

USE OF COAL TAR PITCH COKE FOR PRODUCING PREBAKED ELECTRODES

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Keywords: pre-baked anode, pitch coke, bench scale.

Abstract

The utilization of coal tar pitch coke as a substitute for petroleum coke in anodes was tested in the lab. The study was conducted in order to (1) find an alternative material to petroleum coke due to its high cost and deteriorating properties, and (2) determine the feasibility of using a current Chinese source of coal tar pitch coke for producing aluminum industry anodes.

Introduction

The quality of green petroleum coke for production of prebaked anodes is deteriorating, and this has become an even greater problem for the industry in the last decade or so. Green cokes that would have been considered fuel grade are now being utilized for anode production, leading to a consequential deterioration of anode quality and increases in the variability of the anodes produced. On the other hand, aluminum smelters are now expecting anodes that are being produced by suppliers such as Sunstone to have improved performance levels and more competitive pricing. Thus for anode vendors it is very important to optimize all process parameters, and improve quality, consistency, and customer service.

Alternative raw materials such as coal tar pitch coke could possibly be an option that would help anode producers with their improvement efforts. Also, this technology is not new; being used in the past for producing Russian Soderberg anodes. With the current (and projected future) state of coke quality and pricing, coal tar pitch coke might be an opportunity. The current lab study was initiated to determine if there are any limiting factors regarding baked anode quality that might prevent coal tar pitch coke from being utilized as such a raw material.

Raw Materials

All of the raw materials used in the experiments were obtained locally in China. Properties of the green cokes are listed in Table I. Volatiles contents for the cokes are about the same, about 12.7%. Take special note of the sulfur content, just over 2% for the petroleum coke, but only 0.1% for the pitch coke. Also, contents of ash, vanadium, and nickel are quite a bit lower than that of the petroleum coke. The only metallic impurity that increased was iron, going from 120 to 270 ppm.

Coke samples were calcined in the R&D Carbon RDC-164 Coke Calcining Furnace shown in Figure 1.

The temperature profile for calcining the coke is shown in Table II. Heat-up rate is 100 °C/hr up to the soaking temperature of 1100 °C. The coke is then held at 1100 °C for a period of 20 hours.

Table I. Green Coke Properties

| Properties | | Petroleum Coke | Coal Tar Pitch Coke |
|------------|-----|----------------|---------------------|
| Volatiles | % | 12.70 | 12.71 |
| Ash | % | 0.23 | 0.14 |
| S | % | 2.21 | 0.10 |
| V | ppm | 170 | 2 |
| Ni | ppm | 111 | 23 |
| Si | ppm | 132 | 87 |
| Fe | ppm | 120 | 270 |
| Al | ppm | 154 | 177 |
| Ca | ppm | 199 | 115 |
| Na | ppm | 34 | 30 |
| Zn | ppm | Not Detected | 1 |



Figure 1. Coke Calcining Furnace.

Samples of the calcined cokes were then analyzed with the results shown in Table III. Most significantly, the density of the pitch coke is about 18% higher (1.05 g/cc vs. 0.89 g/cc) than the petroleum coke, and the sulfur content is dramatically lower, 0.13% vs. 1.86%. Vanadium and nickel contents are also much lower in the pitch coke, 4 ppm vs. 167 ppm and 5 ppm vs. 108 ppm, respectively. However, the electrical resistivity of the pitch coke was 44% higher than the petroleum coke (714 μΩm VS. 495

$\mu\Omega\text{m}$). Additional studies will have to be conducted in order to determine the reason(s) for the ER difference.

Table II. Lab Coke Calcining Conditions

| Temperature range, °C | Heat-up rate, °C/hr | Time, hr |
|-----------------------|---------------------|----------|
| Ambient - 200 | 400 | 0.5 |
| 200 - 1100 | 100 | 9 |
| 1100 | Soak | 20 |
| Total | | 29.5 |

Table III. Calcined Coke Properties

| Calcined Properties | | Petroleum Coke | Coal Tar Pitch Coke |
|----------------------------|--------------------------|----------------|---------------------|
| VBD | g/cc | 0.89 | 1.05 |
| ER | $\mu\Omega\cdot\text{m}$ | 495.4 | 714.3 |
| Ash | % | 0.25 | 0.15 |
| RD (Water) | g/cc | 2.08 | 1.99 |
| Air Reactivity | % / min | 0.31 | None Detected |
| CO ₂ Reactivity | % / min | 11.23 | 11.83 |
| S | % | 1.86 | 0.13 |
| V | ppm | 167 | 4 |
| Ni | ppm | 108 | 5 |
| Si | ppm | 142 | 114 |
| Fe | ppm | 88 | 168 |
| Al | ppm | 144 | 109 |
| Ca | ppm | 189 | 151 |
| Na | ppm | 31 | 31 |
| Zn | ppm | 1 | 1 |

Analyses of the pitch used in the lab experiments is given in Table IV. Softening point is typical of what has been used in China historically, 101 °C. QI is about 7% and coking value 56%.

Preparation of Lab Samples

The sizing and blends of the cokes used in the experiments are given in Table V. One experiment was conducted with 100% petroleum coke (0% pitch coke) as a control. An additional four experiments were run with increasing amounts of pitch coke, 13%, 32.5%, 65%, and 100%. Note that the 100% experiment was the only one that utilized pitch coke in the fines fraction. All experiments other than 100% used petroleum coke for the fines fraction.

The sizing and amounts of each size fraction are listed in Table VI. The pitch content chosen by Sunstone for the experiment was 15.2%, but as will be seen later, this pitch % turned out to be significantly higher than the optimum.

Table IV. Pitch Properties

| Properties | | |
|-----------------|-----|-------|
| Ash | % | 0.1 |
| Softening Point | °C | 100.8 |
| VOM | % | 55.9 |
| TI | % | 27.44 |
| QI | % | 7.28 |
| Beta Resin | % | 20.16 |
| Coking Value | % | 55.79 |
| Visc. 140°C | cP | 6073 |
| Visc. 160°C | cP | 1125 |
| Visc. 180°C | cP | 330 |
| S | % | 0.51 |
| Na | ppm | 56 |
| Ca | ppm | 31 |
| Al | ppm | 19 |
| Si | ppm | 19 |
| Fe | ppm | 79 |
| Zn | ppm | 105 |
| Pb | ppm | 99 |

Table V. Proportions of coke aggregate in the lab experiments

| Aggregate (not including fines) | | Fines | | Pitch Coke % |
|---------------------------------|----------------|------------|----------------|--------------|
| Pitch Coke | Petroleum Coke | Pitch Coke | Petroleum Coke | |
| 0 | 65% | 0 | 35% | 0 |
| 13% | 52% | 0 | 35% | 13% |
| 32.5 | 33% | 0 | 35% | 32.5% |
| 65% | 0% | 0 | 35% | 65% |
| 0.65 | 0% | 0.35 | 0% | 100% |

Table VI. Recipe and Pitch Content

| Size | 8-5mm | 5-2mm | 2-0mm | Fines |
|-------|-------|-------|-------|-------|
| % | 12 | 20 | 33 | 35 |
| Pitch | 15.2% | | | |

Mixing of was conducted using an R&D Carbon RDC 161 Bench Scale Anode Production Unit as shown in Figure 2. This unit utilizes a 10 liter lab-scale Eirich mixer for paste production. The coke aggregate was preheated to 200 °C and placed in the mixer which was at 160 °C. The prescribed amount of solid pitch at ambient temperature was also placed in the mixer and mixed for 10 minutes. Final paste temperature was 175 °C.



Figure 2. Lab Mixer.

Paste samples were then formed at 170 °C and 62 MPa using a laboratory press. Ten pieces (50 mm dia. X 120 mm ht.) were produced for each experimental condition.

The anode samples were then baked in an R&D Carbon RDC 166 Anode Baking Furnace, shown in Figure 3.



Figure 3. Anode Baking Furnace.

Each anode sample was encased in 1-2 mm of packing coke to protect against air oxidation and baked using the temperature and heat-up profile listed in Table 7.

Table 7. Baking Profile

| Temperature, °C | Heat-up rate, °C/hr | Time, hr |
|-----------------|---------------------|----------|
| Ambient - 150 | 100 | 1.5 |
| 150 - 300 | 10 | 15 |
| 300 - 1100 | 50 | 16 |
| 1100 | Soak | 20 |
| Total | | 52.5 |

Experimental Results

As can be seen in Figure 4 green densities were quite high for the samples containing pitch coke, indicating that the 15.2% pitch level selected for the experiment was excessive. As they should, GADs continue to increase as the proportion of the more dense pitch coke increases. However, baked densities do not follow this same trend. Baked densities increase up through the point where the anode is made with 65% pitch coke, but no pitch coke fines. When the pitch coke is added as the fines fraction and the resulting anode becomes 100% pitch coke, baked densities drop slightly and the excess pitch, rather than increased coke density, becomes the factor with most influence on the resulting baked density.

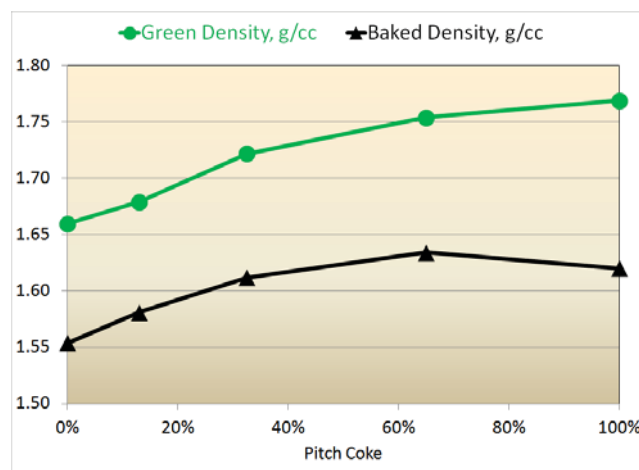


Figure 4. Green and Baked Densities.

Further confirmation of the excessive pitch level can be seen in Figure 5 which shows the baking loss and the difference between GAD and BAD. At optimum pitching levels petroleum coke anodes generally have baked loss of about 3% and the difference between GAD and BAD is no more than 0.05 g/cc. For all of these experimental anodes baked, loss is about 6% or greater and The GAD-BAD difference is 0.10 g/cc or greater. Therefore it's safe to say that the 15.2% level of pitch addition is in excess of the optimum, probably a good bit in excess of the optimum. This over-pitching condition may cast some doubt on the applicability of the baked anode data that follows, but even with this limitation some valid conclusions can be drawn.

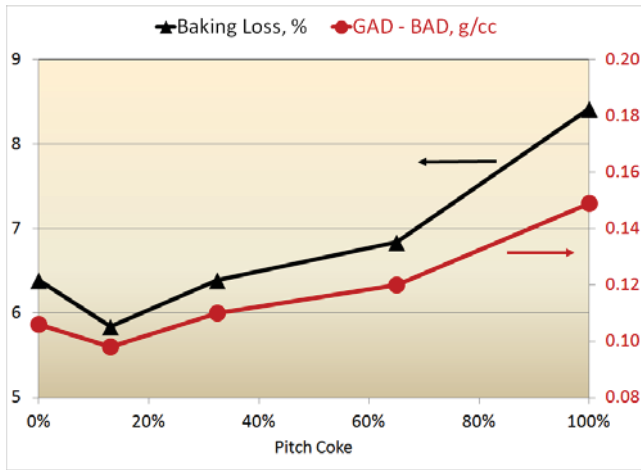


Figure 5. Baking Loss and GAD Minus BAD.

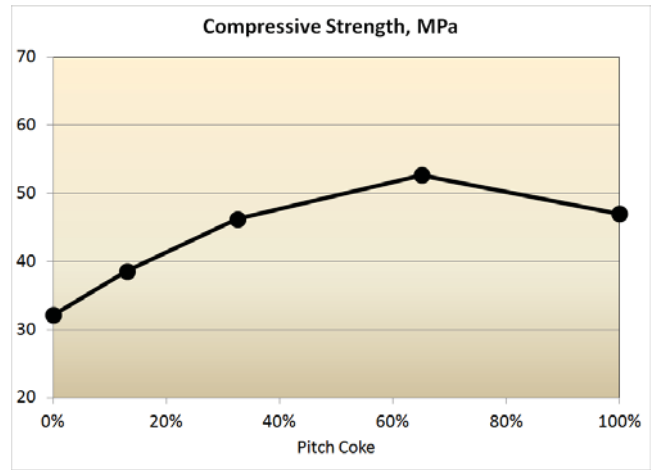


Figure 7. Compressive Strength.

Electrical resistivity for the experimental anodes is shown below in Figure 6.

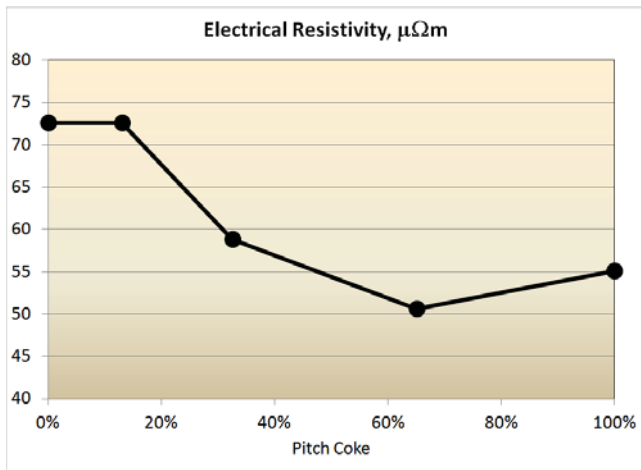


Figure 6. Electrical Resistivity.

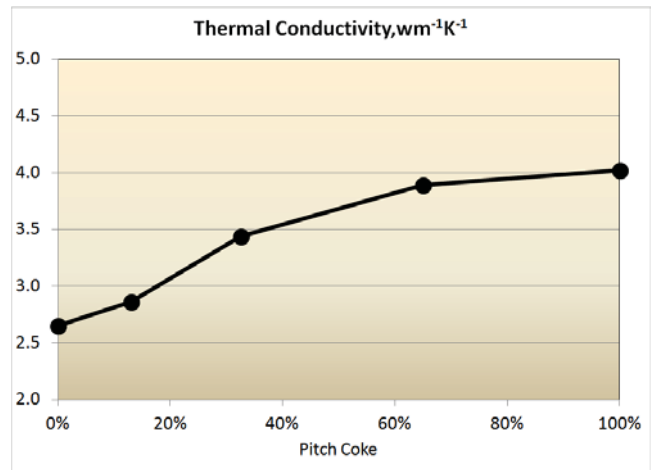


Figure 8. Thermal Conductivity.

There seems to be a decreasing trend in ER as pitch coke % increases; however, ER goes back up slightly as the anode goes to 100% pitch coke. Note this is probably related to the trend in BAD which starts going back down at the 100% level.

Compressive strength for the experimental anodes is shown in Figure 7. The trend for compressive strength follows the same basic trend as for baked density. There is a steady increase up until the point where the anode becomes 100% pitch coke. At 100% the strength decreases slightly, corresponding to the decrease in baked density. Over-pitching of the anode becomes more pronounced as the portion of pitch coke increases and is possibly the reason for this strength decrease.

Thermal conductivity for the experimental anodes displays a steadily increasing trend and is shown in Figure 8. This data implies that anodes made with a portion of their aggregate using pitch coke will show increased thermal conductivity and therefore have lower tendency for thermal cracking.

Reactivity data for the experimental anodes are shown in Figures 9 and 10.

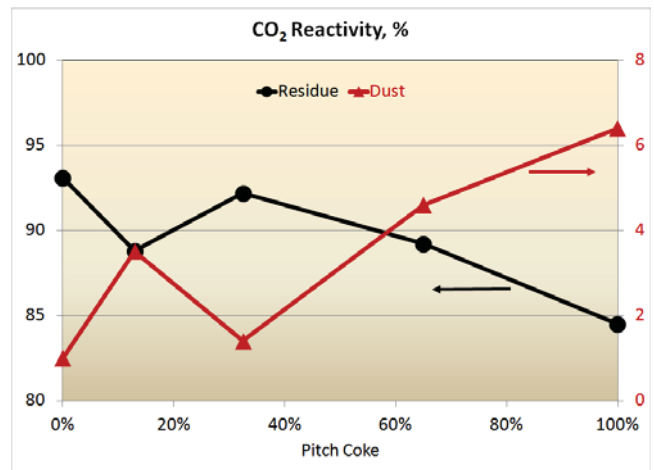


Figure 9. CO₂ Reactivity.

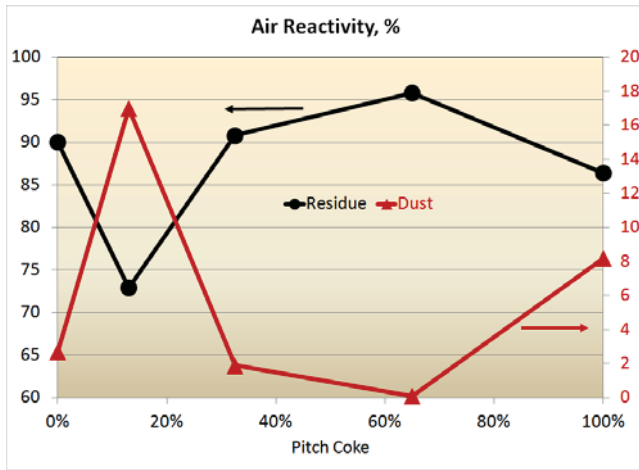


Figure 10. Air Reactivity.

CO₂ reactivity values generally show a negative trend as the portion of pitch coke increases. Air reactivity results are mixed. Values are quite good for the 32.5% and 65% pitch coke anodes, but not so good for the other samples. The authors believe that all of the reactivity results are questionable due to the high pitch content. Additional experiments will be necessary at optimum pitch content for each of the aggregates if a meaningful relationship between pitch coke and reactivity is to be determined.

Air permeability was also run on the experimental anodes, but this property did not show a significant trend due to the high pitch level used.

Data for sulfur, vanadium, and nickel are shown in Figures 11, 12, and 13, respectively. Note that the data and trends in these three figures should not be significantly influenced by the high pitch content of the samples.

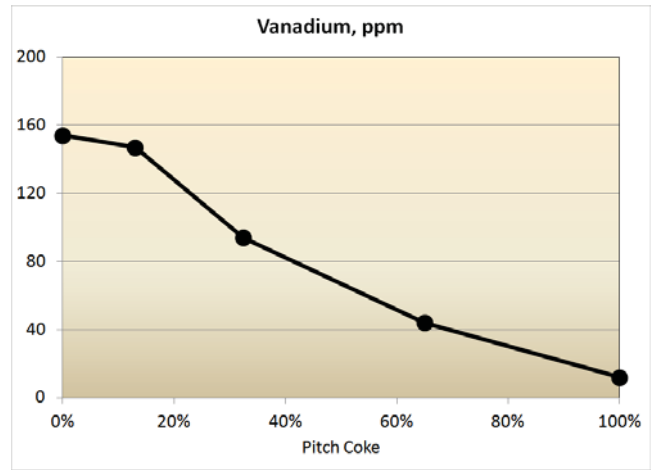


Figure 12. Vanadium Content.

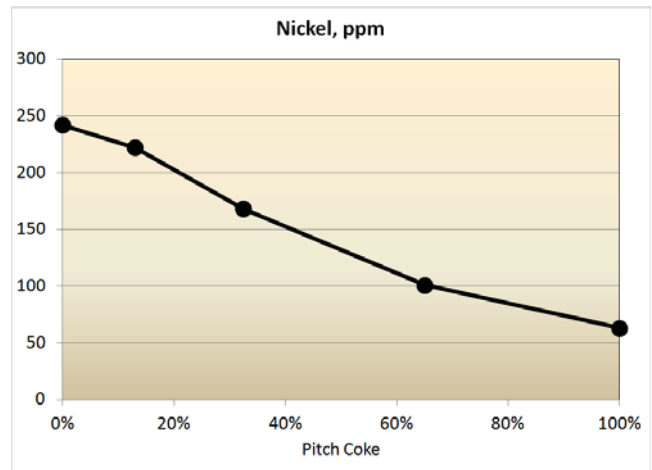


Figure 13. Nickel Content.

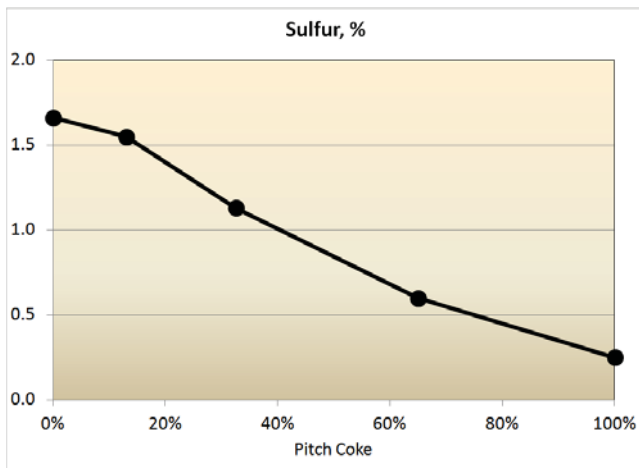


Figure 11. Sulfur Content.

As it should, a common and decreasing trend exists for each of these impurities due to their low levels in the pitch coke.

Sulfur is a major environmental concern for many smelters today and restrictions on sulfur emissions are only expected to get more stringent. Many smelters will be required to either implement more efficient sulfur scrubbing systems (costing \$US MMs) or use lower sulfur coke that is getting much more expensive and more difficult to obtain. Depending upon cost and assuming that there are no smelter performance issues, pitch coke might be an option for blending with higher sulfur petroleum coke in order to reduce sulfur emissions below regulated levels without installing additional capital-intensive scrubbing equipment.

Even though this was not reflected consistently by the CO₂ and air reactivity charts in Figures 9 and 10, both vanadium and nickel are known to be oxidation catalysts for anode carbon. Just as the sulfur is increasing in petroleum residuals and the resulting green cokes, the vanadium and nickel are also increasing. As a result, the tendency for anode oxidation will also be increasing. Similar to the statements on sulfur, pitch coke might be an option for blending with higher V and Ni petroleum cokes in order to reduce the oxidation potential of the baked anodes. This is especially meaningful for older smelters utilizing pot technology where it is more difficult to cover and protect the anodes well.

Conclusions

Additional laboratory studies are needed regarding the use of coal tar pitch coke as a substitute for a portion of the petroleum coke used in anodes. For each blend that is tested, optimum pitch % will first have to be determined in order to obtain more definitive baked anode properties.

With its higher VBD, use of pitch coke as a portion of the anode coke blend has the potential of increasing both baked density and anode strength. Potential for thermal shock cracking may also be reduced due to the increased thermal conductivity of the resulting baked anodes.

Due to its low concentrations of sulfur, vanadium, and nickel, pitch coke has the potential for use in blends to (1) help smelters meet environmental restrictions on sulfur emissions without capital expenditures and (2) reduce vanadium and nickel levels that increase an anode's potential for oxidation. This latter benefit could be especially helpful for older smelters that utilize pot technology where it is more difficult to cover and protect the anodes well.