Considerations in Chemical Coke/Pitch Modification Using Additives for Anode Production

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Abstract

Energy and carbon consumption, production cost, and greenhouse gas (GHG) emissions are some of the major challenges facing the aluminum industry today. These are closely related to the anode quality which depends on the raw material (coke and pitch) quality as well as the operating conditions used in the anode paste plant (recipe preparation, kneading, and forming) and during baking.

The raw material quality has been deteriorating. However, the aluminum industry needs a supply of good quality anodes irrespective of the raw material quality. One possible avenue is to improve the coke/pitch interactions by modifying them with additives. Two studies were carried out: 1) Several types of coke were modified with one additive, and anodes were produced using the same pitch; 2) Several pitches were modified with one additive, and anodes were produced using the same coke. The modified and non-modified cokes and pitches were characterized by means of measuring coke wettability by pitch and studying the surface chemistry of the raw materials using FTIR. Then, anode quality was determined by measuring the anode properties and comparing them with those of the standard anodes, which are produced using non-modified cokes and pitches. Both studies showed that using additives can improve some anode properties such as density, electrical resistivity, reactivity, and flexural strength. Thus, both coke and pitch modifications could help produce better quality anodes. This article presents the factors that affect the anode quality if modified raw materials are used in their production. Also, the advantages and disadvantages of the modifications should be assessed in terms of its application in aluminum smelters.

Keywords: Coke/pitch interactions, Raw material modification, FTIR, Wettability, Improvement of anode properties

1. Introduction

Canada is the fifth producer (3.1 million tonnes in 2021) and the second exporter of aluminum in the world. Three major aluminum producers (Rio Tinto, Alcoa, Alouette) are currently operating nine smelters (eight in Quebec and one in British Columbia) in Canada. Thus, 90 % of aluminum is produced in Quebec. Also, aluminum constitutes 2 % of Canadian exports. Due to the utilization of hydroelectric power and know-how, Canadian aluminum industry is producing the greenest aluminum in the world with the lowest global carbon footprint of 2 tonnes CO_2 equivalent per tonne of Al [1].

Primary aluminum is produced via the Hall-Hérault process, and the overall reaction can be written as shown in Equation 1.

$$2Al_2O_3 \text{ (bath)} + 3C \text{ (anode)} = 4Al + 3CO_2 \quad (1)$$

Carbon anodes are made from two major raw materials, which are coke and pitch. The anode recipe contains 85 % dry aggregate (calcined petroleum coke, butts, and recycled green and baked anodes). Dry aggregate, which has a predetermined particle size distribution, is mixed with 15 % coal tar pitch to produce anode paste. Pitch penetrates between dry aggregate particles and into their pores. Pitch has to wet these particles in order to bind them efficiently. The paste is transferred to a mold and compacted in a vibro-compactor or in a press to form a block, called green anode, prior to baking. During the baking process, the pitch carbonizes (pitch-coke) and forms a solid matrix binding the dry aggregate particles. If dry aggregate (mostly coke) and pitch are compatible (meaning that pitch wets well the coke and penetrates between the particles as well as into the particle pores), good quality anodes are produced (high density, low electrical resistivity, good mechanical properties, and low air and CO_2 reactivities). Good anode quality reduces the energy and carbon consumptions, production cost, and GHG emissions.

Wettability of coke by pitch is an indicator of the coke-pitch compatibility. The better the wettability is, the higher the possibility of producing good quality anodes is. Several researchers studied the wettability of coke by pitch, which depends on their physical and chemical properties [2-8]. Depending on the affinity of the liquid pitch drop with the coke surface, the drop takes a characteristic shape. The degree of a liquid spreading on the surface of a solid is defined as wettability, which is measured by the contact angle (for details see [9]). The wetting behavior of a pitch drop on the surface of the coke depends on the functional groups present on coke and pitch surfaces. In literature, it is reported that hydrogen bonds, electrostatic interactions, dispersion forces, acid-base interactions, and covalent bonds are the principal interactions responsible for the cohesion between coke and pitch [10-13]. Due to these interactions, the solid surface is altered which in turn changes the contact angle with time (dynamic contact angle).

The decrease in the quality of anode raw materials (coke and pitch) affects their compatibility. Coal tar pitch and petroleum coke are by-products of coke production from coal and crude oil refining processes, respectively. Improvements of these processes are leading to a decrease in the quality of their by-products, thus coke and pitch quality. Therefore, the enhancements of raw material properties in order to improve the compatibility of coke by pitch might be one of the avenues to possibly improve anode properties.

Chemical modification of the raw material surfaces using different additives and surfactants was studied by some researchers [14-17]. Only a few researchers worked on pitch modification with the objective of improving the anode properties, especially those of the anodes used in aluminum production.

Malyi et al. [18] worked on the modification of coal tar pitch using carbolic acid for electrodes used in the electrosmelting of steel. The results showed that carbolic acid positively affected the rheological properties of pitch, and thus improved the penetration of pitch and wettability of coke by pitch. They also studied the modification of coal tar pitch with phenolic fraction of slightly pyrolyzed coal tar [19, 20]. The results showed that utilization of 15-20 % additive improved the plasticity of the pitch. It also modified the β fraction of pitch which enhanced the sorption capacity of thermoantracite (solid carbon) used in electrode production, and improved the wettability of thermoantracite by pitch.

functional groups on their surfaces. This likely contributes to the enhancement of coke/pitch interactions.

The anode characterization results demonstrated that modification using an additive could improve some properties. Coke modification slightly improved the BAD compared to that of the standard anode. BAD of the anode made with modified pitch didn't improve. But, it is possible that this anode was over-pitched. The BER, CO2 reactivity (and its dusting), and flexural strength were improved by modifications of pitch with c3 % additive and coke with c1 % additive. These anodes had similar properties. This might be due to the same amount of additive used in both cases, but this was not verified. This study was carried out using the same pitch percentage for all the anodes. But, the pitch requirement for anodes made with modified raw materials might be different than those made with non-modified raw materials. Optimizing the pitch content might further improve the properties of anodes.

The results show that both coke and pitch modifications with additive seem beneficial for anode fabrication. One of the major differences for the application of coke and pitch modifications is the required equipment. It might be possible to realize the pitch modification in the storage silos used presently. On the other hand, coke modification not only requires an additional material (solvent), but possibly additional equipment to dissolve the additive in the solvent and mix with the coke. It was concluded that the advantages and the disadvantages of the modification should be assessed in terms of the limitations for the application of the raw material modification in the plant.

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5. References

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