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IMPROVEMENT OF ANODE PROPERTIES BY COKE MODIFICATION WITH ADDITIVES

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AMÉLIORATION DES PROPRIÉTÉS D'ANODES VIA LA MODIFICATION DE COKE AVEC DES ADDITIFS

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Abstract

In aluminum production, carbon anodes that are made of petroleum coke, coal tar pitch and recycled carbon materials are used to provide carbon required for the electrolysis process. The anode quality directly affects not only the energy consumption and the production cost but also the emission of greenhouse gases. The raw materials quality has a significant effect on anode quality. The good quality anodes should have high density, low electrical resistivity, low air/CO_2 reactivity as well as good mechanical properties. Pitch binds the solid particles together. The quality of raw materials can change depending on its source and the processes parameters used in the refineries. However, industry still has to produce good quality anodes. In general, good coke/pitch interaction results in better quality anodes. This study was undertaken to enhance the wettability of coke by pitch, with the objective of improving the anode properties, based on coke modification by adding additives and surfactants and to determine the effect of additives on anode quality.

The results showed that the wettability of coke by pitch is dependent on the heteroatom containing functional groups present on the coke surface. The interaction between coke and pitch increases with increasing amount of heteroatom-containing functional groups. Thus, it is possible to improve the anode quality by modifying coke with additives.

The study indicated that different cokes have different amounts of functional groups. Therefore, each coke has a different wetting behavior. It was found that, before modifying a coke, its surface chemistry should be taken into account for the determination of suitable additive type and amount. The surface functional groups of pitch are as important as those of the coke, however, this is outside the scope of this project.

In this study, the effect of the contact time between the additive and the coke on the anode quality was also investigated, and a coke modification method was developed. Based on the experimental results, the anode quality improved more when the coke was pre-treated before it was mixed with pitch.

Résumé

Dans la production de l'aluminium, les anodes de carbone qui consistent en coke de pétrole, brai de goudron de houille et matériaux carbonés recycles fournissent le carbone requis pour le procédé d'électrolyse. La qualité des anodes affecte directement non seulement la consommation énergétique et le coût de production, mais aussi l'émission des gaz à effet de serre. La qualité des matières premières a un impact considérable sur la qualité des anodes. Les anodes de bonne qualité doivent avoir de haute densité, de basse résistivité électrique, de basse réactivité à l'air et au CO2 et de bonnes propriétés mécaniques. Le brai lie les particules solides ensemble. La qualité des matières premières peut varier dépendant de sa source et des paramètres des procédés utilisés dans les raffineries. Néanmoins, l'industrie doit produire des anodes de bonne qualité. En général, des fortes interactions entre le coke et le brai résultent en des anodes de meilleure qualité. Cette étude a été entreprise pour accroître la mouillabilité du coke par le brai, pour but d'améliorer les propriétés d'anodes, en modifiant le coke par l'ajout d'un additif ou un tensioactif et aussi pour déterminer les effets de l'ajout des additifs sur la qualité des anodes.

Les résultats ont démontré que la mouillabilité du coke par le brai dépende des groupes fonctionnels, présents sur la surface du coke, qui contiennent des hétéroatomes L'interaction entre le coke et le brai augmente avec la quantité des groupes fonctionnels contenant des hétéroatomes. Donc, il est possible d'améliorer la qualité des anodes en modifiant le coke par des additifs.

Cette étude a indiqué que les différents cokes ont des quantités différentes des groupes fonctionnels. Donc, chaque coke a un comportement de mouillabilité différent. On a trouvé que, avant de modifier un coke, sa chimie surfacique doit être considérer pour la détermination du type et de la qualité appropriés de l’additif. Les groupes fonctionnels du brai sont aussi importants que ceux du coke, mais cela n’est pas inclus dans la portée de ce projet.

Dans cette étude, l’effet du temps de contact entre l’additif et le coke sur la qualité d’anodes est aussi examiné, et une méthode pour la modification de coke a été développée. Basé sur les résultats expérimentaux, la qualité de l’anode a amélioré plus lorsque le coke a été prétraité avant de le mélanger avec le brai.

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List of Abbreviations and Symbols

θ	Contact angle (°)
γ_{LV}	Interfacial tension of the liquid-vapor interface (mN/m)
γ_{SV}	Interfacial tension of the solid-vapor interface (mN/m)
γ_{SL}	Interfacial tension of the solid-liquid interface (mN/m)
V	Volume (cm^3)
d	Diameter (cm)
W	Weight (g)
l	Length (cm)
D	Density (g/cm^3)
I	Current (A)
F_{max}	Maximum force (N)
ρ	Resistivity (μΩm)
σ	Flexural strength (N)
FT-IR	Fourier transform infrared spectroscopy
GAD	Green anode density (g/cm^3)
BAD	Baked anode density (g/cm^3)
GER	Green anode electrical resistivity (μΩm)
BER	Baked anode electrical resistivity (μΩm)

CHAPTER 1

INTRODUCTION

1.1. Background

Aluminum, which has a low weight, good thermal and electrical conductivity and recyclability, is one of the most abundant materials on Earth. Aluminum is used in many sectors such as transport, electrical, construction and packaging because of its properties [1].

Alumina is obtained from bauxite after the process that involves milling, digestion, clarification, crystallization, and calcination. This process is called the Bayer process [2].

Aluminum is produced from alumina by the Hall-Héroult process using electrolysis shown in Figure 1.1. Alumina (Al_2O_3) is dissolved in a bath, which contains molten cryolite (Na_3AlF_6) at about 960°C [2]. Carbon anodes are used as the carbon source in aluminum production and also carry the electrical current to the cell. Different reactions occur at the anode and the cathode (see Equation 1.1, 1.2 and 1.3). The overall reaction is represented as alumina reacting with carbon anodes producing aluminum and CO_2. In order to produce one-ton aluminum, the theoretical amount of carbon required is 334 kg [1]. However, in practice 400 kg of carbon is used. Since carbon anodes are consumed during this process, it has to be replaced approximately every 14-28 days depending on the quality of anode and the technology.

$$At\ anode:\ 2\,O^{-2} + C \rightarrow CO_2 + 4e^- \tag{1.1}$$

$$At\ cathode:\ Al^{+3} + 3e^- \rightarrow Al \tag{1.2}$$

$$Overall\ reaction:\ 2Al_2O_3 + 3C \rightarrow 4Al + 3CO_2 \tag{1.3}$$

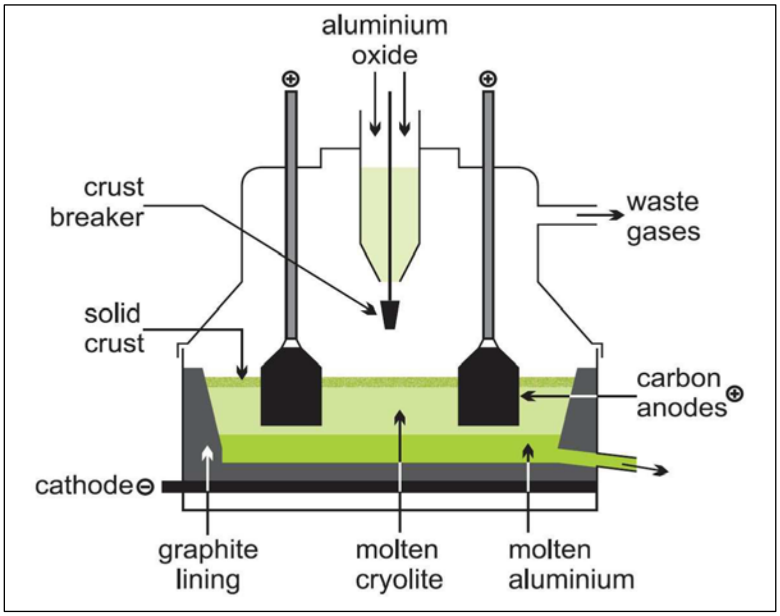


Figure 1.1: Schematic illustration of an electrolysis cell for aluminum production

Aluminum is produced using the electrolysis process with carbon anodes, which consist of a mixture of calcined petroleum coke (60-70%), coal tar pitch (15-25%), and recycled materials (anode butts, green and baked rejects) [2]. The quality of anodes is an important parameter to consider in aluminum production. The good quality anodes should have high density, low electrical resistivity, low air and CO_2 reactivities, and good mechanical properties [2]. In order to manufacture good quality anodes, the coke and pitch must interact well with each other at the mixing stage. The affinity between these two components relies on good wetting properties. To obtain good wettability, pitch, as a binder, should penetrate into the coke particles. The wetting ability of a coke can be improved through its modification.

1.2. Statement of Problem

The carbon anodes play an important role since they provide carbon for the electrolysis reaction in aluminum production. For economical, effective and environment friendly aluminum production, good quality carbon anodes should be fabricated. Carbon anodes are made of calcined petroleum coke and coal tar pitch, and the quality of the resulting anode is dependent on the raw material quality. Therefore, the properties of raw materials should be improved.

The calcined petroleum coke is one of the raw materials for carbon anodes, and its quality has a significant effect on anode properties. Coke and pitch are mixed in a mixer or kneader. Their interaction at the mixing stage has a great impact on the anode quality. The pitch, which is used as a binder, must penetrate into the coke particles to provide better interaction between these two components. Good interaction between coke and pitch requires good wetting properties. The surface tension must be reduced and the coke-pitch interaction should be increased in order to improve the wettability of coke by pitch. Additives and surfactants can be used for this objective in order to create a bridge between coke and pitch.

1.3. Objectives

The main objectives of this study are to enhance the wettability of coke by pitch through the use of additives (surfactants or other chemicals) in order to improve the anode properties and to understand the underlying mechanism so that better quality anodes could be produced with the available raw materials.

The specific objectives are:

- to identify different functional groups on different cokes and pitch in order to determine which functional groups are more significant for the interaction between these raw materials,

- to modify the calcined coke with different additives so that the wettability of coke by pitch can be improved,
- to determine the difference between the non-modified and the modified coke (with different additives at different percentages) spectra,
- to determine the wettability of different cokes (non-modified and modified) by pitch using the sessile-drop technique,
- to analyze the effect of additive quantity on the wettability of different cokes by pitch,
- to improve coke-pitch interaction by modifying the coke with additive,
- to find the best contact time between the additive and the coke before producing anodes to enhance anode quality,
- to improve the anode properties such as density, electrical resistivity, air/CO_2 reactivity, and flexural strength using the coke modified with an additive.

1.4. Methodology

Figure 1.2 shows the schematic of the methodology used in this work. The steps are explained below based on this figure.

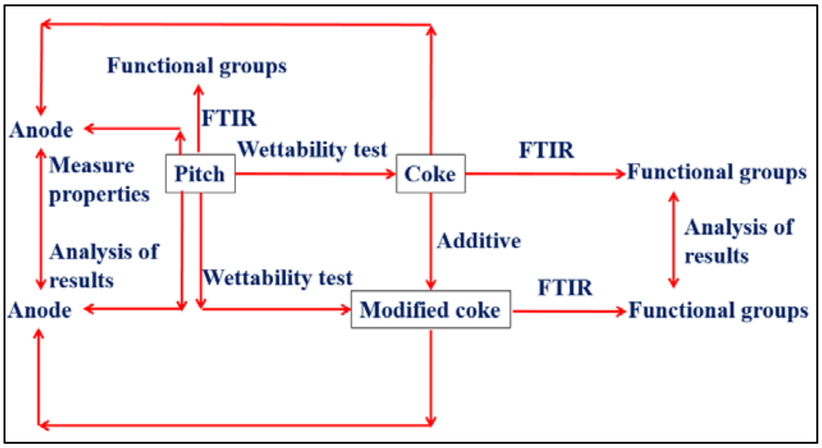


Figure 1.1: Schematic illustration of methodology

- The functional groups of cokes, pitch, and the additives were analyzed by Fourier transform infrared spectroscopy (FT-IR).
- The cokes were modified by different additives to increase the aromatics and heteroatom-containing functional groups. Each additive was dissolved in a solvent before the coke treatment.
- The functional groups of the modified cokes were determined using FT-IR.
- The wettability of non-modified and modified cokes by pitch was studied using the sessile-drop method with a set-up present at the carbon laboratory of Chair CHIMI.
- Based on FT-IR and wettability results, the additive which improved the coke wettability most was chosen. The anodes were produced with the non-modified coke and the coke modified with the chosen additive.
- Two different methods were used to modify the coke for anode manufacturing. The effect of coke preparation conditions on anode properties was examined.
- A standard anode using the non-modified coke and anodes using the coke modified with different quantities of the chosen additive were produced under the same conditions. The effect of the additive amount on anode properties was studied.
- Anodes were characterized based on different properties such as green and baked density, green and baked electrical resistivity, flexural strength, air and CO_2 reactivities, and dusting.

1.5. Scope

In this study, improvement of the wettability of coke by pitch using different additives is investigated. FT-IR analysis was used in order to identify different functional groups in cokes (non-modified and modified), pitch, and different additives. Also, the wetting study was done so that the interaction between coke and pitch could be analyzed before and after the modification of coke by different additives. The results of the study are presented in Chapters 4 to 6 in the form of articles. The section, table, figure, equation and reference numbers in these chapters are different than those in the original articles. This modification was done so that the thesis is easier to follow for the reader.

The thesis consists of seven chapters. The introduction is given in Chapter 1, which includes the statement of the problem, the objectives, the general methodology, and the scope. Chapter 2 gives a detailed literature review on the properties of carbon anodes and raw materials as well as the previous studies reported on the modification of coke. Chapter 3 provides information on the methodology and the experimental systems used in this study. It also presents the detailed information on anode manufacturing steps as well as the characterization methods of coke (Fourier Transform Infrared Spectroscopy and Sessile-drop technique) and anode samples.

Chapter 4 presents the results and the discussion on the modification of one coke by six different additives and the anode produced with the best additive. The effect of different additives on the wettability of the coke by pitch was investigated with FT-IR and sessile-drop tests. Laboratory anodes were produced using the best additive. The anodes were characterized using different tests, and the effect of this additive on the properties of the anodes (density, electrical resistivity, air and CO_2 reactivities and flexural strength) were determined.

The results of the modification of four different cokes using the best additive above and the investigation on the method of modification are presented in Chapter 5. The effect of the additive on different cokes in terms of surface functional groups and wetting was studied. The best coke-pitch pair was chosen, and anodes were produced using this pair and varying the contact time between the additive and the coke during its modification to determine the impact on anode properties.

In Chapter 6, the focus is on the modification of two different cokes by the best additive at different concentrations. Anodes produced using these cokes were characterized (density, electrical resistivity, air/CO_2 reactivity and flexural strength), and the results are presented.

Finally, Chapter 7 gives conclusions and recommendations of the research.

CHAPTER 2

LITERATURE REVIEW

2.1.Anode Properties

Anodes are used in electrolytic cell as the carbon source for aluminum production. Carbon reacts with oxygen coming from the electrolytic reaction; as a result of this reaction, aluminum and CO_2 are produced (see Equation 1.3) [2]. Quality of anode directly affects the quality of resulting aluminum, aluminum production cost, and the amount of greenhouse gases emitted.

In aluminum production, anode manufacturing is one of the most important steps in order to obtain good quality aluminum. There are four major steps to produce anodes: preparation of raw materials, mixing, compaction, and anode baking [2,3]. Each step has a significant effect on anode quality. Carbon anode contains calcined petroleum coke, coal tar pitch, and recycled materials (anode butts and green and baked rejects). Calcined petroleum coke (60-70%) and recycled materials (15-20%) are crushed to attain certain granulometry. These particles are called ‘dry aggregate’. The preparation of dry aggregate has a great impact on packing [4]. Good packing is the first step for good quality anode. The anode recipe is prepared using different fractions of different size coke particles. The medium size particles should fill the void space between the coarse particles, and the space between medium particles should be filled with fine particles. Fine particles (less than 1 mm) fill in the remaining space. If a large amount of fine particles are used in the recipe, the surface area of the recipe will be high. Higher surface area increases the required amount of pitch. Excess pitch causes more volatiles during baking, and it is costly.

The dry aggregate is preheated before mixing to prevent the solidification of pitch. The preheating temperature should be higher than the softening point of pitch. If the pitch stays solid, it cannot mix with the coke particles. Poor mixing (less wetting between coke and pitch) results in low quality anodes. The dry aggregate and the coal tar pitch are mixed at around 170°C-190°C [2]. The mixing temperature should be about 50°C higher than the pitch softening point to ensure the viscosity of the pitch. The adequate low viscosity of pitch allows not only filling of the void space between particles but also the penetration of pitch into the coke particles [2,3]. This provides good mixing and a homogeneous paste. Then, this paste is compacted by pressure molding or vibratory compaction. Vibration is used in the production of large sized anodes, and it is more suitable for aluminum industry. Vibration helps the particles thoroughly settle down to make a dense anode. Compaction of the paste results in the formation of green anodes. The green anode is cooled down below the pitch softening point using a cooling medium. In order to avoid the thermal shock, cooling should be neither fast nor slow. The final step of the process is baking. The green anodes are baked in the baking furnace at about 1100°C. The remaining space between the anodes and the furnace walls is filled with filler (calcined) coke. During baking, pitch carbonizes and binds the coke particles together. Several reactions take place during baking between coke and pitch such as polymerization, cracking, rearrangement and condensation [5,6]. The heating temperature and the heating rate have significant effect on resulting anode. If the heating is fast, the volatiles will be released rapidly. This creates pores and cracks, which increase the electrical resistivity and reactivity and reduce the density and mechanical properties of anodes [7, 8]. After the heating, the anodes are cooled down before rodding and their consequent use in the cells.

2.1.1. Density

The high density is a desired property for a good quality anode. The density is related to anode life. Denser anodes provide longer anode life. The density of green anode is around 1.55-1.65 g/cm^3 and the density of baked anode is 1.50-1.60 g/cm^3 [2,9]. The density of anode is determined by dividing the weight by its volume.

The green density should be high to produce denser baked anodes [2,3]. Raw materials quality, mixing conditions (mixing temperature and mixing time), and forming conditions (compaction time and frequency of compaction) have a significant effect on the green density. The low green density means more porosity, which can create cracks during baking. The baked density also should be high. If the baked density is low, the electrical resistivity is high because of porosity. On the other hand, too high a baked anode density could cause thermal shock.

2.1.2. Electrical Resistivity

The electrical resistivity of anode is related to energy consumption. Decrease in electrical resistivity reduces the energy consumption (and cost) during aluminum production. Electrical resistivity depends on the coke properties, the density of anode, and the pores/cracks inside the anode. Generally, denser anodes have lower electrical resistivity since they have less porosity. The electrical resistivity of anode is around 50-60 μΩm [2,9-11]. The green electrical resistivity is not usually measured, but it is known that the electrical resistivity of green anode is much higher than the electrical resistivity of baked anode.

High electrical resistivity causes more energy consumption. On the other hand, low electrical resistivity means high thermal conductivity. If the thermal conductivity of anode is high, the top temperature of anode increases more and this can cause air burn problems because carbon reacts more with air at higher temperatures [2,3].

2.1.3. Air/CO_2 Reactivity

Carbon anodes are consumed in the electrolytic cell during aluminum production by the reduction of alumina according to Equations 1.1- 1.3 [2]. Air can react with the carbon anode near the top of the anode, and it produces CO_2 (see Equation 2.1). Carbon anode not only reacts with air but also with CO_2. Carbon dioxide, which is produced during aluminum production, can react with the carbon anode and carbon monoxide forms as a result of this reaction (see Equation 2.2). There are three main reasons for excessive carbon consumption: air burn (air reactivity), carboxy attack (CO_2 reactivity), and selective oxidation (dusting) [3, 12, 13].

$$C + O_2 \rightarrow CO_2 \tag{2.1}$$

$$CO_2 + C \rightarrow 2CO \tag{2.2}$$

Air reactivity takes place on or near the top of the anode at around 500°C (see Figure 2.1). The impurities in anode such as sodium, nickel, vanadium accelerates the air burn reaction. On the other hand, sulfur acts as an inhibitor and reduces the air reactivity. The raw materials properties, baking temperature, and cell design have a significant effect on the air reactivity of anode. Unlike the air reactivity, CO_2 reactivity takes place at the bottom of the anode where CO_2 forms as a result of the oxidation reaction at 960°C (see Figure 2.1) [2]. It is also observed that the impurities in anode like sodium, calcium, and sulfur affect the CO_2 reactivity [14-17]. CO_2 reactivity is affected by the raw material properties, the formulation of green anode, and the anode baking temperature. The selective oxidation, which is known as dusting, can be explained by the reactivity difference between coke and pitch [18]. Dusting causes physical loss of coke particles due to the loss of the integrity of the anode structure [2,3].

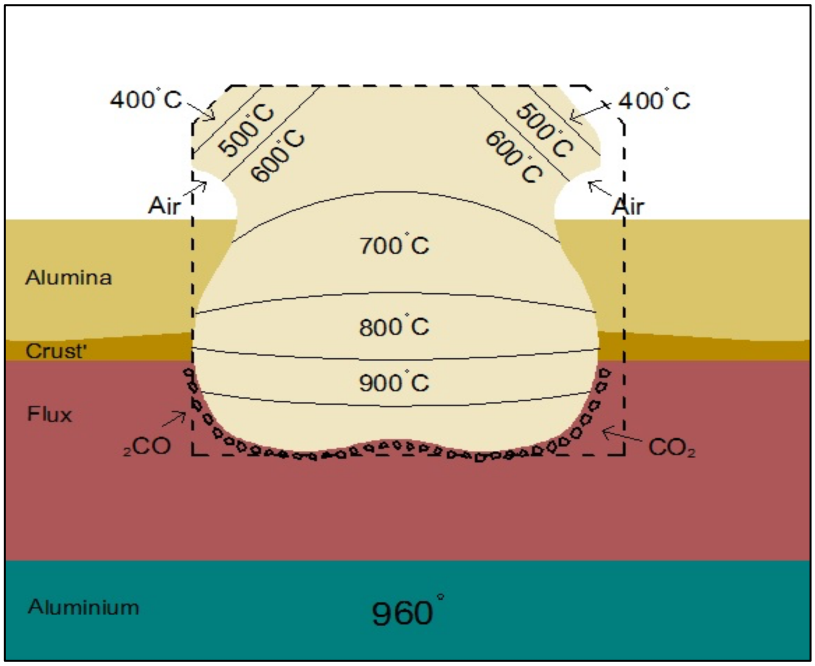


Figure 2.1: Anode behavior in a reduction cell [2, 3]

2.1.4. Mechanical Properties

Mechanical properties of anodes affect their handling and setting, and the rodding processes. Anodes should have adequate strength in order to resist the transportation processes [2]. The micro and macro cracks in anode create low flexural strength. The mechanical properties are affected by the coke properties and the baking conditions of anode. The mechanical properties of anode can be controlled by the raw material properties, forming conditions of anode paste and the baking conditions of anode.

2.2. Raw Materials Properties

Carbon anodes consist of approximately 60-70 % calcined petroleum coke, 20 % recycled anodes and butts, and 15 % coal tar pitch. The properties of these raw materials have a significant effect on resulting anode properties such as density, electrical resistivity, air and CO_2 reactivities, mechanical properties and anode consumption.

2.2.1. Petroleum Coke

Green petroleum coke is a by-product of petroleum refinery, which constitutes about 2% of the overall production [19]. Mechanical and physical properties of petroleum coke are dependent on the source of crude oil, processes within the refineries and the coke calcination conditions [20, 21]. The crude petroleum contains four different groups, namely aliphatic chains (low carbon), napthene (medium carbon), aromatic chains (high carbon), and the mixture. Petroleum cokes obtained from asphaltenes feedstock, which contains higher amount of aromatic chains and impurities, such as sulfur and metals (vanadium, nickel, calcium and sodium).

Green petroleum coke is calcined at a certain temperature (1200- 1300°C) which is usually higher than the anode baking temperature before using it in carbon anodes as one of the main raw materials [2,3]. There are several reasons for calcination such as increasing C/H ratio, removing water and volatiles, decreasing impurities, minimizing the shrinkage during anode baking, and increasing coke strength [22- 24]. Calcination of coke ensures removing moisture and volatile matter from the coke. Therefore, it decreases cracking during the baking of anodes. Also, it helps pitch enter into the pores of coke during mixing stage in anode production.

Petroleum coke comes from different sources, and the calcination conditions of coke can change based on its source. There are several studies about the effect of calcination temperature on coke and resulting anode properties [14, 15, 18, 23, 25]. It was observed that increasing calcination temperature decreases specific electrical resistivity of coke. Dusting during the electrolysis is explained by the reactivity difference between coke and pitch. Generally, the reactivity of pitch is higher than the reactivity of coke. If the reactivity difference between these two raw materials could be reduced, dusting and consequently anode consumption could be decreased.

2.2.2. Coal Tar Pitch

Coal tar pitch is used as the binder in order to create a bond between dry aggregates [2,3]. It is defined by the International Committee for Characterization and Terminology of Carbon as a residue produced by distillation or heat treatment of coal tar. The physical and chemical properties of coal tar pitch are dependent on the processes conditions and the source of tar. It has a complex structure, which contains aromatic and heteroatom-containing functional groups [26]. During anode baking, pitch carbonizes and binds with the complimentary functional groups of coke [2, 10, 27]. The wetting properties of coal tar pitch affect the resulting anode properties. Good wetting properties of coke by pitch means that pitch not only penetrates into the pores of calcined coke but also fills the void space between the particles.

There are some important properties of pitch, which influence the anode properties such as softening point, density, coking value, and impurities. The softening point of pitch varies. Higher softening point pitches usually help produce denser anodes [28]. Coking value of pitch increases with increasing softening point. In order to obtain good anode properties, pitch should have reasonable coking value (54-61) [2]. The density of pitch is 1.30- 1.32 g/cm^3. Better quality anodes can be produced with increasing pitch density, which provides higher aromaticity [2, 28]. Binder pitch should have higher aromaticity to create bonds between coke particles. The impurities in pitch such as sulfur, sodium, calcium, nickel, and vanadium affect the anode reactivity.

2.2.3. Anode Butts

In aluminum production, carbon anodes are used in the electrolytic cells for the reduction of alumina. Carbon anodes cannot be consumed completely because of the cell design. The remaining part of the carbon anodes (unused part) at the end of the electrolysis is called ‘anode butt’ [2]. Anode butts are used in the anode recipe and constitute 15%-20% of the recipe. The quality of anode butts has a significant effect on anode properties. The impurities in anode butts increase the reactivity of anodes [10, 11].

2.3.Wettability of Coke by Pitch

Wettability of a solid surface by a liquid is the function of the surface and interfacial forces which are both adhesive and cohesive (physical wetting) and the chemical interactions (chemical wetting) [29]. Thus, the wettability of coke by pitch can be not only physical due to adhesive and cohesive forces (intermolecular interactions), but also chemical because of the interface reactions between coke and pitch. The spontaneous interaction is observed when the molten pitch contacts the coke surface. This pattern is used to determine the wetting properties of coke. Wettability of coke by pitch determines the quality of interaction between these two components. Better interaction between these raw materials during mixing directly affects the resulting anode properties such as density, electrical resistivity, air and CO_2 reactivities, and mechanical properties [2]. Improved wettability of coke by pitch helps pitch better penetrate into the pores of the coke as well as the void between different particles. The interactions between the pitch and the particles depend on a number of properties of the latter, notably the particle size, the texture, and the chemical functional groups on the surface.

The wettability of coke by pitch can be quantified by the contact angle. Contact angle is the angle between the solid surface (coke) and the liquid (pitch) when the liquid drops on the solid surface [29, 30]. The relationship between the interfacial tensions and the contact angle is expressed by the Young equation (see Equation 2.3). In the equation, γ_{LV} is the interfacial tension of the liquid-vapor interface, γ_{SV} is the interfacial tension of the solid- vapor interface, γ_{LS} is the liquid-solid interface, and θ is the contact angle. The interfacial tension of the liquid-vapor interface is also called the surface tension (γ_{LV}). The force balance given by the Young's equation is applied at the triple point (contact point of solid, liquid, and vapor phases).

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{LS} \tag{2.3}$$

Figure 2.2 shows the different contact angles between the solid surface (coke surface) and the liquid drop (molten pitch). If the value of the contact angle is greater than 90°, it is considered non-wetting. If the contact angle is smaller than 90°, it is considered that the binder wets the solid surface. The contact angle between coke and pitch should be 0° for complete wetting [30]. There are several studies in which the sessile-drop technique is used to determine the contact angle between coke and pitch [31-35]. The contact angle of the pitch drop on coke bed can be measured using sessile-drop technique at a certain temperature under inert gas atmosphere. It was reported by several researchers that the wettability improves (contact angle decreases) with increasing time and temperature.

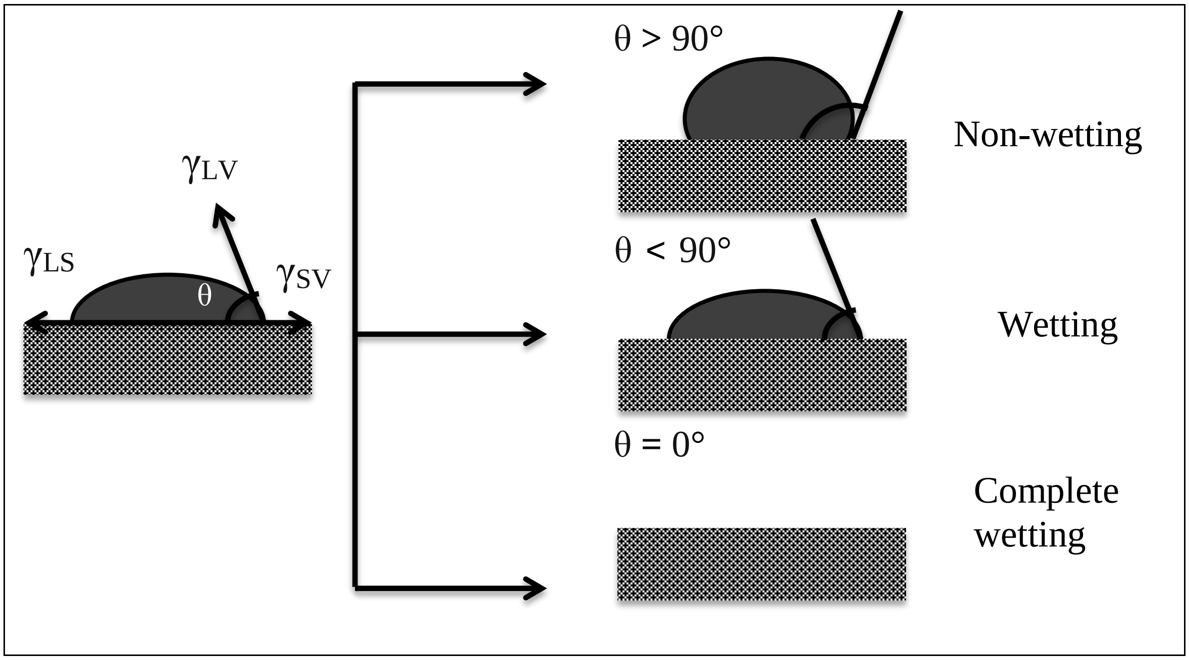


Figure 2.2: Contact angle for a pitch drop on a coke bed

The properties of raw materials (density, viscosity, surface functional groups) have a significant impact on wettability during mixing in anode production [2, 3, 10, 27]. Therefore, improved properties of raw materials provide better wetting. If the wetting between coke and pitch improves, a more homogenous paste can be obtained. In order to obtain good anode quality, pitch should enter the void space between particles as well as penetrate into the pores of coke. The complimentary functional groups of pitch should bond with the complimentary functional groups of calcined coke. There are three kinds of interaction between coke and pitch: hydrogen bonding, electrostatic interaction, and acid-base reactions/condensation. These interactions require aromatics, positive centres, and heteroatom-containing (O, N, S) functional groups [32]. If these functional groups of coke and pitch increase, a better interaction between these two materials can be obtained. This indicates that the modification of raw materials (by adding additives) can improve the wettability of coke and the resulting anode quality.

2.3.1. Modification of Pitch

Coal tar pitch is the by-product of coal tar that is obtained by distillation or heat treatment. It is used as the binder in the anode production so that the coke particles could stick together. The quality of anode depends on the quality of pitch. The properties of pitch such as viscosity, surface tension, penetration ability and the surface functional groups, which can create a bond with coke, play an important role in producing quality anodes. As it mentioned above (Section 2.3), the surface tension is explained in terms of the liquid-vapor interfacial tension (γ_{LV}). It controls the wetting behavior of molten pitch. If the surface tension of the molten pitch is lower than the critical surface tension, the pitch surface is more likely to bind with the coke bed [2]. The viscosity of pitch varies with temperature. The pitch viscosity should be low enough so that it could flow on coke bed for the good wettability of coke by pitch [2, 3].

Pitch has a complex structure that includes aromatic and heteroatom containing functional groups. The structure of pitch has a significant effect on the wettability of coke by pitch. There are several works reported in the literature giving the favorable conditions for better wettability of coke by pitch and the requirements for good mixing [32, 36, 37].

Researchers have studied the improvement of the pitch wetting behavior by the modification of pitch using surfactants and additives. Rocha et al. [37] investigated the effect of two different additives at three different weight percentages on the wetting capacity of petroleum pitch. They found that modification of pitch by additives increased the wettability of coke by petroleum pitch. In the work of Starovit and Maliy [39], the addition of organic compounds such as aceptophene, dimethyl-naphthalene, acenaphthene, fluorine, diphenylene-oxide, α-methyl-naphthalene, and polymeric resins into the pitch was investigated. The addition of additives improved the wetting capacity of pitch through the modification of pitch structure.

Rocha et al. [40] carried out two different studies in order to improve the wettability of coke by pitch. They improved wettability of pitch by the addition of a surface-active agent at different quantities (fatty acid). Also, the pitch with a low wetting capacity was mixed with the pitch with a high wetting capacity to obtain a new pitch with good wetting behavior. In addition, it was reported that during the sessile-drop tests, the use of nitrogen and increase in heating rate helped achieve good wettability.

In the work of Rocha et al. [35] the use of an additive, which is a by-product of the petroleum refining industry, improved the wetting behavior of petroleum pitch (see Figure 2.3). It was also observed by the authors that the quinoline insoluble (QI) content played an important role on the wettability. With a lower QI content, petroleum pitch needed a higher temperature in order to penetrate.

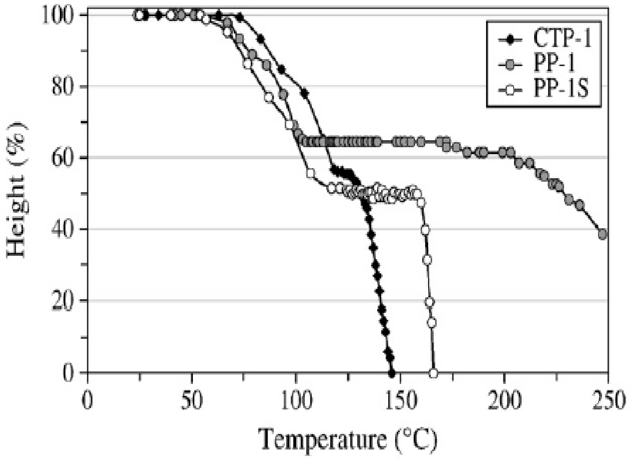


Figure 2.3: Variation of pitch-drop height with temperature for a) coal tar pitch (CTP-1), b) petroleum pitch (PP-1), c) petroleum pitch with an added surfactants (PP-1S) [35]

Another work on the improvement of the wettability of coke by pitch by adding surfactants to pitch was reported by Rocha et al. [41]. The results showed that the addition of the surfactants (two additives were commercial active-surface agents (alkyl/carbonyl and alkyl/sulfur) and one was a product of petroleum refining) at different weight ratios increased the wettability of pitch (see Figure 2.4).

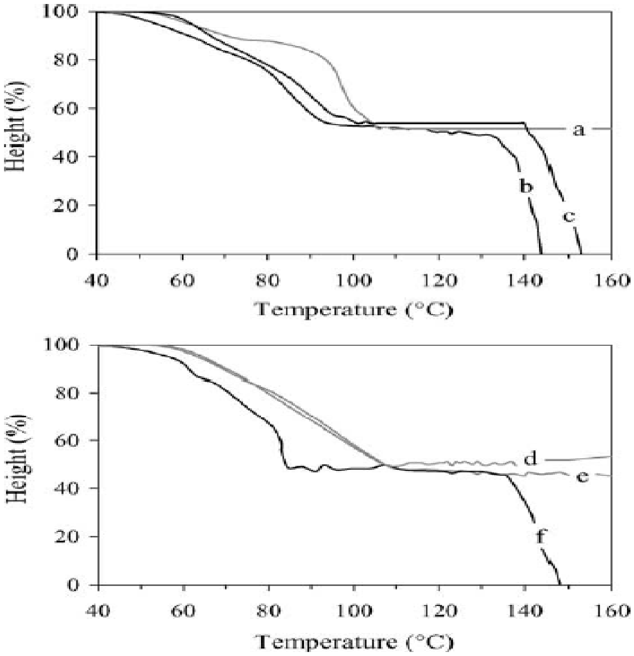


Figure 2.4: Variation of pitch-drop height with temperature for a) non-modified petroleum pitch, b) 5% wt of surfactant B added to petroleum pitch, c) 5% wt of surfactant C added to petroleum pitch, d) 5% wt of surfactant A added to petroleum pitch, e) 10% wt of surfactant A added to petroleum pitch, f) 15% wt of surfactant A added to petroleum pitch [41]

2.3.2. Modification of Coke

Calcined petroleum coke is one of the major raw materials used in the anode recipe. It constitutes about 60-70% of the carbon anodes. The quality of calcined petroleum coke declined over the years [20, 21, 43-45].

In anode production, coke and pitch interact with each other at the mixing stage. The complimentary functional groups of coke bond with the complimentary functional groups of pitch. The interactions between coke and pitch influence the resulting anode density.

Hence, the wettability of coke is an important parameter to consider during the mixing stage [10, 27].

The properties of coke such as porosity, surface chemistry, and density play an important role in the wettability of coke by pitch. The coke porosity should be high enough to allow pitch to enter the pores of calcined coke [2]. The high porosity of coke increases the required pitch amount. Greater amount of pitch might increase the thickness of pitch layer on coke surface if it does not penetrate the pores of the particle.

The surface chemistry has a significant effect on the wetting behavior of coke. It is reported in the literature that the coke surface contains mostly oxygen, nitrogen, and sulfur in addition to carbon [45]. One of the objectives of the calcination of petroleum coke is to increase carbon to hydrogen ratio so that the interaction between coke and pitch can be enhanced. Coke is a highly complex organic material containing different functional groups such as aromatics, heteroatoms and aliphatics. The presence of aliphatic in coke surface creates steric hindrances because of their long chain [10].

There are three kinds of interactions between coke and pitch, namely hydrogen bonding, acid-base reactions/condensation, and electrostatic interaction. These interactions require aromatic and heteroatom-containing functional groups. The increase in these functional groups in coke can increase the possibility to bind with pitch. Table 2.3.2-1 shows the list of functional groups in green petroleum cokes. There is no study found in the literature about the functional groups of calcined petroleum coke from FT-IR study because of its low absorption characteristics to baseline levels [46].

Table 2.1: List of functional groups in green petroleum coke from FT-IR study

Wavenumber (cm^{-1})	Functional groups
750	Ortho-substitution of the aromatic ring [46, 47-49]
830	Aromatic CH out-of-plane vibration frequencies [46, 47]
1126	Esters C-O [48, 49]
1250	C-O-C vibrations in esters or ether [46, 50]
1400-1600	C=C stretching vibrations [46, 49-51]
1600-1700	C=O [49, 50]
2700-3000	Aliphatic C-H [49, 50]
3000-3100	Aromatic C-H [46, 49-51]
3400	N-H groups in secondary amine/OH stretching [47, 49]
3450	OH stretching [50]

Sarkar et al. [32] studied the effect of some coke properties on the wettability of coke by pitch. Figure 2.5 shows the contact angle of three different cokes with increasing time. It was reported in the study that the pitch did not penetrate into Coke 3 because of its lower porosity, lower oxygen content, and higher amount of C-S bond.

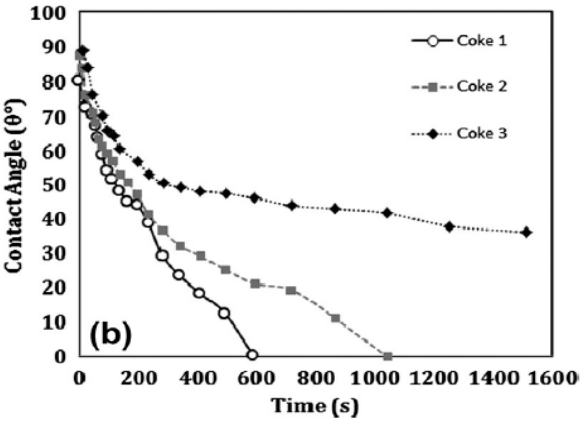


Figure 2.5: Dynamic contact angles of pitch 2 on three different cokes at 190°C [32]

In the work of Jiang et al. [36], petroleum coke was treated by perchloric acid ($HClO_4$) and hydrogen peroxide (H_2O_2). The chemical treatment changed the coke structure. It was observed that the oxygen containing functional groups of coke changed after its modification by chemicals (see Figure 2.6).

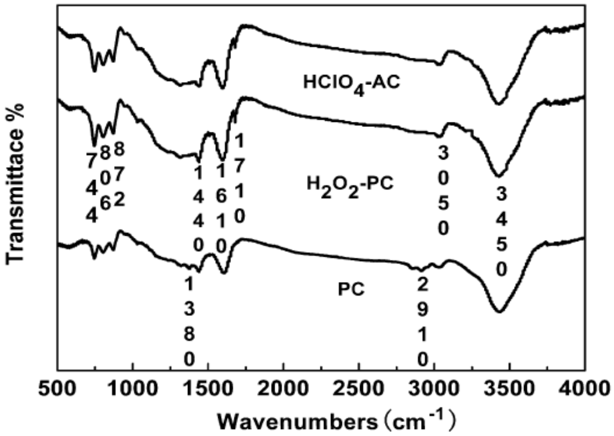


Figure 2.6: FT-IR spectra of petroleum coke with and without modification [36]

As mentioned above, there are a number of studies on the modification of pitch using additives and surfactants in order to improve the wettability of coke by pitch. However, to our knowledge, there is no published study on the improvement of coke properties through the addition of additives, and the use the modified coke in the production of anodes. The current project addresses these issues, coke modification with additives and the impact of using modified coke on the anode properties. Pitch modification is the subject of another project.

CHAPTER 3

EXPERIMENTAL

In this chapter, all experimental systems and characterization methods are explained. The surface characterization of four calcined petroleum cokes (non-modified and modified by additive), one pitch and several different additives was done based on Fourier Transform Infrared Spectroscopy (FT-IR). The cokes were modified using six different additives based on FT-IR results. The wettability of coke (non-modified and modified by additive) by pitch was studied using the sessile-drop system.

Based on material characterization results (FT-IR and wettability), anodes were fabricated with non-modified coke and the cokes modified with additives. The anode fabrication steps such as dry aggregate preparation, modification of coke, mixing, vibro-compaction, and baking are also presented in this chapter. The fabricated anodes were characterized based on apparent density, electrical resistivity, air and CO_2 reactivities, and mechanical properties.

3.1. Characterization of Raw Materials

3.1.1. Modification of Coke with Additives for Characterizations

In this study, four different cokes and six different additives were used to improve the wettability of coke by pitch. In order to modify the coke, additives were dissolved in a solvent using a beaker and a magnetic stirrer (Cole- Parmer stirrer). Then coke was added to the solution. Figure 3.1 shows the modification steps of a coke. It should be noted that this procedure is for the characterization of coke only. During anode manufacturing, the whole dry aggregate (all solid particles) was modified with additives. The details of this procedure are given in Chapters 4 and 5.

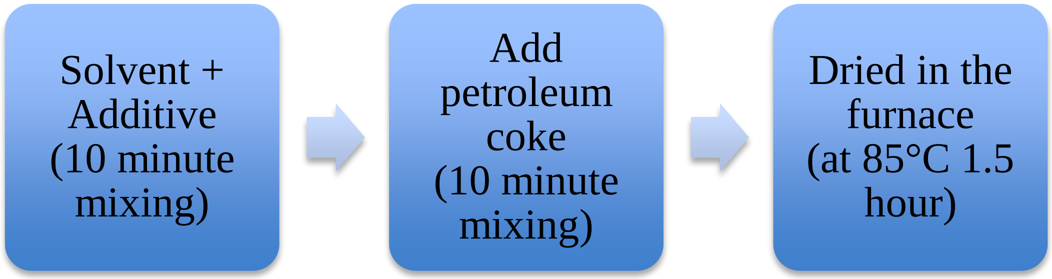


Figure 3.1: Modification steps of coke

3.1.2. Fourier Transform Infrared Spectroscopy (FT-IR)

Coke and pitch are the main components for anode production, and their quality of can directly affect the properties of anode. Both components have complex structures to analyze. The chemical structure of coke and pitch plays an important role in the interaction between coke and pitch at the mixing stage during anode manufacturing. FT-IR is one of the most common, easy, and inexpensive techniques to analyze the structure of materials. It gives an idea about presence of the functional groups, which help coke-pitch interaction, in coke, pitch, and additives. In this study, coke, pitch and additives were analyzed by using Nicolet 6700, which can be seen in Figure 3.2. Characterization was done using KBr, and the ratio of KBr to sample was around 200:1. The number of scans was 36, and the spectra were registered for the wavenumber range of 400-4000 cm^{-1}. Each experiment was repeated two times, and the average value was used for the analysis. Linear baseline correction was carried out for each sample using the Omnic software. The results were presented after the baseline correction in absorbance mode was done.

Figure 3.2: Fourier Transfer Infrared Spectroscopy (FT-IR)

3.1.3. Wettability

Wettability is defined as the ability of a liquid to spread on a solid surface. It represents the interaction between the liquid and the solid surface and can be quantified by measuring the contact angle (θ°) between them. In this study, four different cokes (with and without additives) and one pitch were used to determine the wettability of coke by pitch.

The sessile-drop system is one of the most common systems to determine the wetting properties of materials. In this project, the wettability of coke by pitch was studied using the sessile-drop system (see Figure 3.3). The system consists of a tube furnace (Thermolyne 21100), one graphite crucible for pitch (pitch injection system), a graphite sample crucible (for coke bed), a digital camera (Appro B/W Camera), and a vacuum pump.

Figure 3.3: Sessile-drop experimental set-up at UQAC

The crushed and sieved coke particles (particle size of -125+100 µm) were placed on the crucible. This particle size was also used in other studies [10, 26, 32]. The coke particles were compacted in the same crucible each time to have a smooth surface. The volume of coke samples was identical in each experiment. The bulk density measurement was carried out for different cokes in order to maintain the same porosity between particles and the same packing for all samples. Different packing can give different wetting results. The solid pitch was filled into the injection chamber, which has a small hole for the drop to fall. The coke bed and the injection chamber, which is full of solid pitch, were placed into the tube furnace. Before starting the experiment, vacuum was applied to the tube furnace in order to remove O_2 because O_2 can react with coke or pitch at high temperatures. All experiments were performed under N_2 atmosphere. N_2 was passed through O_2 (Chromatographic Specialties, Chromspec, C36084) and humidity traps to remove from O_2 and reduce the humidity before sending it to the furnace. The system consists two lines for N_2. The first line is connected to the tube furnace to supply N_2 to the inside of the furnace. The second line provides N_2 to the injection chamber. The injection chamber, which contains solid pitch, was placed on top of the coke bed. When the pitch becomes liquid, it falls directly onto the coke bed. The hole of the injection chamber should be the same for each experiment in order to maintain the same drop size. Images of the pitch drop on the coke surface were recorded with a camera. The FTA-32 software was used to measure the contact angle between the pitch drop and the coke bed at different times. The experiments were done at 170°C which is the typical mixing temperature used by the industry. Each experiment was done two times with the same drop size, and the average value of two experiments was used for the study.

3.1.4. Tapped Bulk Density

The tapped bulk density (TBD) measurement was done for four different cokes to maintain the same packing for wetting experiments. The crucible for wetting experiment was filled with coke 1 and the weight was recorded. Then, the volume was calculated by dividing the weight by TBD of Coke 1. The calculated volume was kept the same for the other three cokes. In order to maintain the same porosity between the coke particles, the weight of each coke was calculated based on their TBD at constant volume. If the porosity (packing) of coke particles differs from each other, the wetting results can be misleading.

The TBD measurement device is shown in Figure 3.4. A certain amount of sample was taken and was put in a 250-ml cylinder. The tapping was done for 6 minutes. The TBD (g/cm^3) was calculated by dividing the weight by the volume, which was measured at four different places on the cylinder. The TBD measurement was done based on ISO 10236:1995. The tapped density results are presented in Appendix 1.

Figure 3.4: Tapped bulk density equipment at UQAC

3.2. Preparation of Laboratory Scale Anodes

3.2.1. Dry Aggregate Preparation

The same dry aggregate recipe, a typical industrial recipe, was used for each anode. The anodes were fabricated in the UQAC laboratory under conditions similar to those of the industry. Different fractions of coarse, medium, and fine particles were used to have a certain granulometry. Recipe consists of 15% of pitch and 85% of anode butts, green and baked rejects, and calcined petroleum coke.

3.2.2. Modification of Dry Aggregate with an Additive for Anode Production

Two methods were applied to modify the dry aggregate particles. In both methods, additives were dissolved in a solvent to provide better interaction with coke. The detailed information about the modification of dry aggregate particles with additives for anode production is given in Chapters 4 and 5.

3.2.3. Mixing

The dry aggregate was transferred to the intensive mixer (see Figure 3.5) manually and then molten pitch was added to the mixture. Dry aggregate and pitch were mixed for a certain period of time at 170°C. After mixing, the paste was ready to be compacted in the vibrocompactor.

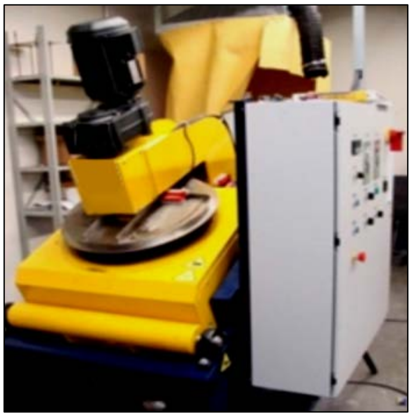


Figure 3.5: Intensive mixer at UQAC

3.2.4. Vibrocompaction

Anode forming was done using the vibrocompactor in the UQAC laboratory (Figure 3.6). The paste was transferred from the mixer into the preheated vibrocompactor mould. The load, which is used as a cover for mould, was placed on the top of the mould. The vacuum was applied to the mould so that there were no trapped gases that can cause cracks during baking. The forming parameters were set always to the same values for each anode. The compaction was carried out. Then, the green anode was left for cooling at room temperature.

Figure 3.6: Vibro-compactor at UQAC

3.2.5. Baking

The green anodes were cored, and the cores were baked in a baking furnace (Pyradia, Model-B07D02029021SVCCH) in the UQAC laboratory (Figure 3.7). Since baking significantly affects the anode properties, the same baking conditions were used for all anodes. The baking conditions were representative of the industrial practice. All cores were placed inside the furnace at the same time. Then they were covered with filler coke so that during baking this material would be consumed instead of cores. Several thermocouples were placed in the furnace at different positions in order to track the temperature distribution. When the furnace reached the desired temperature, 8 hours of soaking was applied.

Figure 3.7: Baking furnace that is used for baking green anodes at UQAC

3.3. Characterization of Laboratory Scale Anodes

The characterization of laboratory scale anode cores was done based on four criteria: apparent density (ASTM D5502-00 (2015)), electrical resistivity (ASTM D6120-97 (2012)), air (ASTM-D6559-00a) and CO_2 (ASTM-D6558-00a) reactivities as well as dusting and flexural strength (ISO N 848).

3.3.1. Sample Preparation

The characterizations work was done on anode cores. Green anodes were cores at four different positions, and 50 mm-diameter and 130 mm-long cylinders were cut from the anode. The core positions and the samples taken from the cores for reactivity tests are given in Figure 3.8.

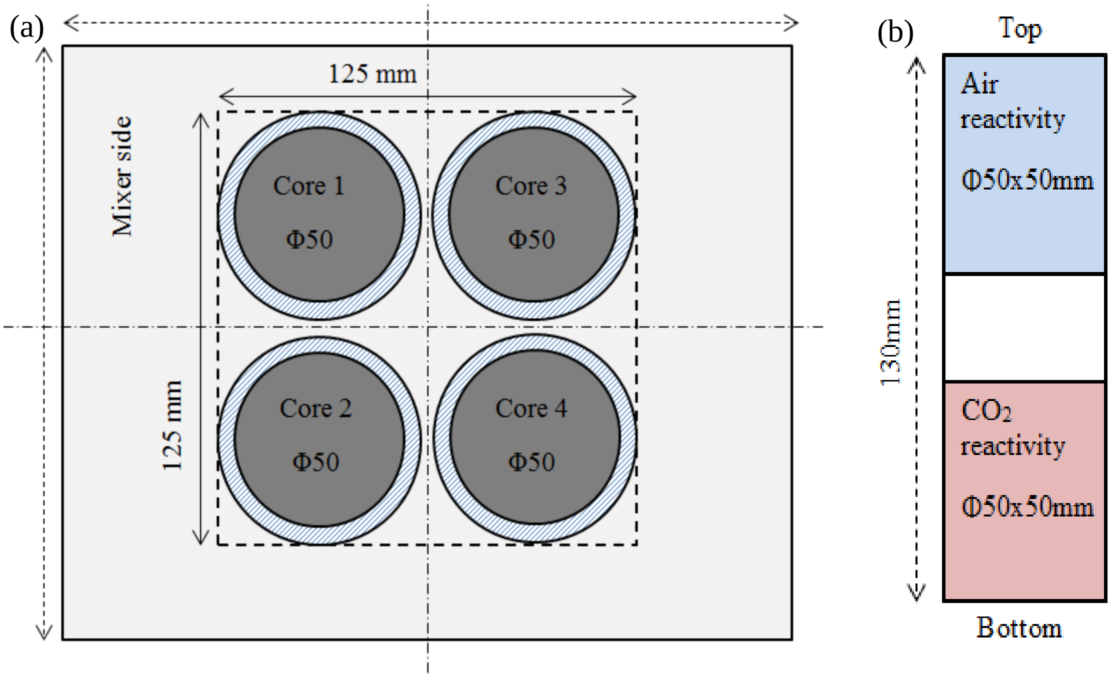


Figure 3.8: (a) Anode coring plan for anode characterization (b) Position of samples used for air/CO_2 reactivity experiments

All cores were dried. Then, green density and green electrical resistivity measurements were carried out for all four cores. Core 2 and Core 3 were baked. Baked density and resistivity of Core 2 and Core 3 were measured. Core 2 was used for reactivity measurements. Samples used for air and CO_2 reactivity experiments are shown in Figure 3.8 (b). The top section of the core (Φ50x50 mm) was used for air reactivity and the bottom section of the core (Φ50x50 mm) was used for CO_2 reactivity measurement. Core 3 was used for the flexural strength test.

3.3.2. Apparent Density

After coring, all cores were dried. Length (l, cm) of the cores was measured at eight different places using the slide caliper as well as the diameter (d, cm) at four different places. The averages of eight measurements for length and four measurements for diameter were taken and used for the volume calculation (see Equation 3.1). Also, the weight (W, g) of the cores was measured using a balance with 0.01 g of accuracy. Density was calculated by dividing by the volume of the sample (see Equation 3.2). Density measurement was performed for green and baked cores.

$$V = \pi \left(\frac{d^2}{4}\right) l \qquad cm^3 \tag{3.1}$$

$$D = \frac{W}{V} \qquad g/cm^3 \tag{3.2}$$

3.3.3. Electrical Resistivity

The resistivity measurements for green and baked cores were carried out using the device developed at UQAC (shown in Figure 3.9). The average diameter, which was calculated for density, was used for resistivity. An electrical current of 1A was passed through the sample and the voltage drop was recorded between two points over a certain length (100 mm). The electrical resistivity (ER) was calculated based on current (I, A), voltage drop between the two points (V), cross sectional area of the sample (a, cm^2), and the length between two points (100 mm) (see Equations 3.3 and 3.4).

$$a = \pi \frac{d^2}{4} \qquad cm^2 \tag{3.3}$$

$$ER = \frac{V\ x\ a}{l\ x\ l} \qquad \mu\Omega m \tag{3.4}$$

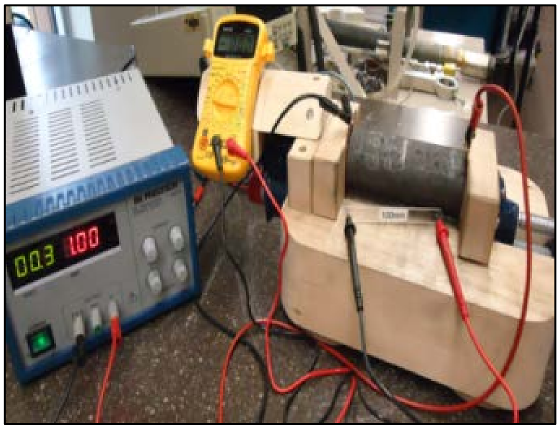


Figure 3.9: Electrical resistivity measurement setup for anode cores at UQAC

3.3.4. Air and CO_2 Reactivities

Air and CO_2 reactivity measurements including dusting for baked cores (Φ50x50 mm) were done using the thermogravimetric (TGA) method (see Figure 3.10). There are several steps for the reactivity experiments based on ASTM-D6559-00a0 and ASTM-D6558-00a;

- The tube furnace (Carbolite) was preheated before starting the experiment (for air reactivity 525°C and for CO_2 reactivity 960°C) under N_2 atmosphere.
- The sample was placed in the tube furnace.
- N_2 was continued to pass for 30 minutes before entering the reaction gases (air or CO_2).
- Then, air or CO_2 was injected to the system at a velocity required by the ASTM standards.
- The initial weight was recorded at 31st minute (W_i) using the balance.

- The air was passed through for 3 h at 525°C for air reactivity measurement and CO_2 was passed through for 7 h at 960°C for CO_2 reactivity measurement.
- The weight of the sample was measured at 210th minute for air reactivity and at 450th minute for CO_2 reactivity (W_f, mg).
- The sample was removed from the crucible inside the furnace, and the exposed dust on the sample surface (W_{d1}, mg) was collected immediately. Otherwise, the air inside the room can affect the dusting results.
- Also during the experiment, the dust was collected inside the furnace in the crucible. This was also measured (W_{d2}, mg).
- The reactivity was calculated based on the exposed surface area of the sample (A), and W_i, W_f, W_{d1} and W_{d2}. Time is 3 h for air reactivity and 7 h for CO_2 reactivity (see Equation 3.5).
- Also dusting was calculated using W_{d2}, empty crucible weight (W_c), exposed surface area of the sample (A), and the test time (3 h for air reactivity and 7h for CO_2 reactivity) (see Equation 3.6)
- For the exposed surface area calculation, the average length (l, mm) and the average diameter (d, mm), determined for density and resistivity measurements, were used (see Equation 3.7).

$$A = \frac{\left(\pi d l + \frac{2\pi d^2}{4}\right)}{100} \quad cm^2 \tag{3.5}$$

$$Reactivity = \frac{[\left(W_i - W_f\right) + (W_{d2} - W_{d1})]}{A\ x\ hour} \quad mg/cm^2 h \tag{3.6}$$

$$Dusting = \frac{(W_{d2} - W_c)}{A\ x\ hour} \qquad mg/cm^2h \tag{3.7}$$

Figure 3.10: Thermogravimetric (TGA) analysis system for air/CO_2 reactivity of anode core samples at UQAC

3.3.5. Flexural Strength

The flexural strength measurement was performed using the three-point bending method based on ISO N 848. A sample was placed inside the device (MTS Alliance RT100) shown in Figure 3.11. The equipment applied a steady and linearly increasing load in the middle of the sample. The maximum load is the load applied when the sample breaks. The flexural strength was calculated using the maximum load (F_{max}, N), support span length (L, m), and the diameter of the sample (d, m) (see Equation 3.8).

$$Flexural\ Strength = \frac{8\ F_{max}\ L}{\pi\ d^8} \qquad N/m^2 \tag{3.8}$$

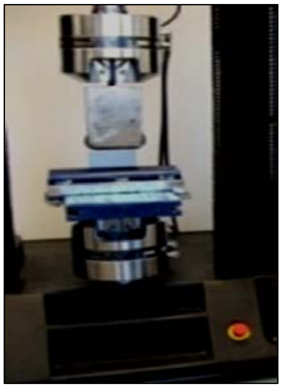


Figure 3.11: Three-point bending test setup at UQAC

CHAPTER 4

MODIFICATION OF COKE BY DIFFERENT ADDITIVES TO IMPROVE ANODE PROPERTIES

(Submitted to FUEL and the first review is completed.)

Abstract

Aluminum is produced in electrolytic cells using carbon anodes, which consist of a mixture of coke, pitch, and recycled carbon material. Anodes play an important role in aluminum production. The quality of raw materials can vary based on the source and the process parameters. In spite of the variations in the raw material properties, the industry has to maintain the quality of anodes. In order to manufacture good quality anodes, coke and pitch must interact well with each other. The affinity between these two components depends on good wetting properties, which will lead to good binding of the particles. The main objective of this work is to modify the coke in order to improve its wetting properties using different additives. An FT-IR study was done to identify certain functional groups in non-modified and modified coke as well as in pitch. The wetting tests were carried out using the sessile-drop method to measure the contact angle between coke and pitch. Based on FT-IR and wettability results, an additive was selected and used for the fabrication of anodes, which were characterized before and after baking. The modification of coke with the selected additive improved the anode properties.

4.1.Introduction

Aluminum is produced by the electrolytic reduction of alumina. In this process, the carbon anodes are consumed according to Equation 4.1.

$$2Al_2O_3+3C = 4Al + 3CO_2 \tag{4.1}$$

The carbon anodes are made of dry aggregate (calcined petroleum coke, butts and recycled anodes) and coal tar pitch. The dry aggregate and pitch are mixed to form the anode paste at around 170°C. The anode paste is compacted in a press or vibro-compactor to produce the green anode. The green anode is baked in a furnace to produce the baked anode. Calcined coke constitutes around 65-70% of the anode raw materials. Carbon anode cost is one of the major elements of the aluminum production cost, which could exceed 20% [52].

In recent years, the demand for anode-quality raw materials has increased due to the increase in aluminum production. The calcined petroleum coke and coal tar pitch are the main raw materials required for the production of carbon anodes. Properties of calcined coke are important since it is present in anodes in large quantity and directly affect the quality of baked anode. It is a solid by-product from oil refineries, representing some 2 % of their overall revenues [19]. Thus, the quality of coke is not a primary concern for the refineries. Its quality depends on the crude oil, processes within the refineries, and calcination conditions. Thus, the quality of calcined coke can change. Pitch is also a by-product of the coal tar industry, and its quality can also change. A good quality baked anode has high density, low electrical resistivity, low air and CO_2 reactivities, and good mechanical properties [2]. In spite of the variation in the raw material quality, the industry has to maintain the anode quality.

During anode manufacturing, calcined coke and pitch interact with each other in the mixing stage. The pitch, which is used as a binder, must not only fill the void space between particles, but also penetrate into the pores of calcined coke [53]. During baking, the pitch carbonizes and binds the coke particles together. This requires good wetting properties between the two components [32]. To achieve this, the surface tension must be reduced, and the interaction between coke and pitch needs to be enhanced. In order to obtain good anode, the raw material properties should be improved.

Wettability of a solid surface by a liquid is the function of the surface and interfacial forces which are both adhesive and cohesive (physical wetting) and the chemical interactions (chemical wetting). When a liquid makes contact with a solid surface, a spontaneous interaction takes place at the interface. The resulting pattern (contact angle) is used to determine the wetting properties of solid [29]. Wettability of coke by pitch controls the interactions between these two components. Improved wettability of coke by pitch helps pitch better penetrate into the pores of the coke as well as the void between different particles. Three kinds of chemical interactions are possible between coke and pitch: hydrogen bonding, electrostatic interaction, and acid-base reactions/condensation. These interactions require aromatics, charged centres, and heteroatom-containing (O, N, S) functional groups [32].

The interactions between the pitch and the particles depend on their properties. Among the properties of coke, the particle size, the texture, and the chemical functional groups on the surface considerably affect the wettability of coke by pitch. In order to quantify the wettability, the contact angle between the solid and the liquid surfaces is measured. If the value of the contact angle is greater than 90°, it is considered non-wetting. If the contact angle is smaller than 90°, it is considered that the pitch wets the solid surface [30].

Coke is one of the major raw materials used in the anode recipe. The interactions between coke and pitch influence the resulting anode density. Hence, the wettability of coke is an important parameter to consider during the mixing stage. In the work of Sarkar et al. [32], the influence of some coke properties on the wettability was investigated. It was observed that porosity, O_2 content, and the amount of C-S bond control the wettability of coke by pitch. Usually electronegative heteroatoms such as O, N and S help formation of hydrogen and covalent bonds between coke and pitch enhancing the coke-pitch interaction. Sarkar et al. [32] identified the role of C-S based on linear multivariable analysis. Jiang et al. [36] studied the effect of chemical treatment of petroleum coke by perchloric acid ($HClO_4$) and hydrogen peroxide (H_2O_2). After the modification, the structure of coke changed, and the specific surface area increased. The oxygen containing functional groups increased due to the chemical treatment. However, they did not use the coke for anode production.

Pitch is also one of the important raw materials in the anode production. Researchers have studied the improvement of the pitch wetting behavior by the use of surfactants and additives [35, 38, 40, 41], and different organic compounds such as aceptophenone, dimethyl-naphthalene, acenaphthene, fluorine, diphenylene-oxide, α-methyl-naphthalene, and polymeric resins [32]. However, to our knowledge, there is no published study on the improvement of coke properties, and use the modified coke in the production of anodes.

The aim of this study is to improve the wettability of coke by pitch using additives. Based on the wettability test results carried out with and without additives, anodes were fabricated and characterized in the carbon laboratory of the UQAC Research Chair on Industrial Materials (CHIMI) to see the effect of coke modification on anode properties.

4.2.Experimental

4.2.1. Material Used

In this study, a calcined petroleum coke and a coal tar pitch were used. They were obtained from the industry. The softening point of the pitch was around 120°C. Six additives and a solvent (aliphatic alcohol) were purchased from Sigma Aldrich. Organic additives that would not leave any inorganic residues during heating at high temperatures (i.e., during anode baking) were chosen. Measured quantities of additives were dissolved in the solvent and were then used to modify the coke. The melting and boiling points and the physical states at room temperature of the six chemicals are presented in Table 4.1. The generic names of the chemicals are presented in Table 4.1 hiding some detailed structural information due to confidentiality.

Table 4.1: Properties of the Additives

Additive	Physical appearance	Melting point (MP), °C	Boiling point (BP), °C	Generic class	Health Risk
A1	Liquid	7.5	248	Phenyl-alkyl-aldehyde	It is a skin irritant at high concentration, it is never been reported anywhere that this compound is a carcinogen or causes a long-term health hazard
A2	Aqueous suspension	~0	310	Polyethylene-glycol-alkyl-ether	Long term exposure at high concentration can affect reproductive functions.
A3	Solid	122	283.5	Dioxin	It may cause skin lesions. Long-term exposure can affect immune system, nervous system, endocrine system and reproductive functions.
A4	Solid	145-170	High	Aliphatic dicarboxylic acid	It can cause blisters. Ingestion can cause sore throat, abdominal pain. vomiting, convulsions, etc.
A5	Solid	101	149	Benzophenone	It may cause irritation when comes in contact to skin, eye etc. There is no report of carcinogenic nature.
A6	Aqueous solution	-114.2	-85.5	Hydrochloric acid	It is corrosive to the eyes, skin, and mucous membranes. Short-term exposure may cause respiratory tract irritation and pulmonary edema.

**The properties given are for hydrogen chloride (HCl) gas. Hydrochloric acis (HCl), which is aqueous (aq), forms when hydrogen chloride gas dissolves in water. Boiling and melting points of aqueous HCl depend on the concentration of HCl gas dissolved in the solution.*

4.2.2. Modification of Calcined Coke with Additive

a) For Wettability Experiment

Calcined coke particles of size less than 1 mm were crushed in a laboratory hammer mill (Retsch SK 100). The crushed particles were sieved using a sieve shaker (Humboldt MFG) and -125+100 µm particles were collected. This particle fraction was modified using the additives for the wettability tests.

Addition of solid or aqueous suspension chemicals directly into coke does not ensure homogeneous mixing and the modification of all coke particles. Thus, the chemicals were dissolved in a solvent. A polar high-dielectric constant solvent with low boiling point was used to ensure that the chemicals will dissolve in this solvent and the solvent will evaporate during drying. The high dielectric constant indicates the high polarity of the solvent, which dissolves polar additive molecules. A measured quantity of the additive was dissolved in a specific volume of the solvent using a magnetic stirrer. Then, measured quantity of coke was added to the solution, which was stirred for 10 minutes. The mixture was dried in a furnace at 85°C for 1.5 h. The modified coke samples were finally cooled to room temperature and used for the wetting experiments.

b) For Anode Preparation

One standard anode (used as a reference) and one anode with the coke modified with a chosen additive were produced to determine the effect of that additive on anode properties. All the other raw materials (pitch, anode butts, green and baked rejects) and fabrication conditions were maintained the same. The optimum pitch content was chosen based on the previous study [27] carried out at UQAC. This study was done using untreated coke and pitch. It was found that 15-17% pitch can help produce good quality anodes with good properties. In this study 15% pitch content was used. The pitch content was not optimized for anode made with the modified coke. Such a study might improve further the properties of the anodes. However, it was not within the scope of this work.

The standard anode was manufactured using non-modified coke. Then, the solution, which contains the measured amount of additive and a certain amount of solvent, was prepared for the modification of the coke. The percentage of the additive was calculated based on the dry aggregate amount. The dry aggregate was placed in a container. Then, the solution was added slowly to the container. The temperature was increased to 50°C and maintained for five minutes. After, the mixture was left at room temperature for 1 day to dry.

4.2.3. Sample Characterization

4.2.3.1.Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR experiments were done to identify different functional groups present in the cokes (modified and non-modified with chemicals), pitch, and additive samples using Nicolet 6700 FT-IR. KBr was used to prepare the sample and the ratio of KBr to sample was approximately 200:1. The number of scans carried out was 36 for each sample to get the average spectra. The IR spectra were collected for the wavenumber range of 400-4000 cm^{-1}. The spectra were smoothened, and linear baseline correction was done using Omnic software. Each sample was analyzed two times at room temperature, and the average value was used.

4.2.3.2.Wettability

Wettability experiments were carried out using the sessile-drop method with a set-up available in the carbon laboratory of Chair CHIMI. The equipment includes one tube furnace, an injection chamber for pitch, a graphite sample crucible, a camera, a vacuum pump, and a nitrogen line. Measured quantity of coke sample was placed into the graphite sample crucible and was compacted to achieve a smooth coke bed surface. The injection chamber contained the solid pitch sample. This chamber has a small hole in its body and is placed just above the coke sample by rotating the injection chamber during the experiment. The coke and pitch were heated in a tube furnace. Since calcined coke or pitch can react with oxygen at high temperature, an inert nitrogen atmosphere was maintained inside the furnace. The nitrogen gas was passed through O_2 and humidity traps before entering the system. The temperature was set to 170°C, which is the average anode paste (mixture of aggregate and pitch) temperature used in industry during mixing. At 170°C, coke will not catch fire, since this temperature is much lower than the auto-ignition temperature of coke. However, there will be loss of coke in presence of oxygen due to formation of CO and/or CO_2. The images of the pitch drop on the coke bed were saved at each predetermined time interval, and the contact angles were calculated at different times using the software FTA-32. Further information about the sessile-drop system was published elsewhere [10, 11, 27]. Each experiment was repeated twice, and the average of the contact angles measured during these two experiments was used for the analysis. If the contact angle value at a certain time differed by more than 5°, the experiment was repeated.

4.2.4. Fabrication of Laboratory Anodes

A measured quantity of dry aggregate (modified or non-modified) was mixed with molten coal tar pitch in a mixer to form the anode paste. The dry aggregate contains calcined petroleum coke, butts, green and baked rejects of certain granulometry (measured quantity of coarse, medium and fine particles) [11]. The paste temperature was maintained at around 170°C. The paste was compacted in a vibro-compactor for one minute. Green anodes (nearly 10 kg) of rectangular cross-section were obtained from the vibro-compactor mould. Four cylindrical cores of 50 mm in diameter were cut from the green anode [10, 27]. The density and the electrical resistivity of the green cores were measured. Two of the cores (same positions for all the anodes) were baked in a baking furnace using a heating rate (11°C/h) similar to that used in the industry. The final baking temperature was 1100°C. After reaching 1100°C a soaking time of 8 h was applied. These baked cores were used for further studies. A detailed description of the anode manufacturing process and the baking conditions was published elsewhere [10, 11, 27].

4.2.5. Characterization of Anode Properties

The density and electrical resistivity of the green anode samples (GAD, GER) (φ50 x 130 mm) were measured according to ASTM D5502-00 (2015) and ASTM D6120-97 (2012), respectively.

The length and diameter of the cores were measured at different places (8 places for length, 4 places at 3 levels for diameter) using a digital slide caliper, and the average length and diameter were calculated. These average values were used to calculate the volume of the core. The density was measured by dividing the mass of the sample by the volume.

The resistivity (ρ) of the cores was measured by the four-point method. A current (I) of 1 A was passed between the two ends of a core. The voltage drops between two points separated by 100 mm was measured at 4 different places to calculate the average voltage drop (V). A custom-made equipment available at UQAC was used to measure the resistivity. The resistivity of the core was calculated using Equation 4.2.

$$\rho = \frac{V}{I}\frac{A}{L} \tag{4.2}$$

where, A is the cross-sectional area and L is the distance between the points where voltage drop was measured. In this case L was 100 mm.

The density, electrical resistivity, and flexural strength of the baked cores (BAD, BAR) (φ50 x 130 mm) were measured based on ASTM D5502-00 (2015), ASTM D6120-

97(2012), and ISO N 848, respectively. The density and resistivity of the baked cores were measured the same way as described earlier the methods for measuring them for the green cores. The flexural strength of the baked cores was measured by 3 point bending method using Instron. The sample was placed horizontally on two pointed blocks separated by 80 mm (l). Then a force is applied on the sample at the middle of the two supports. The maximum force (F), which caused the sample to break, was recorded. The flexural strength (σ) was calculated using Equation 4.3.

$$\sigma = \frac{F\,l}{(d/2)^3} \tag{4.3}$$

where, d is the diameter of the sample.

Then, two φ50 x 50 mm samples were cut (one from the top and another from the bottom) from one of the baked cores (same for all the anodes). The φ50 x 50 mm sample from the top was used for air reactivity measurement (ASTM-D6559-00a), and the sample from the bottom was used for CO_2 reactivity measurement (ASTM-D6558-00a). During the reaction, pitch is usually consumed more compared to the calcined coke. This differential oxidation results in the loss of binder pitch between the coke particles. Consequently, the coke particles fall in the electrolytic cell; this phenomenon is called dusting. The dusting was also measured for the reactivity studies. The reactivities of the samples were measured using a thermogravimetry equipment (Carbolite TVS 12/600 furnace and Mettler toledo model XS2002S balance) available at UQAC. The reactivity and dusting were measured based on the standard procedures (3 h at 525°C for air reactivity, 7 h at 960°C for CO_2 reactivity, gas flow rate 2.2 l/min). The detailed descriptions of the characterization methods were published elsewhere [10].

4.3.Results and Discussions

4.3.1. FT-IR Results

Wetting of coke by pitch can be physical and/or chemical. The physical interaction is controlled by the surface texture and porosity of coke, and viscosity of pitch. The chemical interaction is controlled by the functional groups present in coke and pitch. As same pitch was used in the study, the physical and chemical properties of pitch did not change. Similarly, since the same coke was used, the surface texture and porosity of coke did not change. The treatment of coke by the additives modifies the chemical nature of the coke surface. Thus the property that might change due to the treatment of coke is the functional groups on the coke surface. There are different techniques (such as x-ray photoelectron spectroscopy, nuclear magnetic resonance spectroscopy etc.) to identify and estimate the functional groups. However these methods are costly. FT-IR spectroscopy is a simple, low-cost method for the estimation of these groups, with the available portable FT-IR, this method can be easily utilized in the industry. Thus, in this study the focus was on FT-IR. As the wettability of treated coke by pitch was controlled by the chemical functional groups on the coke surface, the effort was made to correlate the wettability of coke by pitch with the FT-IR results. So far no quantitative study has been reported to correlate the wettability and FT-IR results.

FT-IR spectra can give an idea of the presence of different functional groups in a sample. FT-IR spectra are usually analyzed based on certain fingerprint regions, which are unique to certain functional groups. Due to the presence of different neighboring molecules, steric hindrances, position, and orientation of the functional groups, there might be some shifts in their rotational, vibrational, and stretching energies. These energies correspond to the wavenumbers in the FT-IR spectra. Table 4.2 lists the ranges of wavenumbers for certain functional groups. Thus, a peak in that range will represent the specific functional group.

Table 4.2: List of functional groups in calcined coke from FT-IR study

Wavenumber (cm^{-1})	**Functional group**
700-900	Substituted (ortho, meta, and para) aromatic ring [46]
1000-1300	C-O, -O- [46, 47]
1700-1800	C=O or CO_2 [48]
2700-2950	Aliphatic (C≡C, C=C, and C-C) [49, 50]
3000-3100	Aromatic C=C [50]
3300-3600	N-H group- secondary amine-OH stretching (mostly hydrogen bonded) [47, 50]
3600-3800	Free moisture, phenol or carboxylic acid [36, 49]

For FT-IR spectra using KBr pellet, it is difficult to correlate the peak area with the concentration of the functional group due to the probability of non-homogeneous distribution of the KBr sample and the interaction of the sample with the laser beam. Some researchers normalized the FT-IR spectra based on a certain reference peak [54]. However, this method is difficult to apply in the case of coke and pitch samples. Thus, the absolute value of peak area might not give a reasonable idea of the concentration of a specific functional group in coke or pitch samples. The ratio of two different peak areas can be used to avoid the problem. This ratio can give an idea of the relative amount of a particular functional group. Whatever be the method of analysis, FT-IR peaks indicate the presence of different functional groups.

Figure 4.1 shows the FT-IR spectra of the non-modified coke and pitch. The spectra show that both coke and pitch contain aromatic and aliphatic functional groups (see Table 4.2). They also contain heteroatom (O and N) containing functional groups (see Table 4.2). Aliphatic functional groups do not facilitate the coke-pitch interactions due to the steric hindrances of the long aliphatic chains [10]. Aromatic rings have negatively charged ∏-electron cloud. The electron cloud can form electrostatic bonds with positive centers (such as quaternary ammonium species). Electronegative atoms (such as O and N) attached to hydrogen pulls the electron cloud towards them making hydrogen positively charged. These hydrogen atoms can form hydrogen bond with other electronegative atoms. Two molecules can undergo condensation reactions through the elimination of small molecules (such as water or ammonia). Acid-base reaction can also take place between an acidic functional group (phenolic –OH and pyrrole) and a basic functional group (amine, and pyridine). FT-IR analysis cannot detect the presence of the specific compounds such as pyridine, pyrrole, etc. However, earlier studies showed that the presence of different functional groups necessary to form different types of bonds in coke and pitch samples can be detected using FT-IR [10, 27]. It has also been explained that these types of bonds can take place between coke and pitch. Detailed study of these compounds needs XPS analysis, which is a costly procedure [10, 27]. The objective of this study was to develop criteria for the extent of wettability, which can be applied in industry. FT-IR is a simple technique, and low-cost hand-held FT-IR analyzers are available in the market. Therefore, the functional groups were analyzed using only FT-IR analysis in this study. The FT-IR results showed the presence of aromatic, aliphatic, and heteroatom-containing functional groups in both coke and pitch, which can help coke-pitch interactions. A functional group in coke can bind with the complementary functional group in pitch. Depending on the source and process conditions, the quality of pitch and coke, which depends on the amount of functional groups available on the surface, may vary. Low amounts of aromatics and heteroatom-containing functional groups result in poor coke-pitch interactions. The amounts of these functional groups may vary in different coke and pitch samples. Thus, the focus of this work was on the addition of chemicals (additives) containing these functional groups. The additive binds the functional groups of coke and/or pitch and initiates the interaction between them, resulting in improved wetting. Improvement of the wettability of coke by pitch can help improve anode quality [10, 27].

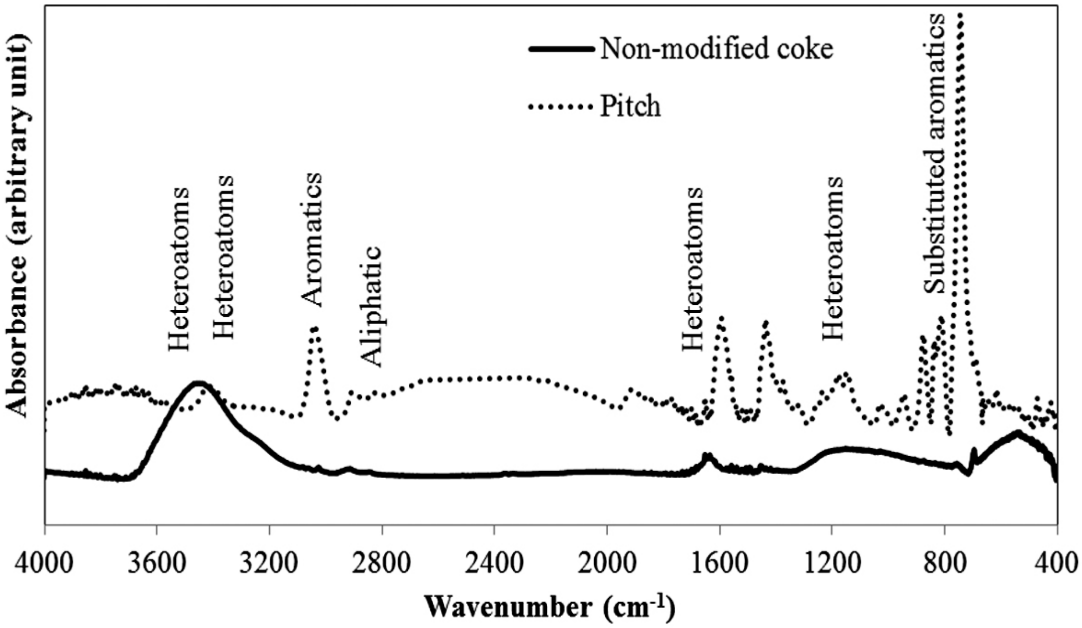


Figure 4.1: FT-IR spectra of non-modified coke and pitch

Six chemicals were chosen to modify coke based on the presence of aromatics and heteroatom-containing functional groups. The FT-IR spectra of the pure chemicals were analyzed. It is possible that the functional groups of the chemicals may not react with the functional groups of the coke. If there is no chemical reaction, then the FT-IR spectra of the modified coke will be a weighted sum of the FT-IR spectra of the non-modified coke and the pure additive. If x wt% of additive is mixed with coke and yc and ya are the absorbances of the FT-IR spectra corresponding to the pure coke and additive respectively corresponding to a particular wavenumber, then the calculated absorbance of the mixture will be (yc*(100-x)+ya*x)/100 at that wavenumber if there is no reaction) [55]. Thus, the FT-IR spectra of non-modified coke and the pure additive chosen were added based on the percentages of the two components. These spectra will be referred as total spectra in the text. The total spectra are presented in Figure 4.2 for the different additives. The spectra show the presence of aromatic, aliphatic, and heteroatom-containing functional groups (see Table 4.2). These spectra show the peaks corresponding to the functional groups of the non-modified coke as well as those of the pure additives. It does not show any new peak or changes in any peak due to interaction.

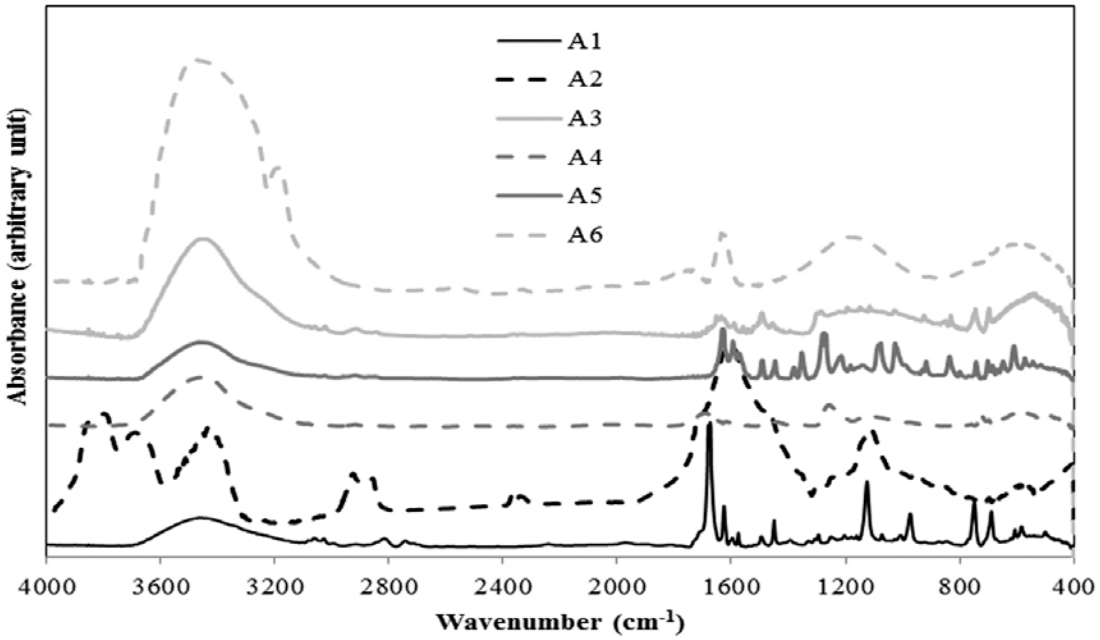


Figure 4.2: FT-IR analysis of total spectra of non-modified coke and pure additives

Figure 4.3 presents the FT-IR spectra of the coke samples modified using the different additives. These spectra also show the presence of aromatic, aliphatic, and heteroatom-containing functional groups (see Table 4.2). However, the total spectra (the weighted sum of the spectra of unmodified coke and the spectra of the additive) differed significantly from the spectra of the modified coke shown in this figure. Some new peaks appeared, and the shape and size of some other peaks changed. This shows the presence of interaction between the coke and the additive. The modified coke samples did not show significant changes in the aromatics region (3000-3100 cm^{-1}) as well as in the aliphatic regions (2700-2950 cm^{-1}) except that for the additive A2. The FT-IR for the additive A6 shows significant difference compared to those for the other additives. This might be due to the water present in A6. However, the total spectra and spectra for coke modified by A6 were similar. This it can be assumed that A6 did not create new bonds. The variations in the peaks corresponding to the aliphatic were not important in terms of the improvement of wettability of the coke by pitch. Some changes were observed related to the substitution reaction of the aromatic ring (750-900 cm^{-1}). These bonds might form due to condensation reactions between heteroatom-containing functional groups. There are significant differences in the regions for heteroatom containing functional groups (1000-1300 cm^{-1}, 1700-1800 cm^{-1}, 3300-3600 cm^{-1}, 3600-3800 cm^{-1}). In spite of the fact that, 3600-3800 cm^{-1} can give some information about phenolic OH and carboxylic acid, this region shows the presence of moisture. Thus, this region was not considered in the study. Also, 1700-1800 cm^{-1} region shows the presence of carbonyls. As this region can show a peak belonging to carbon dioxide, this region was not considered in the analysis. Background correction can reduce the presence of CO_2, but it is difficult to eliminate the peak of CO_2. Thus, the analysis of heteroatom containing functional groups was restricted to two wavenumber ranges: 1000-1300 cm^{-1} and 3300-3600 cm^{-1}.

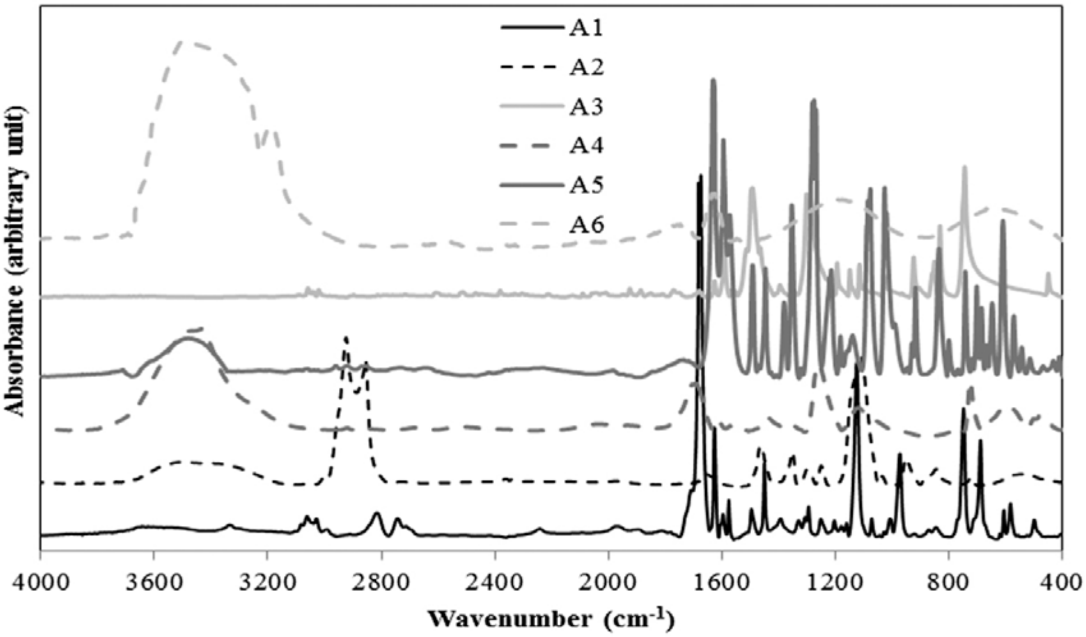


Figure 4.3: FT-IR analysis of cokes modified using different additives

The region of 1000-1300 cm^{-1} represents primary alcohol/secondary alcohol/ether while the surface functional groups in the region of 3300-3600 cm^{-1} represent mostly hydrogen bonded OH and NH. It may be noted that ether shows peak at around 1000-1300 cm^{-1} but does not show peak at 3200-3700 cm^{-1}. It should also be kept in mind that for a vibrational mode to be infrared active the motion must cause a change in the dipole moment of the molecule. Thus an absence of peak in 3200-3700 cm^{-1} region (as seen for coke treated with additive A3) can happen due to presence of ether group or symmetrical vibrations. The functional groups in the range of 3300-3600 cm^{-1} can also show inter/intra molecular hydrogen bonding [32]. The hydrogen-bonded species are not free to bind with the pitch. The functional group of the additive will bind with the complementary functional group of coke. The additives were chosen in such a way that they have minimum two functional groups. One functional group can interact with coke, while the other can interact with pitch. The additive acts as a bridge between coke and pitch.

There is no existing quantitative relation between FT-IR and wettability results. Thus, in this work some ratio was explored to identify relation between FT-IR and wettability results. The area of spectra in the range of 1000-1300 cm^{-1} (Area1) and 3300-3600 cm^{-1} (Area2) were calculated for each sample. Then, the value of *(Area1 / (Area1 + Area 2))* ratio was calculated. This gives an idea of the primary alcohol/secondary alcohol/ether functional groups in the sample, which might not have formed hydrogen bond. This ratio was calculated to find a quantitative criterion for selecting the additive. Other ratios were tried; however, no other ratio, which can be correlated to coke-pitch interactions, was found. An assumption was made that a high value of this ratio is an indicator for improved coke-pitch interaction. Improved interaction can enhance the wettability of coke by pitch.

Table 4.3 shows the value of the ratio for modified coke and the total spectra. The results showed that the values were significantly different for all the cases except that for A3. The similarity in the values for A3 indicates that there was practically no interaction between the additive and the functional groups of coke. For all the other cases, there was interaction between the functional groups of the additive and coke.

The value of the ratio for the modified coke signifies the quality of wetting. As mentioned earlier, a high value will indicate the availability of heteroatom containing functional groups capable of binding with pitch. Thus, the results show that A3 and A6 have low values and will not likely improve the wettability of coke by pitch. On the other hand, A1, A2, A4, and A5 have high values, and it is possible that they can improve the coke wettability.

Table 4.3: Ratios calculated from FT-IR results

	*(Area 1 / (Area1 + Area 2))**	
	Modified Coke	**Total Spectra****
A1	0.083	0.238
A2	0.179	0.316
A3	0.019	0.014
A4	0.113	0.241
A5	0.132	0.290
A6	0.003	0.016

*Area1= Area of 1000-1300 cm^{-1}, Area2 = Area of 3300-3600 cm^{-1}
**Weighted sum of the spectra of unmodified coke and the spectra of the additive

4.3.2. Wettability

Wettability experiments were carried out using the sessile-drop system. The contact angle was measured with respect to time. The contact angle decreased with increasing time for all the samples as expected. FT-IR study showed that A3 and A6 do not improve wettability, and it can be seen from Figure 4.4(a) that they showed poor wettability (higher contact angle) compared to that for the non-modified coke. Also, FT-IR study indicated that A1, A2, A4, and A5 can improve the wettability of coke by pitch (Figure 4.2 and Table 4.3). Figure 4.4(b) shows that A4 and A5 reduced the wettability of the modified cokes compared to that for the non-modified coke, but as it can be seen from Figure 4.4(c), A1 and A2 improved the wetting behavior of the modified cokes (lower contact angle). The actual reason for the discrepancy between the wettability and the FT-

IR results is hard to determine experimentally. The effect of the functional groups and the area ratio on wettability is a hypothesis. One way to validate this effect is to carry out wettability tests at room temperature. However, it was not possible as pitch is solid at room temperature and melts at around 170ºC. Also, molten pitch dropped on cold coke bed will solidify making it impossible to perform the wettability study. Thus, an analysis was performed to identify the reason for the discrepancy based on experimental observations. It was observed that A1 and A2, which improved the wettability of the modified coke, had a low melting point (liquid (A1) or was in aqueous suspension form (A2) at room temperature) and had high boiling points (see Table 4.1). Their boiling points are higher than 170°C. A4 has a high melting point as well as a high boiling point, and it showed poor wetting behavior. Therefore, high melting point of the additive might be the reason for the poor wettability of the modified coke prepared with this additive. A5 has a high melting point but a low boiling point and resulted in poor wettability of the modified coke. It may be noted that after the wettability study with coke modified by A5 some white residue was observed inside the wettability apparatus after cooling. This supports the fact that the additive A5 might have evaporated. Accordingly, in this case, poor wettability can be attributed to the high melting point and the low boiling point. Low melting point of the additive will help liquefy the additive and distribute homogeneously on the coke surface. Hence, liquid (A1) and aqueous suspension additives (A2) spread evenly on the coke surface compared to that for solid additives (A4 and A5). On the other hand, boiling point higher than 170°C will reduce the rate of vaporization of the additive from the coke surface. Thus, high boiling point of the additives helped improve the wettability of the cokes modified with A1 and A2. Based on the experimental observations it can be seen that an additive with a low melting point and a high boiling point (above the mixing temperature) can improve the wettability of coke. The additive should also have high value of (Area 1 / (Area1 + Area 2)) ratio obtained from the FT-IR analysis.

It may be noted that A5 and A6 have boiling point lower than 170ºC. The vaporization of these additives (A5 and A6) cannot justify the reduction in wettability of the modified cokes. If the additive simply leaves the coke surface, the wettability of the modified coke will be the same as that for the non-modified coke. Figures 4.4(b) and 4.4(c) show that this did not happen; the wettability of the modified cokes was less (higher contact angle at a given time) than that of the non-modified coke. This is possible if the additive A5 and A6 modified the coke surface before leaving the coke matrix. Thus the removal of the additives from the coke surface might be associated with chemical reactions that degraded the wettability of the coke surface. The functional groups of the additives can form bonds with the functional groups of the coke particles. As the additives contained heteroatom-containing functional groups, there is the possibility of condensation reactions. During condensation reactions, small molecules such as water or ammonia are released [56]. These losses might reduce the number of heteroatoms of the non-modified coke surface. Thus, the loss of additive will result in a coke surface with low heteroatom content. Fewer heteroatoms will reduce the wettability of the coke surface. The poor wettability of coke modified by the high melting point additive (A3 and A4) might be due to non-homogeneous distribution of the additive in the coke matrix. Another explanation can be removal of water of crystallization (removal of OH) or decomposition of the additive at 170ºC. Crossey [57] found that oxalate (which is a dicarboxylate species similar to A4) can dissociate at even 180ºC following a first order kinetics with a rate constant of 0.0168 h^{-1}. Thus there is a possibility of decomposition resulting in loss of functional groups. This may decrease the wettability of the coke by pitch. This section discussion is based on a number of assumptions and observations, as it is difficult to prove experimentally.

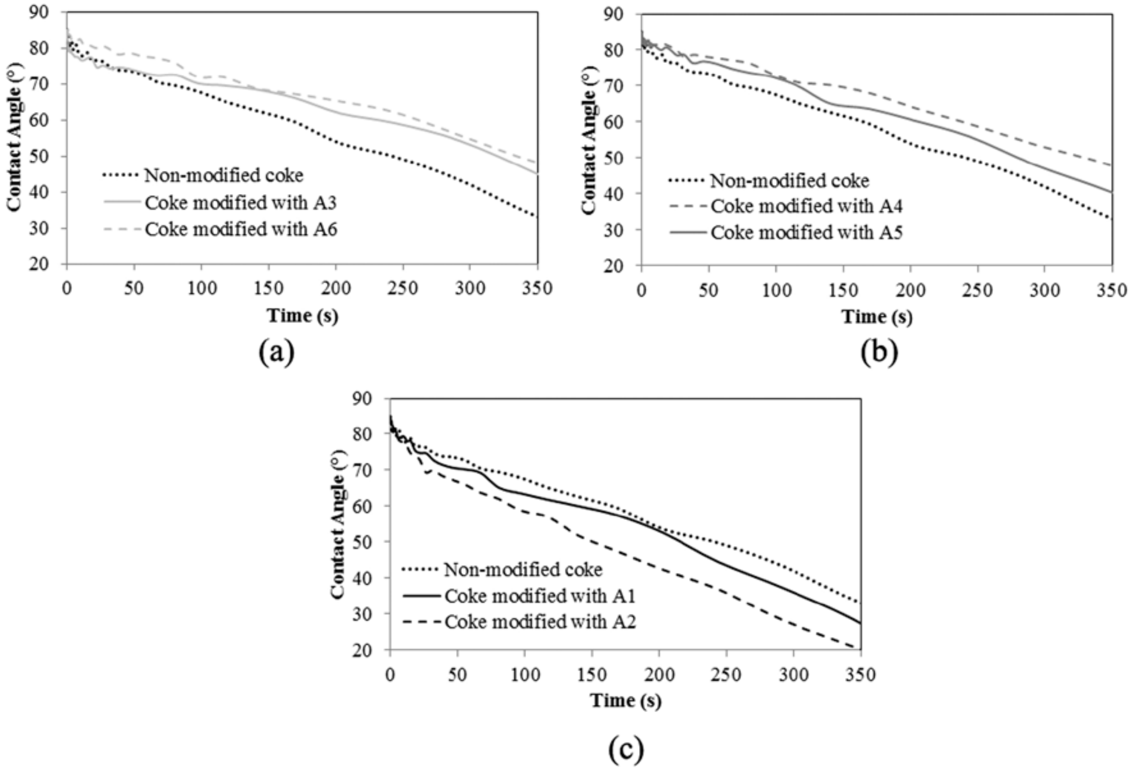


Figure 4.4: Wettability results for non-modified coke and cokes modified with additives (a) A3 and A6, (b) A4 and A5 and (c) A1 and A2

4.3.3. Effects of Additive on Anode Properties

Based on the FT-IR and wettability studies, it was found that A1 and A2 can improve the wettability of coke by pitch. It is true that A2 improved the wettability more than A1 (see contact angle at 350s). However, for anode fabrication, A1 was chosen as its price was lower compared to that for A2. In addition, A2 was no longer available (the production of this chemical stopped) at this point of the study. A1 was a safer choice over A2 as it does not pose any serious health hazard (see Table 1). Another anode was fabricated with (poor wetting) coke modified using A6. The major issue of this anode fabrication with this coke was the release of considerable amount of acidic vapor during coke preheating.

Anodes were produced using non-modified coke and the coke modified with A1 to see the effect of additive on anode properties. All other raw materials and fabrication conditions were maintained the same. Any change in the anode properties can then be attributed to the additive.

As described earlier, cylindrical samples were taken from the green anodes and characterized. The cores were baked and characterized again. The properties of anodes made of non-modified and modified cokes were compared in order to study the effect of additive on anode properties.

4.3.3.1.Green and Baked Anode Density

A good quality anode requires high green (GAD) and baked (BAD) anode density. The anodes with high GAD will result in anodes with high BAD if the baking conditions were optimal. However, anodes with low GAD will never give anodes with high BAD. The anode produced using A6 modified coke had low GAD (1.442 g/cc) compared to that for non-modified coke (1.616 g/cc). Due to the low GAD the anode was not baked for further analysis. This anode proved that the additive A6 had negative effect on anode property. Table 4.4 shows the GAD and BAD for the two anodes (non-modified coke and A1 modified coke). It can be seen from the Table 4.4 GAD and BAD of anode increased after modification of the coke with the additive. It was observed from wettability results that A1 increased interaction between coke and pitch. This additive modified the coke particles and allowed the pitch to penetrate into the coke pores as well as inter-particle spaces easily. Better interaction between the coke and the pitch helped produce a denser anode. For a 1000kg anode (approximate weight of industrial anodes used for over 300 kA cells), an increase in BAD by 0.01 g/cc can increase the carbon content by around 6kg/anode. This will increase the anode life.

4.3.3.2.Electrical Resistivity

Another parameter, which is important for anode quality, is electrical resistivity. Electrical resistivity of baked anode should be low to reduce the energy cost. Usually if the density is high, electrical resistivity is low. Since dense anode has less porosity, current can pass easily through the sample.

Table 4.4 showed that the green anode resistivity (GER) was higher for the anode made with the modified coke compared to that for the one made with non-modified coke. The baked anode resistivity (BER) showed the opposite trend. Pitch, before baking, has high electrical resistivity. Thus, a layer of pitch between the particles can result in high GER. After baking, the carbonized pitch has low resistivity. Hence, carbonization of this pitch layer might reduce BER. BER decreased for the anode after modification of coke by A1. It may be noted that decrease in BER by 1 $\mu\Omega$m may reduce the energy consumption by 0.1%. Considering the volume of aluminum production, this can result in significant amount of energy saving for the industry.

4.3.3.3.Air and CO_2 Reactivity

The theoretical amount of carbon required to produce 1 ton aluminum is 334 kg. Carbon is oxidized to CO_2 during the electrolytic production of aluminum. This CO_2 reacts with the anode inside the cell to produce CO. Air can also react with the exposed surface of the anode to produce CO_2. During the reaction, pitch is usually consumed more compared to the calcined coke. This differential oxidation results in the loss of binder pitch between the coke particles. Consequently, the coke particles fall in the electrolytic cell; this phenomenon is called dusting. This additional consumption of anodes due to air and CO_2 reactivities, and dusting results in excess carbon use increasing the total carbon consumption to more than 400 kg carbon per ton of aluminum. Reactivity of anode is thus related to excess anode consumption and emission of greenhouse gases. High reactivity means that air and CO_2 react more with anode. Table 4.4 shows that the addition of A1 decreased the air and CO_2 reactivities as well as dusting. Reactivity of anode depends on density. Since higher anode density implies presence of less porosity, air and CO_2 could not diffuse easily into the anode. Air usually reacts with any carbon material at high temperature. Researchers have different opinions on the effect of anode density on air reactivity. Sarkar [10] found that the reactivity can increase with increase in anode density whereas Wang et al. reported the opposite trend [58]. For the same coke-pitch pair significant increase in anode density might have reduced the exposed surface area as well as diffusion of air into the matrix of the sample. It is also possible that A1 played a role in reducing the air reactivity. Further study is required to determine the mechanism. Lowe reactivity of the anode resulted in lower dusting. On average, the reduction in reactivity or dusting by 1 mg/cm^2h in a one-ton anode reduces carbon consumption by around 10 kg/anode. This can, in turn, reduce the CO_2 emission by around 35 kg/anode.

4.3.3.4.Flexural Strength

The three-point bending test was carried out to measure the flexural strength of the anodes. The results showed (Table 4.4) that the flexural strength of the anode, which was produced using modified coke, was higher than that for the anode produced using non-modified coke. Addition of A1 improved this mechanical property of the anode.

Table 4.4: Comparison of properties of anodes made with non-modified coke and coke modified by A1

Types	**Properties**								
	GAD, g/cc	GER, μΩm	BAD, g/cc	BER, μΩm	Air reactivity, mg/cm^{2}h	Dusting due to air reactivity, mg/cm^{2}h	CO_2 reactivity, mg/cm^{2}h	Dusting due to CO_2 reactivity, mg/cm^{2}h	Flexural strength, MPa
Non-modified coke	1.616	4805	1.557	58.1	65.5	4.4	31.6	7.1	8.7
Coke modified with A1	1.634	5413	1.566	51.2	63.2	3.4	16.1	1.3	9.4

4.4.Conclusions

The results showed that the additive should have heteroatom-containing functional groups to enhance interaction between coke and pitch. The ratio of peak areas measured from the FT-IR spectra can be an indicator of the effectiveness of the additive in improving the wettability of a coke. The additive should have a low melting point and a high boiling point. Two additives (A1 and A2) were identified, which can improve the coke-pitch interactions. A1 was chosen based on the results and price as well as the availability of the additive. Two anodes were produced using this additive. The modification of coke by A1 increased the green and baked anode densities as well as flexural strength. It also decreased the specific electrical resistivity, the air and CO_2 reactivities, and dusting.

The quality of raw materials plays an important role to produce good quality anodes. This study shows that the use of additives chosen based on certain criteria can improve anode properties. In this case, anode properties were improved without changing any process parameters. Thus, this method can be applied in the industry using the existing facilities.

CHAPTER 5

MODIFICATION OF PETROLEUM COKE BY DIFFERENT ADDITIVES AND THE IMPACT ON ANODE PROPERTIES

(Submitted to Canadian Journal of Chemical Engineering)

Abstract

Anodes, which provide the carbon required for the aluminum production, are made from dry aggregates (petroleum coke, rejected anodes and butts) and coal tar pitch as the binder. Good quality anodes require good interaction between coke and pitch, and this relies on good wetting properties. The objectives of this work are to analyze the wetting properties of four different cokes with and without modification using an additive and to test the effect of the modified coke on anode properties. An FT-IR study was done to identify functional groups in non-modified and modified coke samples since they play an important role on coke-pitch interactions. The wetting tests were done using the sessile-drop method to measure the contact angle between coke and pitch. The results showed that the additive improved the wettability of all four cokes by pitch. The least wettable coke was chosen to produce anodes. For anode production, the entire dry aggregate is modified. The additive was mixed with the dry aggregate using two different approaches (one day earlier and five minutes before mixing). The anodes were characterized before and after baking. The early treatment with the additive was found to be better for the modification of dry aggregate.

5.1.Introduction

In primary aluminum production, alumina is reduced to aluminum in electrolytic cells by using carbon anodes according to the reaction [2].

$$2Al_2O_3+3C = 4Al + 3CO_2 \tag{5.1}$$

There are different steps in anode production: raw material preparation, mixing, compaction, and baking. At the mixing stage, dry aggregate (calcined petroleum coke, butts and recycled anodes) is mixed with coal tar pitch to prepare the anode paste, and this plays an important role in defining anode properties. Pitch, which is used as the binder, must penetrate into the pores of calcined coke and fill the void space between particles [53]. Anode paste is compacted in a vibro-compacter or a press to produce green anodes. Pitch carbonizes during anode baking at high temperature and binds the coke particles together. Good binding between coke and pitch requires good wetting properties between the two components [32]. To achieve this, the interaction between coke and pitch needs to be increased.

Calcined petroleum coke is a solid by-product of the oil refinery, and its quality may vary depending on the source of crude oil and the process conditions used within the refineries [19]. Since it is the major component in terms of mass (around 65-70%) in an anode recipe, properties of calcined coke affects significantly the resulting anode properties. Pitch also plays an important role in anode properties. It is a by-product of the coal tar industry, and its quality can also vary. In order to obtain a good anode, which has high density, low electrical resistivity, low air and CO_2 reactivities, and good mechanical properties, the raw material properties should be improved [2].

The interactions between coke and pitch at the mixing stage have an important effect on resulting anode properties. The wettability gives an indication of the degree of interaction between these two components. If the wettability of coke by pitch improves, pitch can better penetrate into the pores of calcined coke and also fills the void spaces between particles. This results in better quality green anodes. Wettability can be quantified by the contact angle between the solid and the liquid surfaces [29]. The lower the contact angle is, the better the wettability is.

The wettability of coke by pitch is an important parameter to consider in attaining good anode properties. In the work of Sarkar et al [32], the influence of some coke properties on the wettability was investigated. Three calcined cokes with different properties and two different pitches were studied to understand which raw material properties affected the wettability most. Contrary to the other two cokes, the pitch did not penetrate into the third coke, which had lower porosity, lower O_2 content, and a higher amount of C-S bond. Jiang et al. [36] studied the effect of the chemical treatment of petroleum coke by perchloric acid ($HClO_4$) and hydrogen peroxide (H_2O_2). After the treatment, the structure of coke changed, and the specific surface area increased. The oxygen containing functional groups were modified due to the chemical treatment.

Pitch is also one of the important raw materials in the anode production. The quality of anode depends on the quality of pitch as well. Researchers have studied the improvement of the pitch wetting behavior by the use of surfactants and additives. In the work of Rocha et al [38], two additives were used at three different weight percentages to modify petroleum pitch in order to improve its wetting capacity. The results showed that the utilization of additives increased the wettability of coke by the treated petroleum pitch.

Starovit and Maliy [39] investigated the addition of organic compounds such as aceptophene, dimethyl-naphthalene, acenaphthene, fluorine, diphenylene-oxide, α-methyl-naphthalene, and polymeric resins in pitch. When additives were mixed with pitch, the softening point is reduced. After modifying pitch with the addition of the different chemicals, it wetted the coke better.

Two different experiments were conducted by Rocha et al. [40]. First, a non-wetting and a wetting pitch were mixed at different ratios in order to create a pitch with a good wetting capacity. Second, an active surface agent, in this case a fatty acid, was added to the non-wetting pitch. As a result, the wettability of coke by the modified pitch was increased depending on the increase in temperature and the quantity of material added. In addition, during the sessile-drop tests, the use of nitrogen and high heating rate helped achieve good wettability.

In the work of Rocha et al. [35], a coal tar pitch, a petroleum pitch treated with a surfactant (a by-product of the petroleum refining industry), and four substrates (petroleum coke, graphite, carbon black, and magnesia) were used. The use of additives improved the wetting behavior of petroleum pitch. They also observed that the quinoline insoluble (QI) content of pitch played an important role on the wettability of coke by pitch.

Another work on the improvement of the wettability of coke by pitch was reported by Rocha et al [41]. They added surfactants to pitch at different weight ratios in order to modify its properties. One petroleum pitch and three additives were used. Two additives were commercial active-surface agents (alkyl/carbonyl and alkyl/sulfur) and one was a product of petroleum refining. The results showed that the addition of these additives improved the wetting.

As it can be seen from these works, there are some studies on the improvement of coke and pitch properties using different chemicals. However, there is no work reported on the effect of these modifications on anode properties.

In the current study, four different cokes were modified using an additive. The type and the amount of additive were chosen based on the results of the authors' previous work, during which different additives were tested [59]. The wettability of the modified cokes by pitch was improved compared to that for the non-modified cokes. The aim of this study was also to determine the best approach for the modification of the dry aggregate with the additive so that the anodes have better properties compared to those made with the same coke without modification. Anodes were fabricated using non-modified and modified cokes. Then they were characterized in the carbon laboratory of the University of Quebec at Chicoutimi (UQAC) Research Chair on Industrial Materials (CHIMI) to see the effect of the coke modification method on anode properties.

5.2.Experimental

5.2.1. Material Used

In this study, four calcined petroleum cokes (coke 1, coke 2, coke 3, and coke 4) and one coal tar pitch were used. They were obtained from the industry. The softening point of the pitch was around 120°C. The additive and the solvent used were purchased from Sigma Aldrich. As mentioned previously, the additive selection and amount of additive used were based on the previous work of the authors [59]. The additive did not leave any inorganic residue that may contaminate the anodes. A polar solvent with a high-dielectric constant and a low boiling point was used to ensure that the chemicals would dissolve in this solvent. The names of the additive and the solvent are not disclosed due to confidentiality.

5.2.2. Modification of Calcined Coke/Aggregate with Additive

a) For wettability experiments

Calcined coke particles were crushed in a laboratory hammer mill (Retsch SK 100), and the crushed particles were sieved using a sieve shaker (Humboldt MFG). Then, -125+100 µm particles were collected [10, 27]. This particle fraction was modified using the additive for the wettability tests.

The solvent was used since the addition of a small amount of viscous additive directly into the coke would not have ensured homogeneous mixing, and the modification of all coke particles would not have been achieved. A measured quantity of the additive was dissolved in a specific volume of the solvent using a magnetic stirrer. Then, a measured quantity of coke was added to the solution, which was stirred for 10 minutes. The mixture was dried in a furnace at 85°C for 1.5 h. The modified coke sample was finally cooled to room temperature and used in for the wetting experiments.

b) For anode preparation

Coke 1, which was found to be the least wettable coke by the pitch based on the results of the wettability study, was chosen for the anode production. One standard anode (used as reference) and two anodes with modified dry aggregate were produced, all using coke 1. As explained previously, the anodes are made using a dry aggregate composed of coke as well as rejected anodes and butts. It is hard to know the sources of these materials. In this study, all three anodes contained the same recycled material (anodes and butts) so that their impact would be the same. During anode production, the whole dry aggregate was modified before mixing for Anode_1 and Anode_2. The contact time of the additive with the aggregate was changed to determine the approach that would result in better quality anode production. The anode fabrication conditions were maintained the same. Standard anode ($\text{Anode}_{\text{std}}$) was manufactured using non-modified coke 1.

During the production of anodes made with modified coke, the whole dry aggregate was treated with the additive. A certain amount of additive was dissolved in the solvent. The dry aggregate was placed in a container. For the first anode (Anode_1), the solution was added slowly to the dry aggregate. The temperature was increased to 50°C and maintained for five minutes. Then, the mixture was left at room temperature for one day for drying before Anode_1 was produced. The second anode (Anode_2) was manufactured after the additive was mixed with the dry aggregate for five minutes right before the preparation of the anode paste and subsequent anode production. This was done to determine the effect of contact time between the additive and the coke.

5.2.3. Sample Characterization

5.2.3.1. Fourier Transform Infrared Spectroscopy (FT-IR)

An FT-IR study was carried out in order to identify the functional groups in all coke samples (non-modified and modified with additive) using Nicolet 6700 FT-IR spectrometer. The experiments were done using KBr pellet, and the ratio of KBr to sample was 200 to 1. For each sample, 36 scans were carried out. The IR spectra were collected for the wavenumber range of 400-4000 cm^{-1}. The spectra were smoothened, and the linear baseline correction was done using Omnic software. Each sample was analyzed two times at room temperature, and the average value was used.

5.2.3.2.Wettability

Wettability experiments were performed using the sessile-drop method with a set-up available in the carbon laboratory of Chair CHIMI. All experiments were carried out at 170°C under nitrogen atmosphere which is the typical mixing temperature used in industry. The images of the pitch drop on the coke bed were saved at each predetermined time interval. Contact angles were calculated at different times using the software FTA-32. Further information on the sessile-drop system was published elsewhere [10]. Each experiment was repeated twice, and the average of the contact angles measured during these two experiments was used for the analysis. If the contact angle value measured at any given time during the second experiment differed by more than 5° from that of the first experiment, the experiment was repeated.

5.2.4. Fabrication of Laboratory Anodes

A measured quantity of dry aggregate (modified or non-modified) was mixed with molten coal tar pitch. The paste temperature was maintained at around 170°C. The paste was compacted in a vibro-compactor for one minute. Green anodes (nearly 10 kg) of rectangular cross-section were obtained after compaction. Four cylindrical cores of 50 mm in diameter were cut from the green anodes [10]. The density and the electrical resistivity of the green cores were measured. Two of the cores (same positions for all the anodes) were baked in a baking furnace under conditions similar to those used in the industry. These baked cores were used for further studies as explained below. A detailed description of the anode manufacturing process and the baking conditions were published elsewhere [10, 11].

5.2.5. Characterization of Anode Properties

Four cylindrical cores (φ50 mm) were taken from the anodes (see Figure 5.1(a)). Top and bottom of the cores were removed to have a core of 130 mm in length (Figure 5.1(b)).

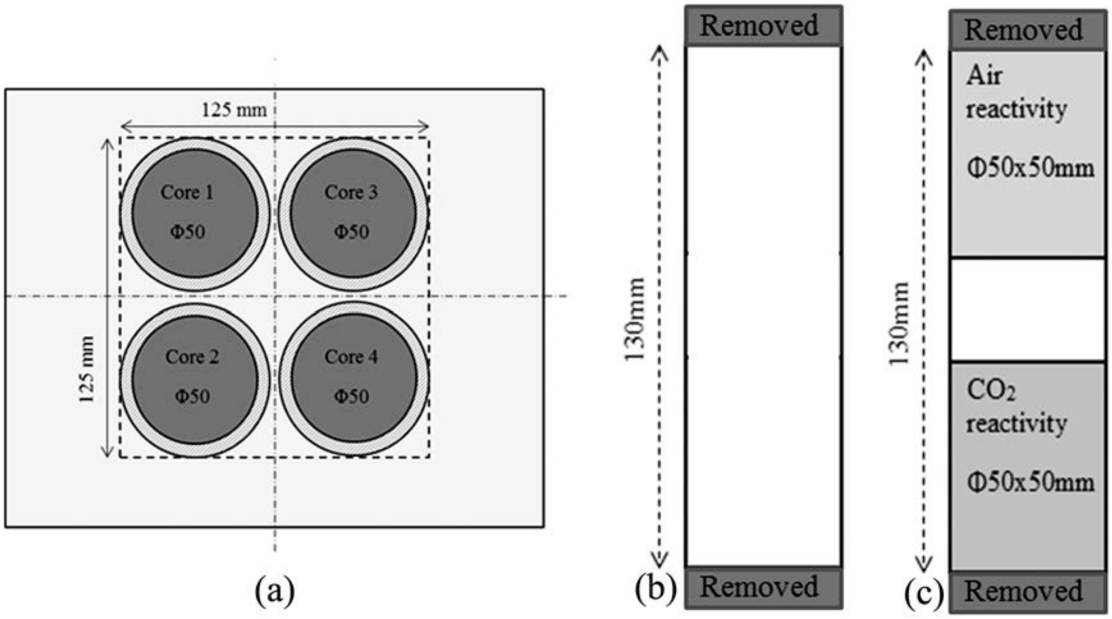


Figure 5.1: (a) Anode coring plan (b) Preparation of green anode cores (c) Anode samples used for reactivity tests

The density (GAD) and the electrical resistivity (GER) of all the green anode cores (φ50 x 130 mm) were measured (cores 1- 4) according to ASTM D5502-00 (2015) and ASTM D6120-97 (2012), respectively.

Cores 2 and 3 were baked. The baked anode density (BAD), the baked anode electrical resistivity (BER) of these cores (φ50 x 130 mm), and the flexural strength of core 3 were measured according to ASTM D5502-00 (2015), ASTM D6120-97 (2012), and ISO N 848, respectively. Then, two φ50 x 50 mm samples were cut (one from the top and the other from the bottom of core 2, Figure 5.1(c)). The φ50 x 50 mm sample from the top was used for the air reactivity measurement (ASTM-D6559-00a), and the sample from the bottom was used for the CO_2 reactivity measurement (ASTM-D6558-00a). The dusting due to both air and CO_2 reactivities was also measured. The detailed descriptions of the characterization methods were published elsewhere [10]. For cases where more than one core was used, the average value and the standard deviation were calculated. The average value gives an idea about the quality of the anode, whereas the standard deviation represents the non-homogeneity of the anode.

5.3.Results and Discussions

5.3.1. FT-IR Results

The presence of different functional groups in coke and pitch can be investigated using the FT-IR analysis. Figure 5.2 shows the FT-IR spectra of non-modified cokes. The results show that all cokes have aromatic and aliphatic functional groups. They also have heteroatom-containing (O and N) functional groups. Three types of interactions are possible between coke and pitch, namely electrostatic interaction, hydrogen bond, and acid-base/condensation reaction [32]. Aliphatic functional groups are usually not favorable for coke-pitch interaction due to the steric hindrances of the long aliphatic chains [10]. However, aromatic and heteroatom-containing functional groups play an important role in these interactions. The differences between the spectra of non-modified cokes in the wavenumber range of 750-900 cm^{-1} (substitution reaction of the aromatic ring) might lead to condensation reactions between heteroatom-containing functional groups [46]. Some differences were observed in the regions for heteroatom-containing functional groups in the wavenumber ranges of 1000-1300 cm^{-1}, 1700-1800 cm^{-1}, 3300-3600 cm^{-1}, and 3600-3800 cm^{-1} [46, 47]. The region of 3600-3800 cm^{-1} mostly shows the presence of moisture. Also, 1700-1800 cm^{-1} region shows the presence of carbonyls. As this region might contain a peak due to the presence of carbon dioxide, this wavenumber range was not considered in the analysis. Thus, the analysis of heteroatom-containing functional groups was restricted to the two wavenumber ranges, 1000-1300 cm^{-1} and 3300-3600 cm^{-1}.

The region of 1000-1300 cm^{-1} represents primary alcohol/secondary alcohol/ether, which can help the interaction between coke and pitch. The surface functional groups in the region of 3300-3600 cm^{-1} represent mostly hydrogen bonded OH and NH. The functional groups of this range can also be due to inter/intra molecular hydrogen bonding. The area of spectra in the range of 1000-1300cm^{-1} (Area1) and 3300-3600cm^{-1} (Area2) were calculated for each sample. In order to have an idea of the primary alcohol/secondary alcohol/ether functional groups in the sample, the ratio given by Equation 5.2 was determined.

$$Area1/(Area1 + Area2) \tag{5.2}$$

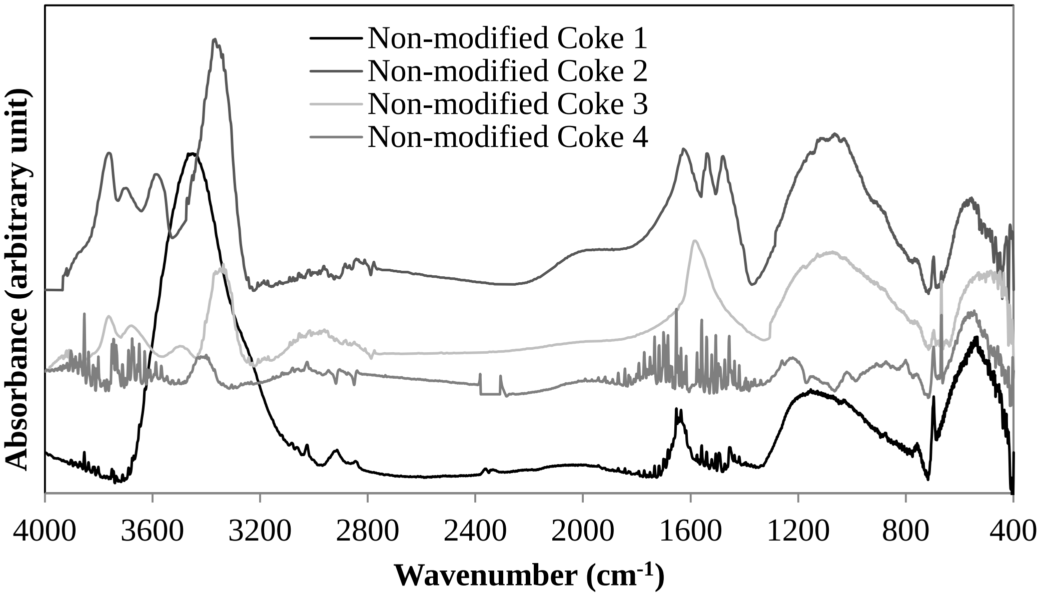


Figure 5.2: FT-IR analysis of four non-modified cokes

The objective of using an additive is to create bridges between coke and pitch in order to enhance the coke-pitch interactions. The additive was chosen in such a way that it has minimum two functional groups to bind with coke and pitch. Figure 5.3 shows the spectra of the cokes modified with the additive. All samples (modified coke 1, modified coke 2, modified coke 3 and modified coke 4) contain aromatic, aliphatic, and heteroatom-containing functional groups. Also, the ratio shown in Equation 5.2 was calculated for the modified coke samples. It was assumed that a high value of this ratio would indicate the availability of heteroatom containing functional groups capable of binding with pitch. This assumption was later validated by the wettability test results. Improved interactions between coke and pitch can result in better wettability of coke by pitch. Table 5.1 shows the values of the ratio for the non-modified cokes and the cokes modified using the additive. The results showed that coke 1 has the lowest ratio in non-modified state and the second lowest in modified state.

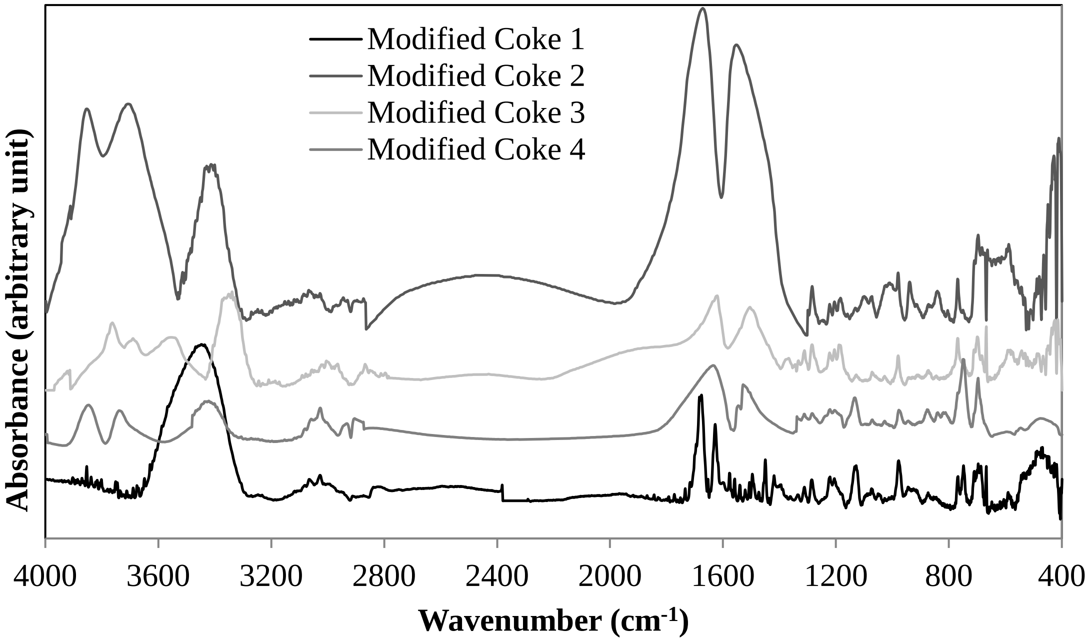


Figure 5.3: FT-IR analysis of four cokes modified using the additive

Table 5.1: Area ratio determined from FT-IR results for four cokes

Sample	***(Area1 / (Area1 + Area2))***
Non-modified Coke 1	0.189
Non-modified Coke 2	0.426
Non-modified Coke 3	0.600
Non-modified Coke 4	0.496
Modified Coke 1	0.083
Modified Coke 2	0.076
Modified Coke 3	0.197
Modified Coke 4	0.226

5.3.2. Wettability Results

The wettability experiments were done using the sessile-drop system. Figure 5.4 shows the wettability results for the non-modified cokes (solid lines) and the cokes modified with the additive (dash lines). The contact angle decreased with increasing time for each coke. Hence, wetting is increased with time. Also, all the modified cokes were wetted better by the pitch compared to the non-modified cokes. It was found that the addition of the additive to coke improved the wettability of coke by pitch.

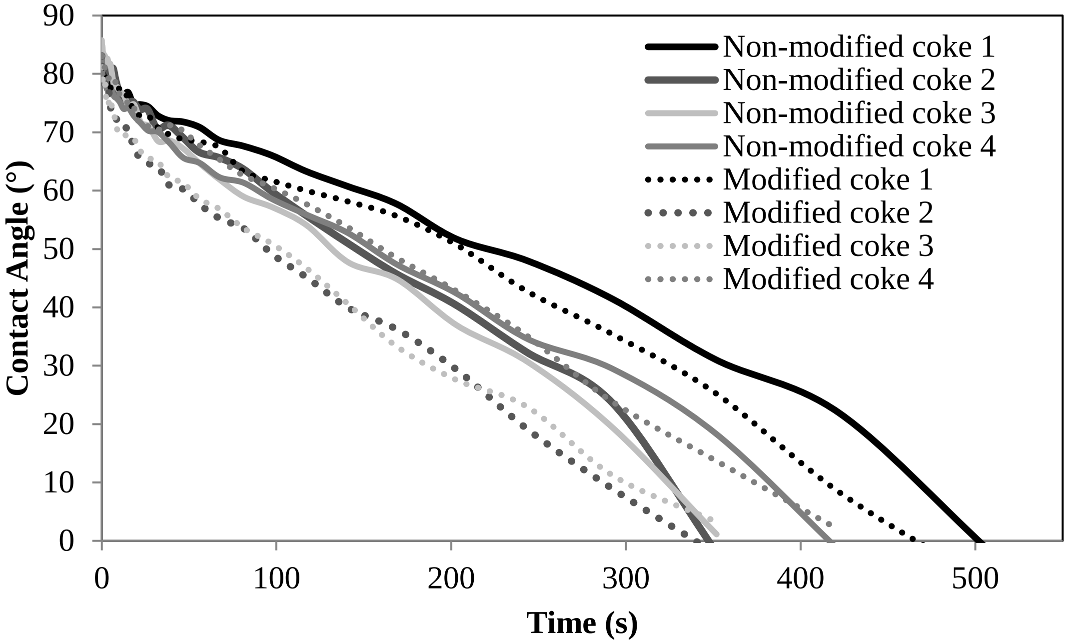


Figure 5.4: Wettability of non-modified cokes and cokes modified with additive

In order to analyze the correlation between the FT-IR results and the wettability experiments, contact angle at 200 second was determined for each sample. Figure 5.5 shows that a lower value of the area ratio determined from the FT-IR spectra corresponds to a higher contact angle at a given time. Similar trend was observed at different times. High contact angle represents weak interaction between coke and pitch (low wettability). If a non-modified coke sample has less heteroatom-containing functional groups (low value of the area ratio), the interaction between that non-modified coke and pitch will be weak. Thus, these results validated the assumption made in section 5.3.

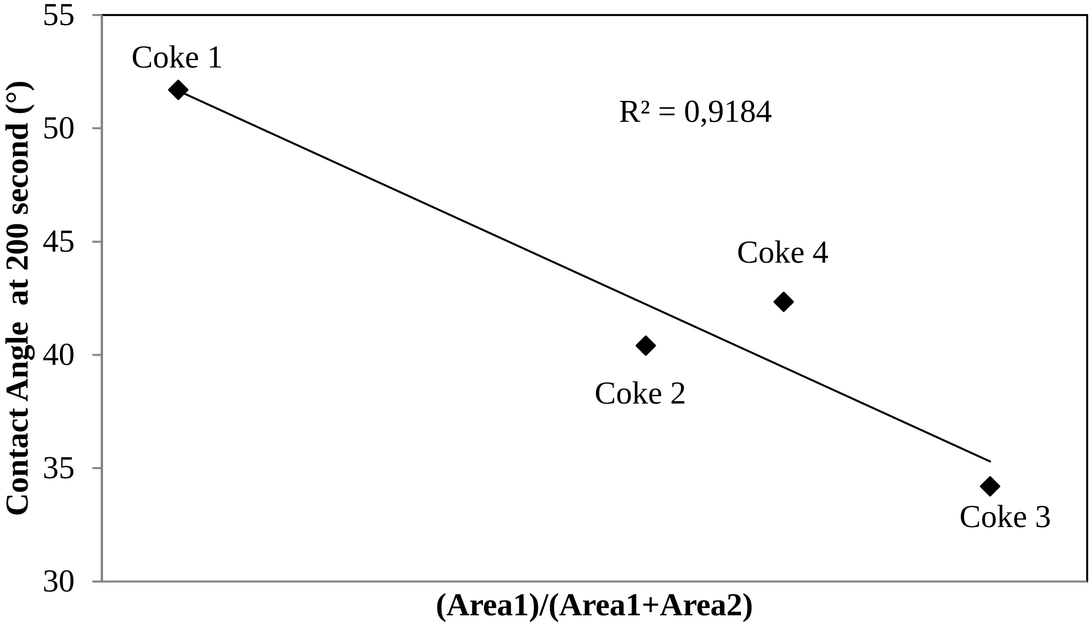


Figure 5.5: Relation between the contact angle and the area ratio at 200 s

5.3.3. Effects of Additive on Anode Properties

It was observed from the FT-IR analysis and the wettability results that the interaction between coke 1 and pitch was poor compared to that of the other coke samples. Thus, coke 1 was chosen to for the anode production. Two approaches were tried to determine the best way to mix the additive with the dry aggregate containing this coke (contact time for the additive-dry aggregate mixture) in order to produce better quality anodes. Table 5.2 shows the characterization results for the standard anode (no additive) and the anodes produced using these two approaches. The table shows that not only the green anode density (GAD) of the modified anodes ($Anode_1$ and $Anode_2$) but also the air and CO_2 reactivities showed significant improvement compared to the anode produced with non-modified coke ($Anode_{std}$). Dusting due to the air and CO_2 reactivities of $Anode_1$ also improved. However, dusting due to the air reactivity of $Anode_{std}$ and $Anode_2$ is quite similar (no improvement). The difference in the electrical resistivity of $\text{Anode}_{\text{std}}$ and Anode_1 is within the range seen in the industry due to the non-homogeneity of raw materials. Their baked electrical resistivities are similar as it can be seen from Table 5.2. The non-homogeneity of Anode_2 was caused due to the vaporization (a lot of vapor was observed during the mixing of the additive) of the solvent as the coke was already hot when the additive-solvent mixture was added. As the solvent evaporated, the additive could not mix uniformly with the dry aggregate. The non-homogeneity of Anode_2 reflected in the texture of the cores (see Figure 5.6). The flexural strength of Anode_2 was not measured due to the visible cracks. The flexural strength of Anode_1 is almost the same with $\text{Anode}_{\text{std}}$. Thus, there is no significant change in the flexural strength after the modification.

It can be seen from Table 5.2 that Anode_1 (treated with the additive one day earlier) showed improvement compared to that for Anode_2 (treated with the additive five min before mixing with pitch) in terms of green and baked anode density, green electrical resistivity, and air reactivity. Anode_2 had high GAD, but low BAD. However, Anode_2 had better for CO_2 reactivity and dusting due to CO_2 reactivity. The physical appearances (visible defects) of $\text{Anode}_{\text{std}}$ and Anode_1 before baking were similar and appeared to be better than that of Anode_2 (Figure 5.6). The standard deviation values for Anode_2 (treated 5 minutes before mixing) were higher compared to those for Anode_2 (treated one day earlier). This shows that Anode_2 was more non-homogeneous with respect to Anode_1. However, the standard anode had the minimum standard deviation values (except for BER).

Improvement of a particular property is not an ideal indicator of an anode quality; a good anode should have reasonable values for all properties. Based on the physical appearance (visible defects), BAD, BER, and the reactivities of anodes made with the modified dry aggregate, the approach for the modification of coke one day earlier was found to be better to produce good quality anodes.

Table 5.2: Characterization results for different anodes

	Properties								
Types	GAD, g/cc	GER, µΩm	BAD, g/cc	BER, µΩm	Air reactivity, mg/cm^{2}h	Dusting due to air reactivity, mg/cm^{2}h	CO_2 reactivity, mg/cm^{2}h	Dusting due to CO_2 reactivity, mg/cm^{2}h	Flexural strength, MPa
Anode$_{std}$	1.616 (0.007)	4805 (204)	1.557 (0.004)	58.1 (1.0)	65.4	4.4	31.6	7.1	8.76
Anode$_1$	1.655 (0.011)	7410 (1230)	1.580 (0.007)	58.4 (0.8)	60.5	3.8	26.0	3.9	8.71
Anode$_2$	1.652 (0.013)	12187 (3830)	1.542 (0.011)	56.1 (1.3)	63.6	4.5	16.4	1.0	*

* Not measured due to visible cracks

Note: The number in each cell denotes the average value. The number in brackets denotes the standard deviation.

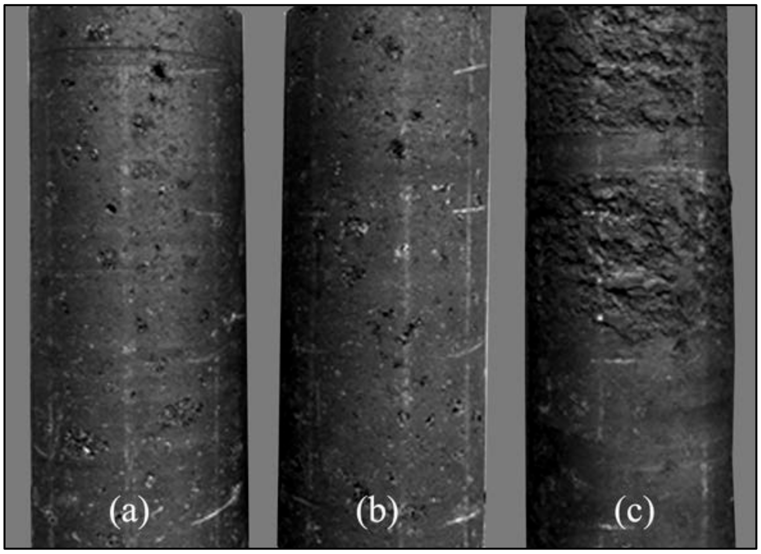


Figure 5.6: Physical appearance of green anode cores (a) Standard anode (b) Anode produced with dry aggregate treated one day earlier (c) Anode produced with dry aggregate treated five minutes before mixing

5.4.Conclusions

In this work, the modification of four different cokes by an additive was studied in order to analyze the effect of coke modification on anode quality. The additive improved the wettability of all cokes for the same pitch. The results showed that the ratio, which represents the heteroatom-containing functional groups in coke, is inversely correlated with the contact angle (wettability of coke by pitch). Better coke-pitch interaction requires a high ratio. Coke 1, which was least wettable by pitch, had the lowest ratio among the cokes studied. It is quite likely that a quick FT-IR analysis can be helpful for the industry in choosing their raw material.

Three anodes were produced with coke 1 to see if the modified coke will improve the anode properties. Anodes made with the chosen additive had better properties compared to those of the standard anode made with non-modified coke (except for GER of both anodes made with modified coke, and BAD for Anode_2). It was also seen that the method of mixing the additive with the dry aggregate has a major effect on anode properties. Additive mixed with coke one day earlier before anode production resulted in an anode with better properties compared to those obtained when the additive was combined with the coke right before the paste preparation (mixing).

Since it is possible to obtain better quality anodes by modifying the coke, this will most likely lead to energy saving, lower carbon consumption, and lower greenhouse gas emissions. However, further study is needed with the other cokes and pitches to study the effect of the additive, and industrial trials need to be carried out to determine the behavior of anodes (made with modified aggregate) during electrolysis.

CHAPTER 6

EFFECT OF THE ADDITIVE CONCENTRATION ON THE MODIFICATION OF PETROLEUM COKE AND ANODE QUALITY

(To be submitted to a journal.)

Abstract

Calcined petroleum coke is one of the major raw materials for anode manufacturing, which is used as the carbon source in electrolytic cells for primary aluminum production. It constitutes around 65-70% of the anode recipe. Therefore, the quality of calcined coke has an important impact on anode quality, which affects the cost, energy efficiency, carbon consumption, and greenhouse gas emissions. Another main raw material for anode production is coal tar pitch. In order to enhance the anode quality, the interaction between these two components should be improved. The objective of this study is to investigate the effect of coke modification and the amount of additive used on anode quality. An additive at different percentages was used to modify two different cokes. Aromatics and heteroatom-containing functional groups of non-modified and modified cokes were identified by FT-IR and compared to see the effect of the additive concentration on anode quality. Wettability experiments were carried out using the sessile-drop method since the wettability of coke by pitch and the anode quality are closely related. Anodes were produced and characterized using non-modified and modified cokes. It was found that the amount of additive used for the coke modification has to be adjusted to improve the anode quality.

6.1.Introduction

Carbon anodes are used in electrolytic cells for the reduction of alumina in aluminum production [2]. During electrolysis, alumina is reduced and aluminum and CO_2 are produced. The quality of carbon anodes affects the quality of resulting aluminum, the consumption of anode, and the production cost. Carbon anodes should have high density, low electrical resistivity, low air and CO_2 reactivities, and high mechanical properties [60].

Carbon anodes consist of approximately 65 % calcined petroleum coke, 20 % recycled anodes and butts, and 15 % coal tar pitch [52]. In the process of anode manufacturing, dry aggregate (calcined petroleum coke, rejected green and baked anodes, and anode butts) is mixed with coal tar pitch. Then, the resulting paste is compacted in a vibro-compactor or a press to produce green anodes. Then, these green anodes are baked in a baking furnace to produce baked anodes, which are used in electrolysis after rodding.

Calcined petroleum coke is a solid by-product from oil refining. The quality of calcined coke depends on the source of crude oil and the process parameters. In recent years, the quality of calcined coke has been decreasing [20, 21, 42-44, 60] since the refineries are forced to accept higher proportion of heavy crudes from different sources. The impurities in the source of crudes directly affect the coke quality [16, 17, 61]. Low quality coke cannot be used in anode production due to the undesirable effects this would have on anode quality and subsequent aluminum production. In any case, the aluminum industry should produce high quality anodes using existing cokes available from the refineries. Thus, the industry needs new techniques to improve the properties of calcined petroleum coke.

In anode production, aggregate containing the calcined coke is mixed with coal tar pitch in a kneader or a mixer to produce anode paste. The mixing enhances the interaction between these components so that better quality anodes can be produced [53]. Wettability of coke by pitch is an indication of the quality of interaction between coke and pitch. The likely interactions between coke and pitch are hydrogen bonding, electrostatic interaction, and acid-base reactions/condensation. When the wettability of coke by pitch improves, pitch can penetrate better into the void spaces between particles and the pores of calcined coke. This helps bind the coke particles together when pitch carbonizes during anode baking. In order to improve the wettability of coke by pitch, the aromatics and the heteroatom-containing (O, N, S) functional groups in coke and pitch, which enhance their interactions, should be increased [10].

The wettability of coke by pitch is an important parameter to consider the production of quality anodes. It represents the level of the interaction between coke and pitch. Improved wettability of coke by pitch ensures better coke/pitch interaction. The contact angle is used to quantify the wettability. When the contact angle is smaller, the wettability is better. The force balance between a liquid and a solid surface is given by the Young equation (see Equation 6.1) [62]. γ_{LV} is the interfacial tension of the liquid-vapor interface, γ_{SV} is the interfacial tension of the solid- vapor interface, γ_{LS} is the interfacial tension of the liquid-solid interface, and θ is the contact angle. The interfacial tension of the liquid-vapor interface (γ_{LV}) is also called the surface tension. The Young equation is applicable for the smooth surfaces [63]. To measure the wettability of granular samples, small particles are packed to approach a smooth surface. However, there is penetration through the bed in these samples in addition to surface wetting. When the wetting is good, the penetration is usually faster.

$$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{LS} \tag{6.1}$$

In the work of Sarkar et al. [32], the influence of some coke properties on the wettability was investigated. There are some studies on the improvement of the wetting properties of pitch using additives [35, 38-41]. The objective of addition of an additive is to increase the functional groups in raw materials and to create a bridge between coke and pitch so that the coke-pitch interaction would improve.

In this study, the modification of coke using additives is investigated. Two cokes and two pitches were used. Two different additive percentages were tested in order to study the effect of additive concentration on anode quality. The wettability of the modified cokes by pitch was also studied and compared to that for the non-modified cokes. Anodes were fabricated and characterized in the carbon laboratory of the UQAC Research Chair on Industrial Materials (CHIMI) to determine the effect of the coke modification and the concentration of additive used on anode properties.

6.2.Experimental

6.2.1. Material Used

In this study, two different calcined petroleum cokes and one coal tar pitch were used. They were obtained from the industry. Also, an additive and a solvent were used to modify the cokes. They were purchased from Sigma Aldrich. An organic additive, which does not leave harmful residue during baking and improves the anode quality according to the results of a previous study, was chosen [59]. A measured quantity of additive was dissolved in the solvent and was then used to modify the cokes. The names of the additive and the solvent are not disclosed due to confidentiality.

6.2.2. Modification of Calcined Coke with Additive

The two calcined cokes were modified with the additive. Calcined coke with a particle size less than 1 mm was crushed in a laboratory hammer mill (Retsch SK 100). Particles in -125+100 µm in size were separated using an automatic sieve shaker (Humboldt MFG). In order to mix the coke and the additive homogeneously, a polar high- dielectric constant solvent was used. A measured quantity of the additive was dissolved in a specific volume of the solvent using a magnetic stirrer. Then, a measured quantity of the sieved coke particles was added to the solution. This solution was stirred for 10 minutes. Then the mixture was dried in a furnace at 85°C for 1.5 h. The modified coke samples were finally cooled to room temperature and used for the wetting experiments.

Two standard anodes ($\text{Anode}_{\text{std1}}$ and $\text{Anode}_{\text{std2}}$) with two different cokes (used as reference) and four anodes with the modified cokes were produced. For each coke, two anodes were prepared using two different additive percentages (a total of four anodes). The type and the quantity of all the other raw materials (pitch, anode butts, green and baked rejects) and the fabrication conditions were maintained the same in order to be able to determine the effect of the additive concentration on anode properties.

For the modified anodes, a measured amount of additive (calculated based on the dry aggregate amount) was dissolved in a certain amount of solvent. Then, the dry aggregate containing the desired coke was placed in a container, and the solution was added slowly on to it. After five minutes of mixing, the mixture was left at room temperature for one day for drying. This method was previously found to be most effective for coke modification [64].

6.2.3. Sample Characterization

6.2.3.1.Fourier Transform Infrared Spectroscopy (FT-IR)

The different functional groups in the cokes (modified and non-modified with the additive) were identified by FT-IR (Nicolet 6700 FT-IR). Pellets with KBr were used and the concentration of the sample in KBr was approximately 0.005%. The number of scans carried out was 36 for each sample to get the average spectra. The IR spectra were collected for the wavenumber range of 400-4000 cm^{-1}. Omnic software was used for the baseline correction. Each sample was analyzed two times at room temperature, and the average value was used.

6.2.3.2.Wettability

The sessile-drop method was used for the wettability experiments. The set-up available in the carbon laboratory of Chair CHIMI was modified and used for this study. The temperature for all experiments was set to 170°C, which is the typical temperature used in industry for coke/pitch mixing. Using the FTA-32 software, contact angles were determined at different times from the images of the pitch drop that was dropped onto the coke bed. Detailed information about the sessile-drop system was published elsewhere [10]. Each experiment was carried out two times, and the average contact angles were used for the analysis. A third experiment was performed if the contact angle value at any time differed by more than 5° between the two previous experiments.

6.2.4. Fabrication of Laboratory Anodes

A measured quantity of dry aggregate (non-modified and modified) containing different particle fractions according to a standard anode recipe, which is similar to that used in industry, was mixed with a certain amount of molten coal tar pitch at 170°C. This anode paste was compacted in a vibro-compactor for a certain time and green anodes were obtained. Four cylindrical cores (φ50 x 130 mm) were cut from the rectangular green anodes for characterization. The density and the electrical resistivity of all the green cores were measured. Two cores taken from the same positions of all anodes were baked in a baking furnace using a heating rate similar to that used in industry. Then, density, electrical resistivity, air and CO_2 reactivities, dusting due to these reactivities, and the flexural strength were measured for the baked cores. A detailed description of the anode manufacturing process and the baking conditions were published elsewhere [10, 11]. The preparation of cores is explained in detail in a previous publication [64].

Two standard anodes ($Anode_{std1}$ and $Anode_{std2}$), two anodes with coke 1 modified by 5% additive ($Anode_1$) and 1% additive ($Anode_2$) and two anodes with coke 2 modified by 1% additive ($Anode_3$) and 2% additive ($Anode_4$) were produced. First, coke 1 was modified using the additive at two different percentages (1% and 5%). It was observed from FT-IR results that the heteroatom-containing functional groups of coke 1 didn’t change significantly. Thus, the additive amount for coke 2 was changed to 1% and 2%. All the other raw materials (pitch, anode butts, green and baked rejects) and fabrication conditions were kept the same. Therefore, the modification of the entire dry aggregate instead of only coke does not hinder the investigation of the effect of coke modification on anode properties.

6.2.5. Characterization of Anode Properties

The green anode density (GAD) and green anode electrical resistivity (GER) of the green anodes cores (φ50 x 130 mm) were measured according to ASTM D5502-00 (2015) and ASTM D6120-97 (2012), respectively.

The baked anode density (BAD), baked anode electrical resistivity (BER), and the flexural strength of the baked cores (φ50 x 130 mm) were measured based on ASTM D5502-00 (2015), ASTM D6120-97 (2012), and ISO N 848, respectively. For the reactivity experiments, two φ50 x 50 mm samples were cut from one of the baked cores, which was taken from the same position of each anode. The air reactivity measurement was done using the core sample from the top of the core according to ASTM-D6559-00a. The CO_2 reactivity of the core sample taken from the bottom of the core was measured based on ASTM-D6558-00a. Also, the dust produced during both air and CO_2 reactivity tests (dusting) was measured. The detailed descriptions of the characterization methods were published elsewhere [10, 11, 27].

6.3.Results and Discussions

6.3.1. FT-IR Results

The FT-IR study was done to identify different functional groups of different cokes (non-modified and modified with an additive). The objective of the FT-IR study was to analyze the difference between the spectra of non-modified coke and the coke modified with the additive using different concentrations.

In anode production, coke and pitch interact with each other at the mixing stage. Three types of interactions are likely to take place between coke and pitch: hydrogen bonding, electrostatic interaction, and acid-base/condensation reaction. Electronegative atoms (such as O and N) attached to hydrogen, pull the electron away from hydrogen. As a result, hydrogen becomes positively charged. These positively charged hydrogen atoms can create bonds with other electronegative atoms, which is called hydrogen bond. Aromatics, which have a negative charged electron clouds, can react with positive centers of other atoms, and this is called electrostatic interaction. Also, acidic functional groups can react with basic functional groups. During these interactions, small molecules (such as water or ammonia) can be eliminated, which is known as condensation reactions [10]. All these reactions require aromatic and heteroatom-containing functional groups.

The FT-IR spectra of coke 1 and coke 2 (non-modified and each modified with the additive using two different concentrations) are presented in Figure 6.1 and Figure 6.2, respectively. All samples contain aromatics and heteroatom-containing functional groups. In the FT-IR spectra of calcined coke, the wavenumber range of 700-900 cm^{-1} represents substituted (ortho, meta, and para) aromatic rings, which can form because of condensation reactions between heteroatom-containing functional groups [46]. It can be seen from Figure 6.1 and Figure 6.2 that there are significant differences between non-modified samples and the cokes modified with additive in some regions such as 1000-1300 cm^{-1}, 1700-1800 cm^{-1}, 3300-3600 cm^{-1}, 3600-3800 cm^{-1}. The 1700-1800 cm^{-1} shows the presence of carbonyls [47]. Although peaks in the range of 3600-3800 cm^{-1} can give an indication about phenolic OH and carboxylic acid, this region is mostly present due to the presence of moisture [36]. Therefore, it was not considered in this study. Thus, the identification of heteroatom containing functional groups was limited to two wavenumber ranges: 1000-1300 cm^{-1} and 3300-3600 cm^{-1}.

The area of spectra in the range of 1000-1300cm^{-1} (shows the primary alcohol/secondary alcohol/ether functional groups [43, 44]. The region of 3300-3600cm^{-1} represents mostly hydrogen bonded OH and NH, which are not free to bind with pitch [29].

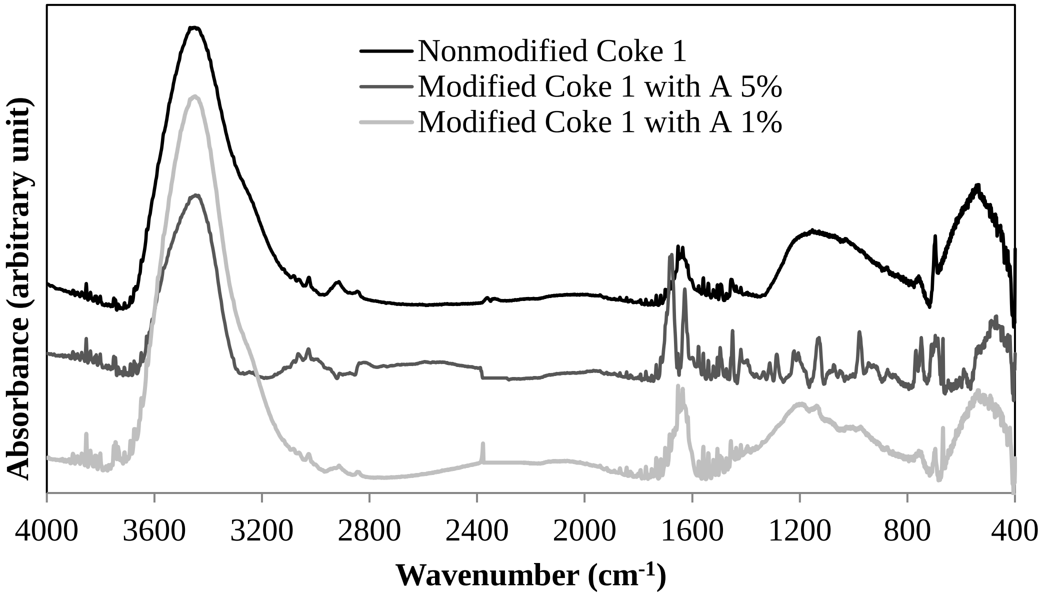


Figure 6.1: FT-IR analysis of non-modified coke 1 and coke 1 modified using the additive (1% and 5%)

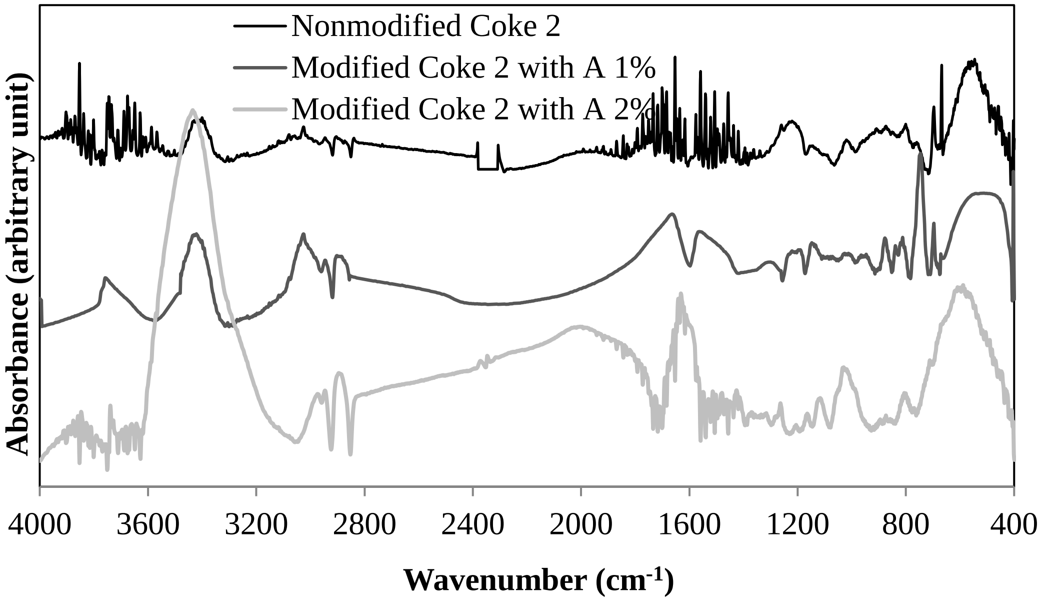


Figure 6.2: FT-IR analysis of non-modified coke 2 and modified coke 2 by an additive (1% and 2%)

6.3.2. Wettability Results

Wettability experiments were carried out using the sessile-drop method. The effect of additive on the wettability of coke by pitch was studied. The contact angle was recorded with respect to time. Also, a study was done to analyze how the molten pitch penetrates through the coke bed. The volume of the molten pitch (V_0) was calculated, when it touches to the surface of the calcined coke (t=0). Then, it starts to penetrate into the bed. The volume of the pitch above the surface (V_s) (see Figure 6.3) and the volume ratio based on Equation 6.2 were calculated as a function of time. In this equation, ($V_0 - V_s$) represents the volume of the pitch below the coke surface (the part that has penetrate into the bed) at a given time. This variation of V with time shows how fast pitch penetrates into the coke bed.

$$V\,(t) = \frac{V_0 - V_s}{V_s} \tag{6.2}$$

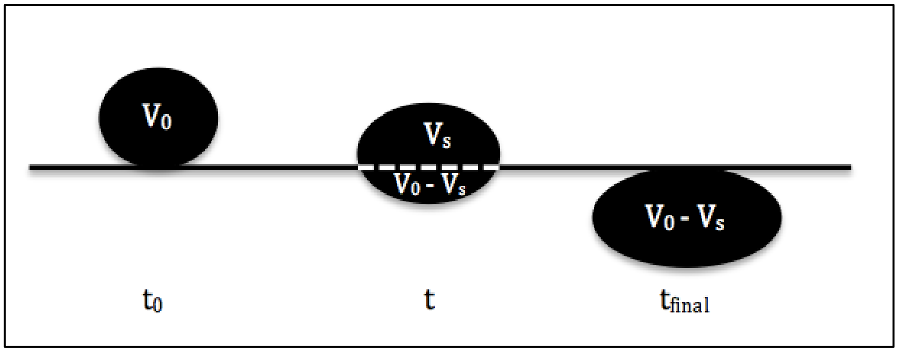
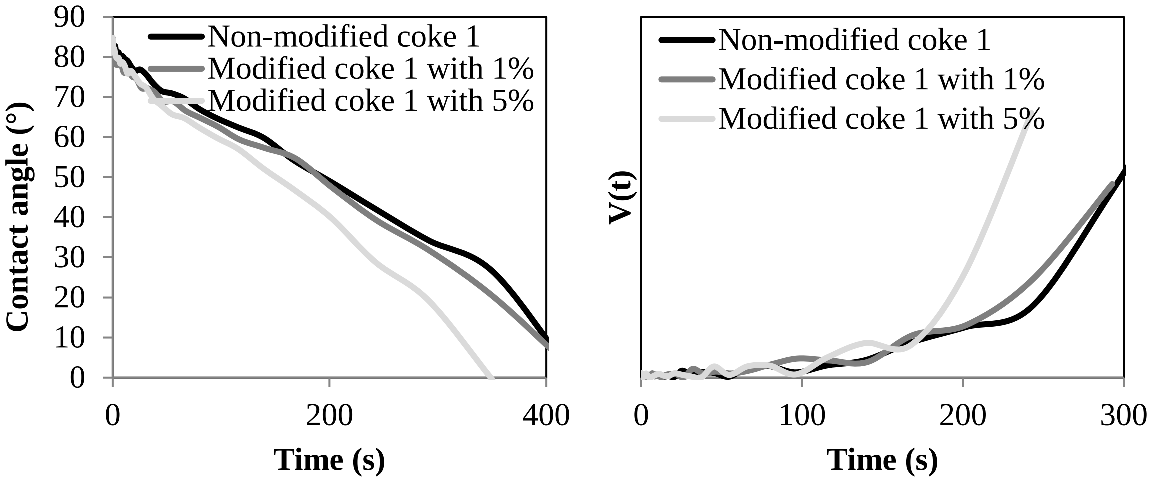


Figure 6.3: A schematic illustration of the penetration of pitch into the coke bed

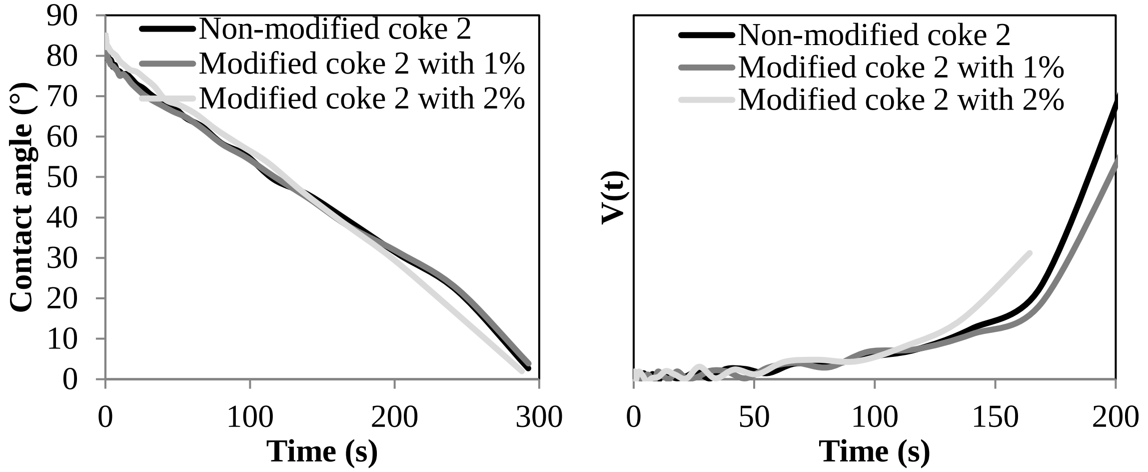
Figure 6.4 shows the wettability results of non-modified coke 1 and modified coke 1 with additive (1% and 5%). The contact angles of modified cokes were smaller than those of the non-modified coke (better wettability, Figure 6.4 (a)). Also, pitch penetrated faster into the coke 1 bed modified using different percentages of the additive than into the non-modified coke 1 bed. Also, it can be seen from this figure that the pitch penetration is faster into the coke 1 bed modified using 5% additive compared to the other two.



(a) (b)

Figure 6.4: (a) The contact angle and (b) the penetration results for non-modified coke 1 and coke 1 modified using the additive (1% and 5%)

Figure 6.5 shows the wettability results of non-modified coke 2 and modified coke 2 with additive (1% and 2%). The contact angle and the penetration time for each sample were almost same. It was observed that pitch penetrated slightly faster into the coke 2 bed modified using 2% additive.



(a) (b)

Figure 6.5: (a) The contact angle and (b) the penetration results for non-modified coke 2 and coke 2 modified by the additive (1% and 2%)

6.3.3. Effects of Additive on Anode Properties

Table 6.2 shows the characterization results of the anodes produced using coke 1. It can be seen from Table 6.2 Anode$_1$ (modified using 5% additive) and Anode$_2$ (modified using 1% additive) showed improvement compared to Anode$_{std1}$ (non-modified coke 1) in terms of green and baked anode densities (GAD and BAD), air and CO_2 reactivities and dusting. Also, baked anode resistivity (BER) and the flexural strength of Anode$_2$ (modified using 1% of additive) were better compared to those of Anode$_{std1}$ (non-modified coke 1). However, the BER and the flexural strength of Anode$_1$ (modified using 5% additive) did not show improvement.

Table 6.1: Characterization results for anodes produced using coke 1

Types	GAD, g/cc	BAD, g/cc	GER, μΩm	BER, μΩm	Air reactivity, mg/cm^{2}h	Dusting due to air reactivity, mg/cm^{2}h	CO_2 reactivity, mg/cm^{2}h	Dusting due to CO_2 reactivity, mg/cm^{2}h	Flexural strength, MPa
Anode$_{std1}$	1.616	1.557	4805.7	58.13	65.46	4.45	31.65	7.06	8.7
Anode$_1$	1.655	1.579	7410.4	58.43	60.53	3.78	26.05	3.91	8.2
Anode$_2$	1.633	1.566	5412.9	51.25	63.20	3.40	16.14	1.34	9.4

Table 6.3 represents the characterization results for anodes produced using coke 2. The CO_2 reactivity, dusting due to both air and CO_2 reactivities of Anode$_3$ (modified using 1% additive) improved only compared to those of Anode$_{std2}$ (non-modified coke 2). The flexural strengths of Anode$_{std2}$ and Anode$_3$ are almost the same. On the other hand, almost every property of Anode$_4$ (modified using 2% additive) improved compared to that of Anode$_{std2}$ except for the flexural strength.

Table 6.2: Characterization results for anodes produced using coke 2

Types	GAD, g/cc	BAD, g/cc	GER, μΩm	BER, μΩm	Air reactivity, mg/cm^{2}h	Dusting due to air reactivity, mg/cm^{2}h	CO_2 reactivity, mg/cm^{2}h	Dusting due to CO_2 reactivity, mg/cm^{2}h	Flexural strength, MPa
Anode$_{std2}$	1.615	1.555	5576.6	56.01	59.39	5.04	19.36	2.35	10.0
Anode$_3$	1.595	1.552	6076.0	58.42	60.48	3.56	18.46	1.32	10.2
Anode$_4$	1.617	1.565	4972.4	54.80	56.23	3.63	17.52	1.44	8.3

The results showed that there is potential for the improvement of anode properties using additives, however, it may not possible to improve all properties. Based on the anode characterization results, it was found that the properties of Anode$_2$ (modified with 1% additive) for coke 1 and Anode$_4$ (modified with 2% additive) for coke 2 have been improved compared to those of the other samples.

An additive may also help pitch penetrate more rapidly into the coke bed due to improved wetting. This may affect the distribution of pitch between the fraction entering into the pores of calcined coke particles and the fraction that remains between the particles. This should be investigated further. If more pitch remains outside the particles (i.e. less in the particle pores) due to rapid penetration, the amount of volatiles increases during baking. Higher amount of volatiles creates cracks in anodes with adverse impact on a number of properties.

6.4.Conclusions

In this study, the modification of two cokes using different additive percentages was studied in order to analyze the effect of coke surface functional groups and the amount of additive on anode quality.

It was found that the modification of coke using an additive improves anode properties. Three anodes were produced with coke 1 by modifying with 5% and 1% additive. Both anodes (Anode_1 and Anode_2) showed significant improvement in most properties compared to those of the standard anode ($\text{Anode}_{\text{std1}}$) made with the non-modified coke. Also, three anodes were produced with coke 2. Anode_3 (modified using 1% additive) showed improvement only in terms of CO_2 reactivity and dusting due to air and CO_2 reactivity. On the other hand, the anode modified using 2 % additive (Anode_4) improved almost all the properties except for the flexural strength. Thus, it is not always possible to improve all the properties of anodes: but a good anode should have reasonable values of all the properties.

Improvement of anode quality not only increases the productivity, but also ensures energy saving, less carbon consumption, and lower greenhouse gas emissions. This study provides a new technique involving coke modification in order to improve anode properties, and this without making any significant changes in the process or the operating conditions in industry.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

In aluminum production, the quality of carbon anodes has a significant impact on the production cost, energy consumption, and the environmental emissions. The improvement of anode quality decreases the energy consumption, increases the efficiency of the process, and decreases the emission of greenhouse gases. The quality of raw materials plays an important role on anode quality. In this work, the focus was on the improvement of the wettability of coke by pitch using additives. The major conclusions of the study are presented below.

- The FT-IR study showed that both coke and pitch have aromatic, aliphatic and heteroatom-containing functional groups.
- It was obtained from the FT-IR and wettability results that the additive should have heteroatom-containing functional groups to enhance coke-pitch interaction. Also, it was found that the wettability of pitch is significantly affected by two wavenumber ranges: 1000-1300 cm^{-1} (Area1) and 3300-3600 cm^{-1} (Area2). The value of *(Area 1 / (Area 1 + Area 2))* ratio measured from the FT-IR spectra is a possible indicator of the effectiveness of an additive in improving the wettability of coke.
- It was observed from the wettability experiments of coke modified by six different additives that the additive should have a low melting point and a high boiling point. Also, the additives should be organic in nature, and they should not leave any residue which would contaminate the anode and harm the environment.

- It was observed from the FT-IR results that the functional groups in different cokes vary. Selection of an additive for the treatment of coke should be based on these functional groups. Thus, coke modification for the improvement of anode quality can be realized by the use of different additives at different concentrations.
- The results showed that the modification of coke by an additive in general improved anode properties. The green and baked anode densities were increased, the specific electrical resistivity, the air and CO_2 reactivities and dusting decreased. Also, the flexural strength of anode was improved in some cases.
- A study on the contact time of the additive with the coke before producing an anode was carried out. The results showed that the additive mixed one day earlier showed better improvement in anode properties compared to that added 5 minute before mixing.
- In this study, the additives, which improved anode quality, were chosen based on not only the functional groups, but also the cost and the environmental factors. The utilization of low cost and environmental-friendly additives has the potential for the industry.
- In addition, this method can be applied in the industry without making changes in the process or the process parameters. Thus, it can readily be integrated into the existing facilities.

7.2.Recommendations

In this study, the calcined petroleum coke was modified using different additives in order to improve the interaction between coke and pitch. Additives were chosen based on FT-IR analysis, which is a simple and low-cost technique available in the market. The criteria for the development of wettability of coke by pitch are done based on the FT-IR results. However, a more detailed study of coke, pitch and additives can be carried out using the XPS analysis.

Anodes made with the modified coke by an additive in general showed significant improvement in terms of density, electrical resistivity, air/CO_2 reactivity, and mechanical properties. More laboratory anodes can be produced using different cokes modified by different additives and different concentrations of these additives. In addition, the method needs to be tested on industrial anodes to verify the results obtained from the laboratory anodes.

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Appendix 1

The tapped bulk density results

Table A.1.1: The bulk density results for four cokes

Samples	**Tapped Bulk Density, g/cm^3**
Coke 1	0.8994
Coke 2	0.8853
Coke 3	0.8385
Coke 4	0.8737