites and to slow down the carboxy gasification [31]. In the electrolysis conditions, anode is not only oxidized from the surface, but also the reacting gases diffuse into its pores and react over its internal surfaces. These reactions inside the anode may result in generation of CO inside the pores, influencing the reaction rate. In other words, in order to assess the overall reactivity of the anode constituents, the effect of CO should also be considered.

In industrial practice, the CO_2 reactivity of coke is usually assessed using a standard method ISO 12981-1. In this method, about 5 grams of coke particles with a size comprised between 1.0 and 1.4 mm is placed in a tube and reacted with CO_2 at 1,000 °C. CO_2, with a flow rate of 50 L/h, passes through the powder bed (from the bottom to the top), with a thickness of about 2 cm. The major difference between this method and the TGA experiments presented above is that the concentration of CO resulting from the reaction increases from the bottom to the top of the particle bed. Thus, the particles at the upper layers are not exposed to the same gas composition as are the particles at lower layers. Although this method dose not either represent the real anode conditions, it can reveal the effect of CO gradient within the powder bed.

The ISO 12981-1 standard test was used to evaluate the CO_2 reactivity of the same samples; all tests were performed with a pre-calibrated instrument using a standard sample provided by R&D Carbon. A reaction time of approximately 83 minutes was selected and the reactivity test was conducted at 1,000 °C, as specified in the standard. Table 4 shows the percentage of the mass loss of the samples after 83 minutes of reaction. For comparison purpose, the mass loss corresponding to 83 minutes of reaction during TGA test were also presented in this table. Although the standard reactivity test was carried out at higher temperature (1,000 °C), it can be seen that the gasification percentage of all samples during the standard tests are significantly lower than those obtained by TG analysis, carried out at 960 °C. The results reveal the inhibiting effect of CO on the overall reactivity and the external mass transfer resistance in the powder bed. In other words, the concentration of CO in the standard test increases from the bottom to the top of the powder bed and influences the overall reactivity of bed. It can also be seen that, except for butt samples, the order of the reactivity of the samples is similar in two experiments; pitch showing the lowest reactivity followed by anode and coke. The butt sample, however, exhibited the highest reactivity, being approximately 50% higher than that of coke. This very high reactivity of butt is again justified by the catalytic effect of sodium. Since the equilibrium constant of reaction 6 is temperature-dependent, it is expected that the catalytic effect of sodium during the standard test be higher than that during TGA tests. This is the reason why the butt sample showed the highest reactivity.

Table 4: Comparison of the CO_2 reactivity based on the standard test 12981-1 at 1000 °C and performed on the TGA instrument at 960 °C for the baked anode, baked coke, baked pitch and butt crushed and sieved between 1.0 and 1.4 mm.

Sample	Anode	Coke	Pitch	Butt
Gasification percentage with ISO Standard 12981-1 after 83 minutes, 1,000 °C	18.6 +/- 0.5	23.1 +/- 0.5	15.6 +/- 0.3	32.3 +/- 0.8
Gasification percentage with TGA after 84 minutes, 960°C	37.6. +/- 5.8	63.5 +/- 10.8	22.2 +/- 1.9	57.6 +/- 10.1

The results obtained so far confirmed that the baked pitch, when it is baked alone, is not more reactive than other anode constituents and should not be preferentially consumed in the anode. However, the dusting phenomenon and the preferential consumption of the binder matrix (mixture of fines coke and pitch) are well-documented phenomena, regularly observed in industrial practice [32-34]. Based on the reactivity results obtained in this work, two hypotheses could be proposed to explain the results.

1) The structure and morphology of the baked pitch could be fundamentally different when it is baked alone and it is baked in the presence of coke particles, leading to a more reactive material within the anode. This hypothesis stands on the fact that the specific surface area of the anode does not obey the rule of mixtures and it is higher than those of all its constituents (Table 3). It seems that the baked pitch exhibits higher surface area when it is baked in the presence of coke particles, compared to that when it is baked alone. In order to verify this hypothesis, some coke particles trays (8 and 16 US Mesh; 2.4 and 1.4 mm) were enveloped with liquid pitch prior to baking and their surface area was compared with that of the particles baked without pitch. The mass fraction of the pitch over the enveloped particles was

estimated to be less than 20%. The uncovered particles exhibited a specific surface area, measured by N_2, of around 1 m^2/g while the covered particles exhibited a very large surface area of 14 m^2/g. This observation confirmed that pitch has not the same properties when it is baked alone and baked over a solid coke particle, possibly because of the template effect of the coke surface on the pitch baking process. More investigation is required to elucidate the co-baking process of pitch and coke and its effect on the structural development of pitch coke.

2) The seconded hypothesis is based on the possible catalytic effects of the coke impurities on pitch gasification. Since in a binder matrix fine coke particles are distributed within the pitch, after baking, the pitch coke would be in intimate vicinity of fine coke particles. The catalytic impurities of coke may influence the gasification reaction of the neighbouring baked pitch, thus increasing the overall reactivity of the binder matrix, resulting in dusting. Work is in progress to assess the catalysis effect of the impurities on the gasification of baked pitch.

Conclusion

The objective of the present study was to understand the source of the dusting phenomenon, by preparing all anode constituents, separately, and assessing their reactivity. The reactivity of the samples was assessed using both TGA analysis of separate particles and standard reactivity test on a powder bed. The experimental results showed that coke is the most reactive constituent of anode for air reactivity, followed by anode itself, butt, and baked pitch. For CO_2 reactivity at 960 °C, butt is as reactive as coke and its reactivity exceeds that of coke when the reaction temperature increases to 1000 °C. The increase of butt reactivity with temperature was ascribed to the presence of sodium and its catalytic effect on carbon-CO_2 reaction.

The baked pitch showed the lowest reactivity in these experiments; however, some evidence suggests that the pitch baked alone may be different from the pitch baked in the presence of coke particles. One of these evidences is the high specific surface area that a baked pitch exhibits when it is baked in the presence of coke particles. Thus, the fact that the baked pitch is less reactive than other anode constituents does not necessarily mean that it would also be less reactive within an anode.

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