



Full Length Article

Anode coke from coal – A low cost approach



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ABSTRACT

Declining quality and availability of petroleum cokes, which have traditionally been used for the production of carbon anodes, is forcing aluminum producers to use cokes previously regarded as unsuitable. Domestic reserves of coal represent a potential alternative carbon resource for anode production, provided coke specifications can be economically achieved. Previous studies have shown that the solvent refining of coal could produce carbons suitable for aluminum production. To conform to coke specifications (e.g. metals content), it was necessary to remove mineral matter in the coal by a costly filtration step. This adds significantly to the cost of the process, making it uncompetitive with coke from other sources. However, cokes with properties very similar to the required specifications have been produced from very low ash coals by solvent extraction, but without the uneconomic solids removal step. Extraction in a suitable solvent was used to produce a coal digest, which when injected at high temperature into a coking vessel generated the anisotropic needle structure characteristic of high quality cokes. Reported herein are the results of our investigation into using low-ash coals (1–2 wt.%) from the south-eastern Kentucky coalfield to produce anode-grade cokes using similar methods. The high cost filtration step was omitted, but the resulting coke did not meet the anode grade specifications.

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1. Introduction

Carbon anodes used in the primary smelting of aluminum have traditionally been manufactured from calcined petroleum coke [1]. The electrodes are made by blending the coke with a small fraction of coal tar pitch as binder. The green anodes are then baked to produce carbon anodes with sufficient density to meet the required performance standards. Consumption rates of the anodes during primary aluminum smelting, in the molten fluoride salt electrolysis cell are high, approaching 0.5 ton of carbon for each ton of aluminum produced [2]. Hence, large quantities of coke are required for carbon anode manufacture to satisfy the demands of the aluminum industry. Worldwide, the majority (>85%) of calcined petroleum coke is used to produce anodes for the primary smelting of aluminum from alumina in the Hall-Héroult process [3].

Petroleum coke is a by-product from the oil refining process. Modern refinery practice, controlled by the economics of the petroleum market, is aimed at maximizing the yield of lighter high value products. Therefore, emphasis is placed on the conversion of the heavy liquids from the distillation columns such as middle distillate, oil and residuum to higher value products by one of several

cracking processes; fluid catalytic cracking (FCC), hydrocracking or thermal cracking (coking). The heaviest material (bottoms) is fed to a delayed coker where thermal cracking of the large molecular species occurs, which yields high value lighter products. Consequent polymerization of the residuum results in the formation of coke as a by-product. This 'green coke' is mechanically removed from the coking drum and calcined by heating to ~1300 °C to remove volatiles and produce a material suitable for anode production. Impurities in the crude oil become concentrated in the coke and can have undesirable effects on aluminum production. For example, metal impurities such as vanadium and nickel catalyze carbon oxidation reactions, causing higher carbon consumption in the electrolysis cell [4]. Stability of the coke in air and carbon dioxide is a vital consideration in the economics of its use in anodes. Other impurities collect in the refined aluminum and can lower its value. Table 1 shows generic acceptable levels of impurities in the coke.

Impurity levels in petroleum cokes have been progressively increasing in recent years as the refineries have been obliged to accept a higher proportion of heavy sour crudes [6,7]. This trend and changes in refinery practice have resulted in an increase in the sulfur content of the petroleum coke, and/or an increasing coke cost [1]. An alternative supply of anode coke is desired to supplement calcined petroleum coke supplies, provided defined

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Table 1
Generic coke specifications for anode production [5].

| Component | Value |
|------------|-----------|
| Ash | ≤0.1 wt.% |
| S | ≤1.0 wt.% |
| Fe | ≤300 ppm |
| Si, V & Ni | ≤200 ppm |
| Na | ≤100 ppm |
| Ca | ≤50 ppm |
| P | ≤5 ppm |

specifications can be met and at a cost that is economically sustainable. The significant domestic reserves of coal could represent a viable carbon source for anode production. Specifically, the Blue Gem coal in southeastern Kentucky is of initial interest due to its inherently low ash content [8]. Cokes with properties very similar to the required specifications have been produced from very low ash coals by solvent extraction, in the absence of the uneconomic solids removal step [9,10].

The principal objective of this research effort was to determine whether Kentucky coal resources could be converted into coke suitable for anode fabrication through a mild solvent extraction process. Previous work has shown that the solvent refining of coal yields carbons suitable for aluminum production [5]. Low ash coals were extracted in a process solvent at relatively low pressure and without the use of hydrogen gas. *In addition, the uneconomic solids removal step commonly used to separate any undissolved solids present in the coal digest from the coal solution was omitted.* Coals for these tests were selected based on their inherently low mineral matter content and their known coking behavior on the premise that the structure and properties of the cokes produced from them would likely be suitable for anode fabrication. High volatile A bituminous coals of Eastern Kentucky produce anisotropic cokes, and many have been used as blend constituents for production of metallurgical coke and were thus selected as prime candidates for this application. Current anode coke specifications require very low metals and sulfur contents, with V, Ni, Na, Ca, Si, and Fe being of particular importance (see Table 1). To achieve anything close to the current pet coke specs in terms of metals content, it was essential to use feed coals with minimal mineral matter content. To further reduce the mineral matter content of the low-ash feed coals, a coal cleaning procedure, selective oil agglomeration, was used on the finely milled coals. This further cleaning of the coal would remove mineral matter, which can poison the formation of the anisotropic needle-like carbon structure [11] formed during coking and required in a high quality anode coke. Removal of particulates from the feed that inhibit growth and coalescence of the developing mesophase in the coking process, would lay the foundation for achieving these goals. The as-received and cleaned coals were analyzed for composition and compared. A bench scale mild solvent extraction process developed by University of Kentucky Center for Applied Energy Research (CAER) to convert bituminous and subbituminous coals to high value carbon products was used as the basis for the work [5].

The work presented here addressed the issue of whether this process could be used to produce cokes that exhibit the properties and structure required for fabrication of carbon anodes and at an economically viable cost, achieved by omission of the costly filtration step. The coal digests derived by this process were converted into green coke by heating, under a N₂ sparge of 230–260 SCCM to promote solvent stripping and to simultaneously shear the polymerizing residue, at 380 °C for 1.5, 2.5 and 5.0 h, and then at 500 °C for 2.5 h. Subsequently, the green cokes were heat treated, under an inert atmosphere to 1300 °C at 50 °C/min with a 1-h soak time, to produce calcined cokes. The final cokes were characterized

by X-ray diffraction, optical microscopy and compositional analysis.

2. Experimental

2.1. Identification, selection and procurement of candidate coals

Low ash coal samples from sites in the southeastern Kentucky coalfield were identified and sourced. Three coals were selected from the suite of candidate samples for conversion into coke by solvent extraction and coking. Candidate coals were limited to low-ash, low-S, high volatile A bituminous coals from southeastern Kentucky: the Blue Gem coal from the Logan Hollow and Harps Maple Creek mines, and the Jellico coal (sample no. 3037). These coals were known to contain very little mineral matter (ash); in the 1–2 wt.% range. The mineral content in the Blue Gem is marked by low amounts of aluminosilicates and is dominated by siderite [5,12–14]. Conversely, efforts have been made to arrive at low-ash coal by chemically and thermally treating lower cost, high-ash coals [15,16]. Other solvent extraction of coal research has focused on producing one- and two-ring compounds for the jet fuel industry [17].

Ash is known to hinder the formation of long-range anisotropy in the final cokes [11]. Further, a central hypothesis was that the ash content could be reduced even further, perhaps to <0.1 wt.% through a coal cleaning (oil or pentane agglomeration) procedure, to separate the ash fines from the coal. The cleaned ultra-low ash coal would then be used to produce anode grade coke *without the need for a costly filtration step to remove ash from the coal digests.* The results of compositional analyses of the three starting coals are shown in Table 2a. The native ash contents of the Logan Hollow Blue Gem, Harps Maple Creek Blue Gem, and Jellico coals were 1.02, 1.42, and 2.31 wt.%, respectively. Similarly, the metals contents of these coals, stemming from the ash, were higher than the generic coke specifications (Table 1). However, the sulfur content of the coals was quite low at 0.77, 1.08, and 0.99 wt.%, respectively. The total vitrinite content (mineral-free basis) of the three coals ranges from ~71% for the Jellico coal to 75.4–77.6% for the two Blue Gem samples (Table 2b). The Blue Gem samples have lower inertinite content than the Jellico sample.

2.2. Coal cleaning: Pentane agglomeration procedure

Pentane agglomeration, commonly referred to as oil agglomeration, was investigated as a method to reduce the ash content of the selected coals to produce a desirable coking feedstock. Ash levels of less than 0.1 wt.% were targeted, starting from coals containing 1–2 wt.% ash. Oil agglomeration is a procedure commonly used to separate finely disseminated hydrophobic and hydrophilic minerals [18]. The procedure consists of adding hydrophobic oil to a finely ground coal and water slurry. Upon agitation hydrophobic agglomerates are formed. The mineral matter liberated from the coal particles by the fine-grinding procedure accumulates in the hydrophilic fraction of the product and can then be separated from the organic hydrophobic fraction by decantation. The process has been used successfully in the past at the industrial scale; however no commercial installations are currently operating.

Pentane was used as the agglomerating oil, due to its low boiling point and the fact that it leaves no residual components to interfere with other upgrading processes. The parent coal was slurred with water and ground (33% solids w/w) in a ball mill to a size sufficient for liberation of the finely disseminated mineral matter. Approximately 0.5 L of the ground slurry was transferred to a blender, ~25 ml of pentane added and the mixture was subjected to intense agitation at 1000 rpm for 30 s to form

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