The Use of Gasification Pitch and Coal Tar Pitch in Carbon Anodes

Uthaiporn Suriyapraphadilok, Colin Jennis-McGroarty, Adam Zel, and John M. Andresen

The Energy Institute
Pennsylvania State University
407 Academic Activity Building
University Park, PA 16802

Introduction

Carbon anodes are manufactured from calcined petroleum coke, butt fillers and coal tar pitch[1]. Since the demand of the coal tar pitch in the aluminum industry accounts for about 75% of the pitch market and the production of coal tars is rapidly decreasing in the United States as well as throughout the world, the development of alternative binders were considered in this work. Standard binder pitches are obtained from coal tars that are the by-product of bituminous coal coking process used to make coke for blast furnaces in iron production. Coal tars are then distilled to produce distillate products and a residue that is coal tar pitch. Coal tar pitch is mixed with calcined petroleum coke, and recycled anode butts. Petroleum coke is the by-product from the delayed coker in a refinery. Delay coking is a severe thermal cracking process of heavy feedstocks such as vacuum residue. The residue is converted into valuable light products and a by-product petroleum coke. This green coke is then calcined, i.e. heated to about 1250°C, in an inert atmosphere to remove all volatile matters. The mix of binder, filler and some additives are heated to about 50°C above the softening point of the pitch, typically 160°C. This temperature is sufficient to enable the pitch to wet the carbon particles.[3] The mix is then either extruded, vibrated or pressed to form a green anode. The wetting of coke by pitch is very important to the anode property. The pitch has to flow over the coke surface and has to enter into the surface porosity to generate a cohesive paste. Quinoline insolubles or QI play an important role in filling the spaces between petroleum and recycled anode coke particles on which the pitch is supported and prevent the pitch from fully penetrating the pores of the coke particle.[3] It is generally accepted that pitches with up to 15 %wt QI yield better anodes.[4]

The demand of the coal tar pitch in the aluminum industry is accounted for about 3/4 of the pitch market.[5] However, the production of coal tars is rapidly decreasing in the United States as well as throughout the world.[6] Therefore, the development of alternative binders from coal gasification pitches are considered in this work. Gasification pitches are distilled by-product tars produced from the coal gasification process. Since gasification pitches have low QI, it is of interest to mix the gasification pitch with the higher QI coal tar pitch. This would give a flexibility and sustainability to the development of the anode production in the future. The optimum use of pitches and coke is studied in this work to obtain the maximum baked density of the anodes.

Experimental

Materials. There are two types of pitch used in this study: coal tar pitch (CTP) and gasification pitch (GP). Two gasification pitch were used, namely GP 1 and GP 2 with softening points close to a standard coal tar binder pitch.

Petroleum coke and recycled anode butts were crushed and aggregated into three different: (i) Fines: >200 Tyler mesh size; (ii) Intermediate: 60-200 Tyler mesh size; and (iii) Coarse: <60 Tyler mesh size

Optimum Composition. The optimum size distribution of the aggregate (filler) was first determined. Laboratory-scale anodes were made at different size distributions using petroleum coke by keeping the ratio of pitch and coke constant. After the optimum size distribution of the aggregate had been obtained, this distribution was fixed and the amount of binder was varied to optimize the final anode properties.

Mixing and Forming. The aggregate fillers and binders, which weigh about 15 grams in total, were mixed at about 160°C. The CARVER cylindrical mold with an inside diameter of 28.58 mm is preheated to 110-120°C. The hot mix is placed into the mold and rapidly pressed at 9,000 psi for 3 minutes. The final green anode is cylindrical in shape with typically 28.60 mm. in diameter and 13.00-14.00 mm in height.

Baking. The green anodes are baked with a low heating rate to about 1075°C over a period of 5-6 days prior to cooling. The temperature profile is 25°C/hr from 25°C to 575°C and 3.5°C/hr from 575 to 1075°C. The anodes are baked between temperature of 950 and 1075°C for 6 hours and are cooled down in the furnace.

Apparent Density. The apparent densities of both green and baked anodes are calculated using the diameter and height measurement. The amount of pitch loss after baking is calculated by assuming that all the weight loss is resulting from the pyrolysis of pitch. Finally, the volume change of the baked anodes relative to the green ones are calculated.

Results and Discussion

Size Distribution. The optimum size distribution of the aggregate was obtained experimentally. The ratio of fines:intermediates:coarse was 40:35:25. This ratio was held constantly for all anodes studied in this work.

Optimum Pitch Content. **Figure 1** shows the apparent densities of green anodes at various percentages of pitches. The ratio of Butt:Coke is about 3:5 for all compositions. It is shown that all pitches used here represented similar trends where GP 1 gives the best densities and followed by GP 2 and CTP, respectively.

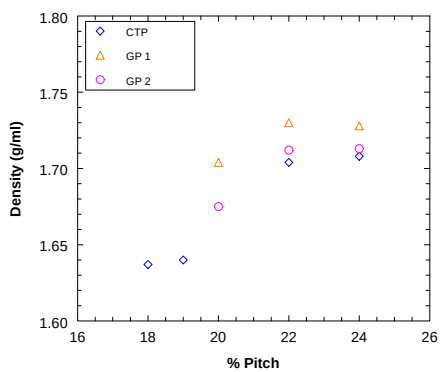

Figure 1. Apparent densities of green anodes at various percentages of pitches. Three different types of pitches are demonstrated: CTP, GP 1 and GP 2

The optimum percentage of pitch for the laboratory setup was found to be 22% somewhat higher than that used by the industry. The pitch concentration of laboratory mixes was a few percentages higher than in a commercial mix due to the finer size particles of the filler for the smaller diameter anodes (< 2 inch) used in this study.[3] The results indicate that the gasification pitch forms a denser green anode than that obtained by a standard coal tar binder pitch. Presumably, the gasification pitch has better wetting ability towards the coke filler particles and is able to penetrate further into the pores of the coke.

Pitch Mixture. Gasification pitch and coal tar pitch were mixed at various percentages while maintaining the total pitch content of 22%. Butt and coke compositions and their size distribution were also held the same as above. Figures 2 and 3 show the apparent densities of the green and baked anodes from the CTP + GP 1 and CTP + GP 2 mixtures, respectively.

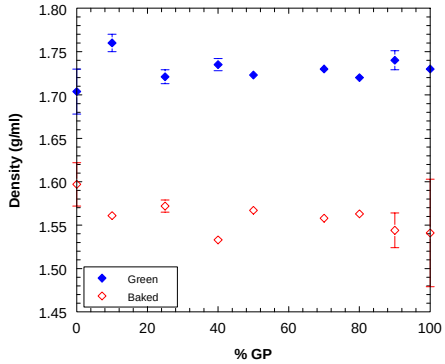

Figure 2. Apparent densities of green and baked anodes: 22% Pitch (CTP and GP 1); 29% Butt; and 49% Coke. The error bars show the standard deviations of each experimental set.

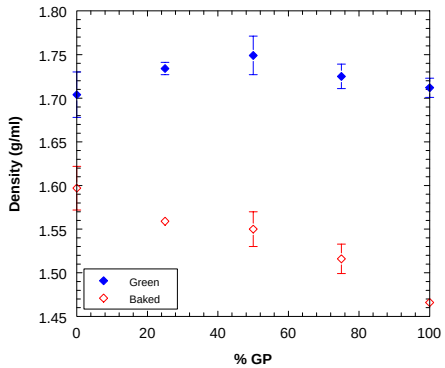

Figure 3. Apparent densities of green and baked anodes: 22% Pitch (CTP and GP 2); 29% Butt; and 49% Coke. The error bars show the standard deviations of each experimental set.

For both mixtures the addition of gasification pitch give an improvement in the apparent densities of the green anodes. For GP1 the green apparent density increases from 1.70 g/cm^3 for SCTP only to about 1.74 g/cm^3 for the GP1 only (Figure 2). Similar results were observed for GP2 (Figure 2). However, this trend does not keep up for the densities after baking. For the GP1 there is a slight reduction in the baked density from 1.60 g/cm^3 for the SCTP to 1.55 g/cm^3 for the GP1 only. For the GP2 there is a significant reduction in the baked density from 1.60 g/cm^3 for the SCTP to 1.46 g/cm^3 for the GP1 only.

The measurements indicate that the main factors for the reduction in baked density is due to increased loss of binder and increased volume during baking as shown in Table 1. The pitch loss was defined as reduction in anode weight over initial pitch content (22%) since the weight loss of the coke material can be neglected. For the baked anodes with increasing GP content the pitch loss increases from 27.9% for SCTP to 46.2% for GP1 only and 53.2% for GP2 only. Also, for most of the GP mixtures a increase in the volume was observed that was not the case for the SCTP (Table 1).

The reason of the high loss of pitch content in the anodes with higher gasification pitch concentration may result from the lack of QI as well as difference in molecular composition. The QI plays a very important role in how pitches perform excellent binder functions, i.e. wetting and penetrating petroleum coke particles during mixing and forming, and bridging between pitch-coke particles during baking.[3] Although the importance of QI is well established, the optimum amount of QI in binder pitch is still not clear.[3] Because pure gasification pitch gives higher apparent green density, it can be hypothesized that this type of pitch wet and penetrate petroleum coke better than SCTP. However, gasification pitches need to be optimized in terms of pitch loss prior to commercial interest. The results indicate that reducing the gasification pitch loss below 40% could make a binder pitch that can compete with SCTP in terms of density.

Table 1. Volume Changes and Amount of Pitch Losses of Baked Anodes: CTP + GP 1 and CTP + GP 2 pitch mixtures.

CTP + GP 1			CTP + GP 2		
% GP	$\frac{\text{Baked Volume}}{\text{Green Volume}} \times 100\%$	% Pitch Loss*	% GP	$\frac{\text{Baked Volume}}{\text{Green Volume}} \times 100\%$	% Pitch Loss*
100	100.65	46.18	100	102.4	53.2
90	102.60	41.33			
80	99.69	41.92			
70	102.21	35.56	75	101.5	48.3
50	102.11	31.65	50	103.5	37.2
40	103.33	33.33			
25	101.82	31.27	25	103.3	31.9
10	105.33	29.53			
0	100.02	27.91	0	100.0	27.9

* reduction in anode weight over initial pitch content

Conclusions

Anodes with pure gasification pitches gave higher apparent green densities than those with pure coal tar pitch. However, baked anodes with gasification pitches lost higher pitch content compared to the anodes with coal tar pitch. This effect was assigned to the effect of reduced QI with increasing gasification pitch content as well to structural differences between the pitches. It seemed that gasification pitch could wet and penetrate petroleum coke very well but it is poor remaining in the anode during baking. This resulted in a high loss of pitch content in baked anodes. The results indicate that reducing the gasification pitch loss below 40% could make a binder pitch that can compete with SCTP in terms of density.

Acknowledgement. The authors would like to thank Kopper Industries and.Sasol CarboTar for the coal tar pitch and gasification pitches, respectively, and Alcoa for the calcined petroleum coke and recycled carbon anode butt material.

References

1. Weng, T. L., and Vera, V. M. *Light Metals* **1984**, 1005-1013.
2. Gary, J. H. Petroleum Refining Technological and Economics; 4th ed.; Marcel Dekker, Inc: New York, 2001.
3. Gray, R. J., and Krupinski, K. C. In Introduction to Carbon Technologies; Marsh, H., Heintz, E. A., and Rodriguez-Reinoso, F., Ed.; Secretariado de Publicaciones, 1997, pp 329-424.
4. Grjotheim, K. a. W., B. J. In Aluminum Smelter Technology; 2nd ed.; Aluminum-Verlag: Dusseldorf, 1988, pp 75-118.
5. CRU International, Carbon Products – Aluminum Raw Materials, London, U.K., May 2002.
6. Rusinko, F., Andresen, J.M. and Adams, A., Ch. 13 in Great Lakes Carbon Corp. 6th Carbon Conf., Sept. 26-28, 2000, Houston, USA.