

ANODE BINDER COKE REACTIVITY

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Introduction

Baked carbon anodes, made from a mixture of petroleum coke and coal tar binder pitch, are consumed in the production of aluminum at a minimum theoretical rate of 334 kg C/tonne Al produced. The real net consumption is, however, from about 400 kg anode/tonne Al and up. The difference, the excess anode consumption, is caused by the current efficiency being less than 100%, gasification reactions by CO₂ and air, and anode "dusting". Anode carbon "dust" is normally petroleum coke particles that are coming detached from the anode and accumulate in the electrolyte. The cause is selective reactivity of the binder coke, *i.e.* the coked pitch binder is consumed faster than the aggregate coke, thus destroying the petroleum coke particle anchor to the binder matrix. Anode "dust" can cause severe problems for cell operation, particularly in sodberg cell operation (where the process temperature of about 960°C is the maximum baking temperature), but also in prebaked anode cells where the anode heat treatment temperature has been considerably higher.

The baked anode may consist of less than 10% pitch binder coke, the balance being the calcined petroleum coke aggregate. During laboratory reactivity testing of baked anodes, the contribution of the binder coke to the overall anode properties are hence often overshadowed by the large amount of petroleum coke. In order to evaluate the specific reactive properties of the binder coke in the granular composite anode, a number of industrially used and prospective anode binder pitches were coked alone and tested for CO₂ and air reactivity.

Experimental

When coked at atmospheric pressure most binder pitches are turned into foam-like carbons with low bulk density and with gas reactivity properties that are difficult to reproduce. Anode binder pitch coke yields are typically 55-60% under these conditions. Controlled carbonization at high pressure will turn the same binders into denser cokes with a calcined coke yield of 88-90% and bulk densities comparable to the anode petroleum coke aggregate. Such cokes were better suited for excess gas reactivity studies.

A special coking reactor was built for this purpose where pitches could be coked under 15 bar of inert gas pressure [1]. The green cokes were then calcined to 1010°C, crushed and screened. The -2+1 mm fraction was used for reactivity measurements in a modified Hydro

Aluminium air/CO₂ reactivity apparatus. Air reactivity was measured at 475°C and CO₂ reactivity at 960°C, the apparatus and experimental procedure were otherwise as described in Ref. [1].

Fifteen anode pitches from four different pitch distillers and four petroleum pitches from two distillers were coked, calcined and tested for air and CO₂ reactivity. The pitches had softening points in the range 110-140°C. Sulfur and trace metal analysis were done on the calcined cokes as well as their precursors.

Results and Discussion

A simple correlation analysis made between all reactivity parameters, sulfur and trace metal analysis showed that air and CO₂ reactivity had a medium to strong positive correlation with the impurity content of Na, K, Mg, Ca, Fe, Zn and Pb in the cokes. With the exception of Zn, all these other elements are known to catalyze the air and CO₂ gasification reactions. The reason why Zn showed up in the correlation analysis is its covariance with Pb. In coal tar anode pitches the Zn and Pb impurity levels tend to follow each other (the Pb-Zn correlation coefficient was 0.934). While Pb is the strong oxidation catalyst, Zn should not display this type of catalytic ability [2].

Sulfur comes out with a negative correlation coefficient for both air and CO₂ reactivity, weak for air but medium strong for CO₂. The correlation between reactivity parameters and sulfur were less than expected, since sulfur is a known metal catalyst poison and it has been reported to inhibit both air and CO₂ reactivity of petroleum cokes and anodes [3,4,5]. The sulfur content of petroleum cokes (and anodes) is, however, generally higher and covers a broader concentration range than normally found in coal tar pitches (and pitch cokes).

The reactivity (R, air or CO₂) data was then fitted to two types of empirical equations, one through a simple linear multi-regression analysis,

$$R = A_0 + A_1M_{Me(1)} + \dots + A_nM_{Me(n)} + A_S M_S \quad (1)$$

and the second through a non-linear fit with the sulfur concentration term as the denominator,

$$R = A_0 + \frac{A_1M_{Me(1)} + A_2M_{Me(2)} + \dots + A_nM_{Me(n)}}{A_S M_S} \quad (2)$$

where the A's are regression parameters and M_{Me} and M_S are metal impurity and sulfur concentrations in the cokes.

In view of the correlation analysis it is not surprising that Eqn.1 makes the best fit for air reactivity while Eqn.2 fits the CO_2 reactivity data best. The simplest CO_2 reactivity expression that has a satisfactory correlation coefficient is Eqn.2 containing the constant term and Na,

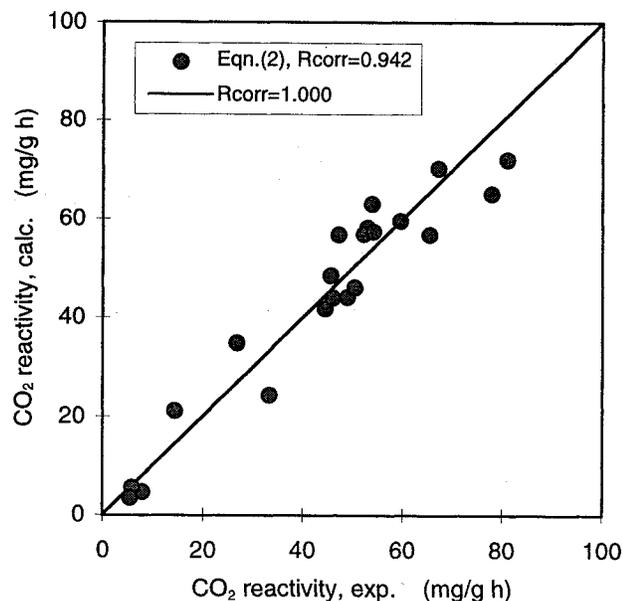


Figure 1. Experimental CO_2 reactivity plotted against calculated CO_2 reactivity according to Eqn.2. Solid line is ideal 1:1 correlation ($R_{corr} = 1.000$).

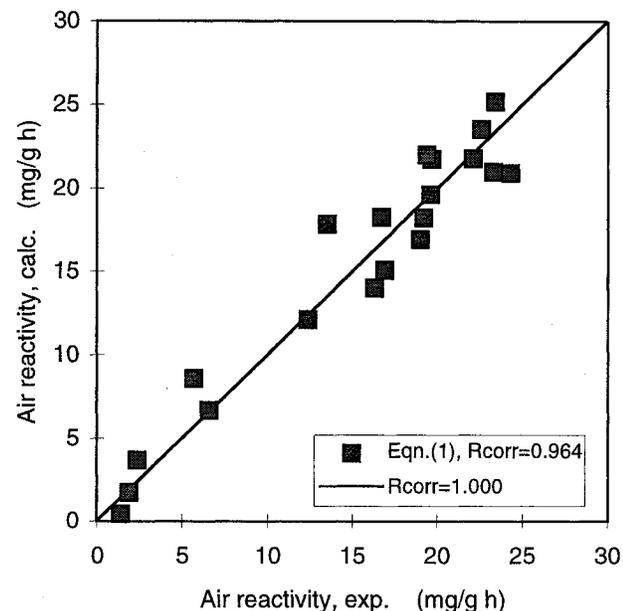


Figure 2. Experimental air reactivity plotted against calculated air reactivity according to Eqn.1. Solid line is ideal 1:1 correlation ($R_{corr} = 1.000$).

Ca, Fe, Pb and S terms (Figure 1). The correlation coefficient $R_{corr} = 0.942$. Further omission of any of the remaining coke impurity terms results in a significantly reduced correlation.

The simplest equation that describes the air reactivity data with good correlation is Eqn.1 with the constant term and the Na, Ca, Fe, Pb, Mg and S terms. The correlation coefficient $R_{corr} = 0.964$ (Figure 2). Unlike the CO_2 reactivity, the air reactivity is dominated by one metal impurity; the concentration of Na. If all other terms, also the constant term A_0 , are removed from Eqn.1 the air reactivity of the cokes can be described by a simple proportional relationship to the Na impurity content with a correlation coefficient $R_{corr} = 0.899$. This should be of particular importance in regard to anode pitch quality and specifications since the major part of Na found in anode binder pitches is added by the pitch distiller as soda to reduce corrosion on the still.

Conclusions

The concentration of some catalytically active elements in pitch binder cokes almost fully describe the excess air and CO_2 reactivity of the coke.

While sulfur seems to play a part in inhibiting the CO_2 gasification reaction of the pitch binder cokes, it is not significantly correlated to the air-burn reaction of the binder cokes.

Most air-burn reactivity in the binder cokes can be attributed to the concentration of Na alone. This is of particular importance since most Na is introduced in the tar distilling process.

Acknowledgments

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