ANODE FILLER COKE POROSITY STUDIES

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Porosity of calcined coke used as filler in aluminum reduction cell anodes is influenced by the following factors: (a) nature of coke precursor, (b) volatile content of the green coke, (c) heating rate during calcination, (d) calcination temperature, and (e) degree of sulphur removal during calcination. The relative significance of these factors in coke porosity development and the resulting effects on bench-scale anodes are discussed.

## INTRODUCTION

Calcined coke porosity is important with respect to prebaked anode and Soderberg-paste binder requirement and anode properties, particularly apparent density. It has been reported in the past that porosity is very sensitive to green coke volatile matter content at high heating rates during calcination and other factors such as coke source, final calcination temperature, and thermal desulphurization can also have a significant effect on porosity development.[1] The relative effects of the above parameters on calcined coke porosity have been more recently further investigated and are presented in this paper including the effects of filler coke porosity on binder requirement and properties of bench-scale anodes.

## EXPERIMENTAL

An Aminco-Winslow mercury porosimeter was used in this study with the operating range shown in Table I. Determinations were done on minus 830 plus 420 micrometer (-20 + 35 Tyler mesh) granular coke. Calculation of pore sizes was based on assuming cylindrical pores (Washburn equation).[2] Prosity results given in volume percent (P) can be converted to pore volume in $cm^3/g$ ($\varepsilon$) by the equation $\varepsilon = P/\delta \times 10^2$ where $\delta$ is the apparent density of particles including pores smaller than 100 micrometers in diameter, determined with the mercury porosimeter and expressed as $g/cm^3$. The coefficient of variation of the measurement was 2% for laboratory-calcined coke and 4% for coke less uniformly calcined in rotary kilns.

The Aminco-Winslow porosimeter with an upper limit of 211 $kg/cm^2$ (3,000 psi) pressure covers the total porosity and pore size distribution normally found in calcined petroleum coke. This pressure, however, is not sufficient to penetrate with mercury the fine pores of thermally desulphurized cokes. For this purpose a Quantachrome scanning mercury porosimeter was used with an upper limit of 4,220 $kg/cm^2$ (60,000 psi) pressure, equivalent to a pore diameter of 0.003 μm.

Laboratory calcinations were done in an induction furnace. The apparatus and technique has been described elsewhere.[1,3]

## RESULTS

The effect of coke precursor on the porosity of laboratory-calcined coke is shown in Table II. Calcination temperature was 1250°C, heating rate 10°C/min and holding time at calcination temperature 30 minutes. Thermal desulphurization did not occur during calcination. A significant but relatively small increase in porosity is indicated as the coke precursor changes from asphaltic to paraffinic nature, accompanied by an increase in the degree of anisotropy of the calcined coke. It can also be seen that the porosity of the green coke is insensitive to the change in the nature of precursor.

Table I.  Pore Size Ranges Determined Using the Aminco-Winslow Mercury Porosimeter
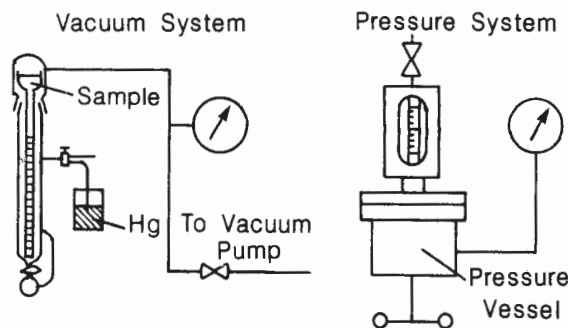
| Absolute pressure$^{(p)}$ | kg/cm$^2$: | 0.126 | 1.30 | 211 |
| | psi: | 1.8 | 18.5 | 3,000** |
| Equivalent pore diameter$^{(d)*}$ | μm: | 100 | 10 | 0.05 |

$$* \ d = \frac{-4 \ \gamma \cdot \cos \theta}{p}$$

where:

γ = surface tension, 480 dynes/cm

θ = contact angle, 140°

Vacuum System    Pressure System

Sample

Hg  To Vacuum Pump

Pressure Vessel

**   A Quantachrome scanning mercury porosimeter with an upper limit of 60,000 psi pressure
     (d = 0.003 μm) was used to measure fine porosity of desulphurized coke.

Table II.  Effect of Precursor on Coke Porosity and Other Properties (Laboratory Calcination)

| Nature of precursor (delayed coker feed) | | asphaltic | inter-mediate | paraf-finic |
| --- | --- | --- | --- | --- |
| **Green Coke** | | | | |
| Volatile matter | wt% | 12.4 | 14.3 | 12.3 |
| Porosity | vol% | 8.3 | 8.9 | 7.8 |
| Sulphur | wt% | 0.81 | 0.30 | 3.40 |
| **Calcined Coke** | | | | |
| Texture: | | isotropic | mosaic | sponge |
| Real density | g/cm$^3$ | 2.03 | 2.05 | 2.06 |
| Mean crystallite thickness, $L_c$ | Å | 31.5 | 30.3 | 33.3 |
| Vibrated bulk density | g/cm$^3$ | 0.952 | 0.880 | 0.840 |
| Porosity | vol% | 15.2 | 16.3 | 18.6 |

Figure 1 shows calcined coke porosity as a function of volatile matter content of the green coke and heating rate. The chart was constructed using the results of measurements made on numerous samples from laboratory induction furnaces, commercial rotary kilns and from an experimental fluidized bed calciner. As would be expected the effect of heating rate becomes more and more pronounced as the volatile matter content of the green coke increases. Thus there is considerable incentive to reduce the rate of heating in commercial rotary kilns when calcining delayed coke typically containing 10 to 12 wt% volatile matter. On the other hand, fluid coke with usually 6 wt% volatile matter content can be calcined in a fluidized bed (direct feed to the bed) without an appreciable increase in porosity.

The effect of final calcination temperature on coke porosity over the temperature range where thermal desulphurzation does not occur is relatively small. Table III gives experimental data obtained in the laboratory with low and high-sulphur coke. The increase in mercury accessible pore volume for the low-sulphur coke remains monotone up to 1500°C, even though at this temperature a noticeable decrease in sulphur content takes place. On the other hand, for the high-sulphur coke, a sharp increase in pore volume is evident at 1450°C where sulphur content
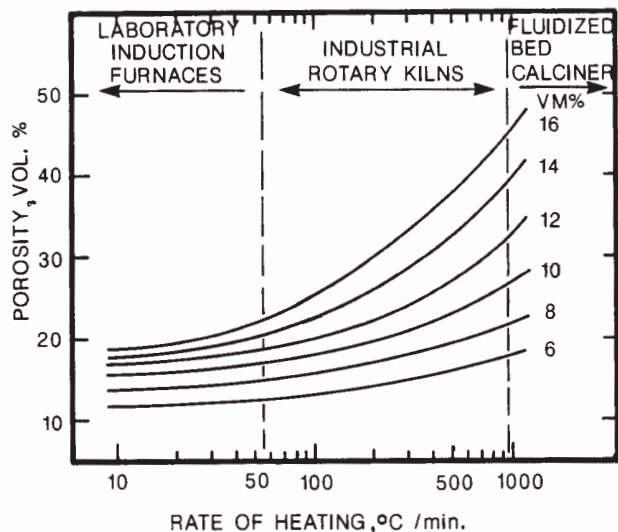
Figure 1 – Porosity of calcined coke as a function of heating rate and volatile content of the green coke (VM = Volatile matter content of green coke)



Figure 2 – Coke porosity as a function of calcination temperature.

Figure 3 illustrates the change in pore size distribution when green coke is calcined (a) in the laboratory, (b) in a rotary kiln, and (c) is thermally desulphurized. It is seen in the figure that the fine pores developed as a result of desulphurization are not totally penetrated by mercury at 211 kg/cm² (3,000 psi) pressure which is the upper limit of the Aminco-Winslow porosimeter used. Further determinations made with a Quantachrome scanning mercury porosimeter

Table III – Experimental Data Obtained on Low and High Sulphur Coke Calcined in the Laboratory

| Volatile matter in green coke wt% | Calcination temperature °C | Sulphur wt% | Kerosene density g/cm³ | Pore volume cm³/g |
|---|---|---|---|---|
| | 1050 | 2.37 | 1.92 | 0.110 |
| | 1150 | 2.40 | 2.03 | 0.119 |
| | 1270 | 2.51 | 2.06 | 0.128 |
| 10.5 | 1300 | 2.43 | 2.08 | 0.129 |
| | 1450 | 2.54 | 2.12 | 0.142 |
| | 1510 | 1.50 | 2.05 | 0.151 |
| | 1175 | 5.14 | 2.04 | 0.104 |
| | 1200 | 4.69 | 2.02 | 0.119 |
| | 1250 | 4.72 | 2.04 | 0.112 |
| 10.2 | 1325 | 4.53 | 2.06 | 0.116 |
| | 1450 | 2.20 | 1.98 | 0.147 |
| | 1475 | 1.68 | 1.95 | 0.179 |
| | 1500 | 0.90 | 1.99 | 0.195 |



Figure 3 – Pore size distribution of calcined coke. (a) laboratory calcination, (b) rotary kiln, (c) laboratory, 55% of sulphur removed.

commences to decrease substantially. Figure II illustrates the change in porosity expressed in volume percent with calcination temperature for the two types of coke.
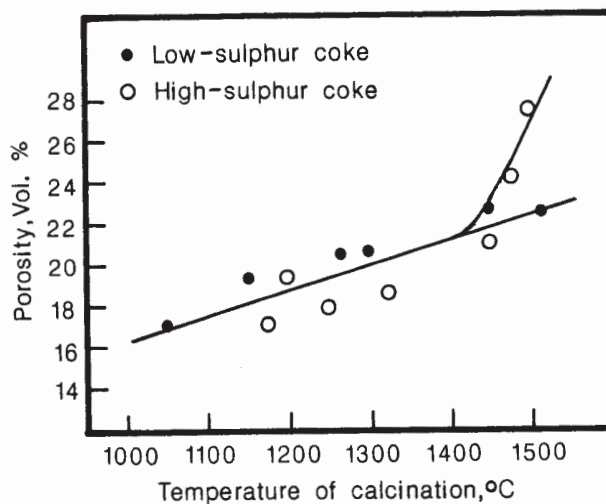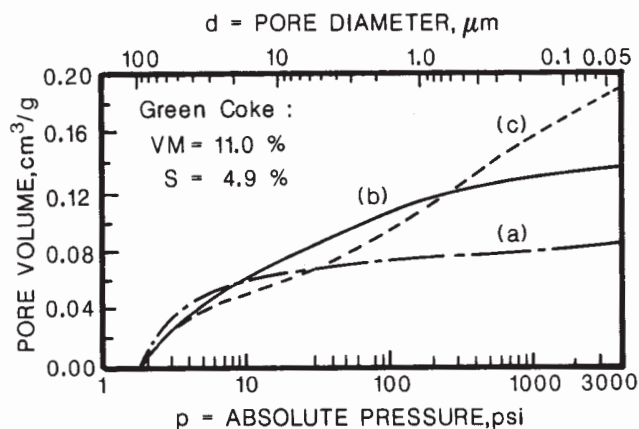
(operating limit 4,220 kg/cm$^2$ or 60,000 psi) revealed that the desulphurization-induced porosity is in the range of 0.5 to 0.02 μm (diameter) pore sizes.* Table IV gives typical results.

Table IV. Effect of Desulphurization on Coke Porosity and Pore Size Distribution (Green Coke: VM = 12.0 wt%, Sulphur = 5.0 wt%)

| Porosity, vol% | Calcined | Desulphurized** |
|---|---|---|
| 100 to 10 μm diameter | 13.4 | 9.3 |
| 10 to 0.5 μm diameter | 9.4 | 12.5 |
| 0.5 to 0.02 μm diameter | 2.2 | 11.2 |
| Total | 25.0 | 33.0 |

** Approximately 50% of sulphur removed

The effect of volatile-matter-induced coke porosity (typically 100 to 0.5 μm pore diameter range) and of desulphurization-induced porosity (presence of 0.5 to 0.02 μm diameter pores) on Soderberg-type bench-scale anodes was next investigated. The results are given in Tables V and VI, respectively. Target paste elongation was 60% in both cases.

Inspection of data in the two tables reveals a striking difference in Soderberg paste binder requirement. In the case of devolatilization (Table V) pitch binder requirement increases at a rate of 0.4 wt% per 1 vol% porosity increase, while in the case of desulphurization (Table VI) the rate of increase is twice as high, 0.9 wt% per 1 vol% porosity, for the same paste elongation. Although the rates of heating were not identical in the two cases as indicated by the different porosity levels, this factor is not expected to influence binder requirement. It was shown in earlier work[1] that the latter can be expressed by the equation y = 17.4 + 0.45× independently of heating rate as long as thermal desulphurization does not occur. In the equation y represents wt% binder requirement and × is vol% porosity. The higher binder requirement for the desulphurized coke is attributed to the high surface area pore structure[4] and to the opening-up of closed porosity present in this coke[1] when it is ground to the anode aggregate granulometry.

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* This can be compared with a range of 0.1 to 0.015 μm obtained by other investigators under different experimental conditions.[4,5]

Table V. Effect of Volatile-Matter-Induced Coke Porosity on Bench Scale Anodes (Green Coke Sulphur Content: 1.2wt%)

| | | |
|---|---|---|
| Green coke VM content wt% | 9.6 | 23.0 |
| Calcined coke porosity, vol% | 16.1 | 29.0 |

Test Electrodes

| | | |
|---|---|---|
| Binder content wt% | 28.0 | 33.7 |
| Green apparent density g/cm$^3$ | 1.64 | 1.49 |
| Baked apparent density g/cm$^3$ | 1.45 | 1.29 |
| Compressive strength kg/cm$^2$ | 315 | 254 |
| Electric resistivity μΩm | 62 | 81 |
| Anode consumption %+ | 124.1 | 125.5 |

+ Percentage of that corresponding to formation of $CO_2$, (0.112 kg/kAh).

Table VI. Effect of Desulphurization-Induced Coke Porosity on Bench Scale Anodes (Green Coke Volatile Matter Content: 10.0 wt%)

| | | |
|---|---|---|
| Calcined coke S content wt% | 4.1 | 1.2 |
| Calcined coke porosity vol% | 29.6 | 38.2 |

Test electrodes

| | | |
|---|---|---|
| Binder content wt% | 30.1 | 38.0 |
| Green apparent density g/cm$^3$ | 1.63 | 1.51 |
| Baked apparent density g/cm$^3$ | 1.47 | 1.39 |
| Compressive strength kg/cm$^2$ | 296 | 302 |
| Electric resistivity μΩm | 66 | 59 |
| Anode consumption % | 119.6 | 122.0 |

The adverse effect of coke porosity on green paste and baked anode apparent density is evident in Tables V and VI. Concerning other properties of the baked anodes, lower strength and higher electric resistivity are indicated for the high-volatile coke, while there is no difference in these properties in the case of desulphurized coke. The relatively small increase in laboratory baked anode consumption with increased filler coke porosity is considered only moderately significant in both cases.

CONCLUSIONS

The nature of coke precursor and maximum temperature of calcination have a significant, but relatively small effect on filler coke porosity. Green coke volatile matter content, heating rate during calcination and sulphur removal at elevated calcination temperatures cause far more significant increases in coke porosity. From a practical point of view, at calcination temperatures normally used in rotary kilns for anode filler cokes, the most important parameter is green coke volatile matter content, causing an increase of 1 vol% porosity per 1 wt% increase in volatiles. In turn, 1 vol% increase in coke porosity calls

for an increase of 0.4 wt% in Soderberg paste binder requirement. A significant decrease in apparent density and compressive strength and a significant increase in electric resistivity of bench scale anodes were observed when filler coke porosity increased from 16 to 29 vol% due to increased volatile matter content in the green coke.

### REFERENCES

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