

REDUCTION OF PUFFING BY NITROGEN COMPOUNDS IN COAL-BASED NEEDLE COKE PRECURSORS FOR ELECTRODE GRAPHITE

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Introduction

Graphite electrodes are used for the generation of heat in the electric arc furnace in the melting and recycling of scrap steel. During the graphite electrode fabrication process, binder pitch and calcined needle coke filler are mixed and extruded into cylinders. The article is baked, impregnated with pitch and rebaked, then graphitized to produce the final product.

The vast majority of the needle coke is derived from petroleum sources through the delayed coking process. Globally, about one million metric tons of needle coke is required as the filler material in which only about 15 % is supplied by coal-based precursors. Coal-tar distillates recovered from metallurgical coke making could, after removal of particulate matter, be used to produce high-quality needle coke with exceptional low coefficient of thermal expansion, a major indicator of electrode graphite quality. Nevertheless, coal-based needle cokes can exhibit unacceptably high puffing behavior in the graphite manufacturing process.

Puffing is an irreversible expansion that damages the electrode during graphitization and is partially linked to sulfur and nitrogen contents in the calcined coke. Generally, calcined coal-based cokes contain more nitrogen than calcined petroleum cokes. Herein we report on our efforts to remove nitrogen compounds through adsorption from needle coke feedstocks prior to conversion into coke and its effects on graphite properties.

Experimental

Two disparate raw materials were chosen for treating with adsorbent: decanted oil and heavy coal-tar distillate. Both of these heavy oils have been shown to produce high-quality needle cokes. The adsorbent was a commercial activated carbon, which was dried in a vacuum at elevated temperature before use.

Preliminary experiments were conducted by contacting the decanted oil and heavy coal-tar distillate with the activated carbon. The slurry was stirred for several hours at elevated temperature followed by removal of the activated carbon. Nitrogen content before and after adsorption was determined by an Antek analyzer.

The decanted oil and heavy coal-tar distillate were thick, viscous fluids at room temperature and were judged not to have sufficient fluidity for contacting with the adsorbent even at elevated temperature. To reduce the viscosity, increase mobility, and improve blending with the adsorbent, the

decanted oil and heavy coal-tar distillate were diluted with a solvent before contacting with the activated carbon. The mixture was conveyed to and sealed in a vessel that was gently stirred above room temperature and slight pressure for several hours. The mixture was cooled and centrifuged to remove the adsorbent. The mixture was then filtered through filter paper. The filtrate was collected and heated slightly to evaporate the toluene or until constant weight was achieved. For the heavy coal-tar distillate a portion of the filtrate from the first adsorption was subjected to a second adsorption. Thus, materials from one-stage and two-stage nitrogen removal of the heavy coal-tar distillate were carbonized and converted into green coke.

The treated and untreated feedstocks were converted into green coke in a pilot-scale coker under conditions consistent with delayed coking. A known quantity of feedstock was placed in a stainless steel capsule and sealed loosely with a cover. The capsule was placed in the pilot-scale coker, a cover installed and bolted, and the system purged of air with flowing nitrogen. A computer system and associated software controlled heating rate, soak temperature, and pressure.

After the coking cycle, the coker was cooled and vented to atmospheric pressure. The capsule with the carbonized product was weighed and coke yield calculated based on the initial and final masses. The cokes were calcined, milled into flour, and hot-mixed with a conventional coal-tar binder pitch. The mix was extruded into 19-mm diameter rods, which were baked, and then graphitized. The bulk density (ASTM C-559) and specific resistance (ASTM C-611) were measured on the graphitized rod. The coefficient of thermal expansion was determined on the graphitized rod using a capacitance method as reported elsewhere [1]. Puffing behavior was determined on calcined cokes using a proprietary test developed by GrafTech.

Results and Discussion

In Table 1 elemental analysis shows that the heavy coal-tar distillate is more aromatic and contains more sulfur and more than twice the nitrogen as the decanted oil.

Table 1. Elemental Analysis of Needle Coke Feedstocks.

Feedstock	H wt%	C wt%	S wt%	N wt%	H/C Atomic
Heavy Coal-Tar Distillate	5.81	92.72	0.65	1.11	0.75
Decanted Oil	7.86	91.68	0.48	0.44	1.02

Figure 1 shows the reduction in nitrogen content for the decanted oil and heavy coal-tar distillate following contact with activated carbon above room temperature. The concentration of nitrogen decreased for the decanted oil from 1,990 to 1,707 ppm, an 18.8 % reduction. The concentration of nitrogen for the heavy coal-tar distillate decreased from 11,078 to 8,141 ppm, a 26.5 % reduction.

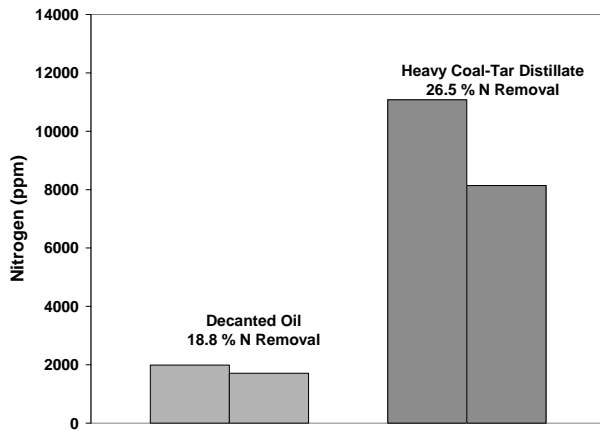


Fig. 1 Nitrogen removal from decanted oil and heavy coal-tar distillate after contacting with activated carbon.

The feedstocks that were diluted with the solvent and contacted with the activated were carbonized and the yields of pilot-scale coking of these materials are shown in Table 2. The yield of green coke appears to be affected by treatment with activated carbon and could be attributed to the adsorption of feedstock onto the surface of the activated carbon.

Table 2. Green Coke Yields from Pilot-Scale Coking.

Feedstock	Number Adsorptions	Green Coke Yield wt%
Heavy Coal-Tar Distillate	0	74.0
Heavy Coal-Tar Distillate	1	55.9
Heavy Coal-Tar Distillate	2	61.5
Decanted Oil	0	47.6
Decanted Oil	1	32.5

Following pilot-scale coking of the feedstocks, the green cokes were calcined and nitrogen content of the calcined cokes determined. The relative puffing was measured using GrafTech's proprietary method. The results are provided in Table 3 where it can be seen that the relative puffing for the heavy coal-tar distillate without nitrogen removal was 3.7. After one-stage and two-stage adsorption the relative puffing was reduced to 2.1 and 1.8, respectively. The one-stage adsorption was more effective reducing puffing than two-stage adsorption. On the other hand, for the decanted oil, one-stage adsorption had minimal affect on reducing puffing probably because the nitrogen content was relatively low to begin with.

Table 3. Characteristics of Calcined Cokes: Heavy Coal-Tar Distillate (HCTD) and Decanted Oil (DO).

Feedstock	Number Adsorptions	Calcined Coke Yield wt%	N Content wt%	Relative Puffing
HCTD	0	90.3	NA	3.7
HCTD	1	94.0	0.67	2.1
HCTD	2	91.6	0.51	1.8
DO	0	91.3	0.21	1.0
DO	1	94.7	0.18	1.0

The results of characterization of the 19-mm diameter graphite test specimens are presented in Table 4. The coefficient of thermal expansion (CTE) for the heavy coal-tar distillate graphite following one-stage and two-stage adsorption (0.074 and $0.128 \cdot 10^{-6}/^{\circ}\text{C}$, respectively) is considerably lower than that of the decanted oil with or without nitrogen removal (0.164 to $0.250 \cdot 10^{-6}/^{\circ}\text{C}$, respectively).

Table 4. Properties of Graphite Test Specimens.

Feedstock	Number Adsorptions	CTE $10^{-6}/^{\circ}\text{C}$	Density (g/cm^3)	Specific Resistance ($\mu\Omega\text{-m}$)
HCTD	0	0.286	1.440	9.66
HCTD	1	0.074	1.466	8.92
HCTD	2	0.128	1.443	9.56
DO	0	0.250	1.460	8.88
DO	1	0.164	1.481	8.24

Conclusions

Coal-based graphite can have significantly lower coefficient of thermal expansion than graphite from decanted oil. Although adsorption by activated carbon reduces nitrogen content in heavy coal-tar distillate, the puffing characteristic is still considered too high.

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References

- [1] Wagoner G, Sprogis, G, Proctor, DG. Capacitance Bridge Measurement of Thermal Expansion. Carbon 1986 Proceedings, Baden-Baden, 1986; 234-236.