COMPARATIVE STUDY ON CALCINATION OF LOCAL AND IMPORTED INDIAN PETROLEUM COKES[+]

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Abstract

This research involves procedure used for calcination by USING a laboratory shaft furnace at 500-1300 ˚C .This procedures is conducted to determine the suitable calcination temperature for petroleum coke. Two types of petroleum coke; local sponge and Indian needle petroleum coke are used to apply calcination process for 30 minutes to all specimens. The calcination process is achieved at a temperature of 1250 ˚C for the above two coke types to reach a product with 0.5 % volatile matter. This percent is acceptable within the national standard specification . The produced calcinide coke is a raw material for manufacturing carbon electrodes.

المستخلص

تضمن البحث إجراء عملية الكلسنة باستخدام فرن مختبري من النوع (shaft furnace) بدرجات حرارة من ٥٠٠ – ١٣٠٠ درجة مئوية لأستخراج درجة حرارة الكلسنة المناسبة للفحم النفطي. استخدم نوعين من الفحم النفطي، فحم اسفنجي محلي (sponge petroleum coke) وفحم ابري مستورد(needle petroleum coke) لغرض إجراء عملية الكلسنة ولمدة ٣٠ دقيقة لكافة العينات. تم الحصول على الكلسنة بدرجة حرارة ١٢٥٠ درجة مئوية لنوعي الفحم بدلالة الوصول الى نسبة ٠,٥% مواد متطايرة متبقية في النموذج بعد عملية الكلسنة.إن النسبة أعلاه مقبولة وهي ضمن النسبة القياسية العالمية .يستخدم هذا الفحم المكلسن كمادة أولية لتصنيع الأقطاب الكاربونية.

Introduction

Shortly after the discovery of crude oil in Pennsylvania, early "refineries" which boiled crude oil to recover kerosene produced the first petroleum coke in the 1960's. Before 1935, some petroleum coke was claimed in slot ovens similar to units using calicle coal. Attempts had been made to calicle petroleum coke (lump only) in vertical shaft furnace by passing hot combustion gases up through a moving bed of coke, [1,2].

A small amount of coke was claimed in electric furnaces, but this was an expensive process. A rotary furnace was started up in October 1935 becoming the first rotary furnace in the world to produce claimed petroleum coke, [3,4].

As the claimed petroleum coke was used in making anodes for the aluminum industry, new furnaces had been built from 1937 to 1943. The growth of the construction of the cooker part of the furnace was delayed from 1935 to 1975, also the growth of fuelling of petroleum coke

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calcinations continued until the early 1970's. Another development in 1950's that spurred the growth of petroleum coke claiming was the development of synthetic graphite from special kinds of petroleum coke called "needle coke". This special kind of petroleum coke could be produced by delaying cookers and being claimed for making graphite electrodes used in steel arc furnaces and as graphite quality improved and min-mills became more efficient in their use of graphite electrodes, the demand for claimed needle decreased in the late 1980's, [3].

Calcination of Petroleum Coke

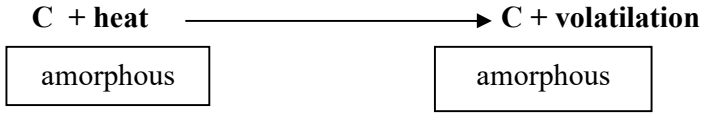
Petroleum coke is calcined (roasted at high temperatures, 1200 to 1350 ˚C) usually in a gas fired rotary furnace or rotary hearth [2, 3]. It is customary to calcine the coke by heating to high temperature in shaft calciners, rotary calciners or electric furnace (the last type of furnaces is used for some types of coke), [1], to remove moisture, drive off volatile matter, increase the density of the coke structure, improve physical properties and increase the electrical conductivity of the material. The result is a hard, dense carbon (calcined petroleum coke) with low hydrogen content and good electrical conductivity. These properties along with low metals and ash contents make calcined petroleum coke the best material currently available for making carbon anodes for smelting of alumina to aluminum [3,5,6].

Green raw filler materials may have a volatile content ranging from 5 to 15%. Hydrocarbons are removed and the coke shrinks in volume resulting in a density increase, the weight loss may be 25% or higher. If calcination is not done, the release of volatile and excessive shrinkage in the subsequent thermal operations cause cracked structure of the baked carbon body [3,7].

In the initial stages of calcination, the coke softens slightly and the latent crystallinity is disrupted, but as the process proceeds to higher temperature further polymerization, crystallization and cross-linking occur, and the number of aromatic rings per layer plane increases over that in the raw coke. A final temperature of 1250 ˚C is typical for a petroleum coke used in graphite manufacture. Calcination conditions have a significant effect on final graphite properties [3,8].

The optimum conditions will also vary somewhat for cokes from different crude sources, different calciner designs. The chemical reaction in calcination process is:

Calcination



The primary use of calcined petroleum coke is in making carbon anodes for the aluminum industry. Calcined petroleum coke is also used in making graphite electrodes for arc furnaces, titanium dioxide, polycarbonate plastics, steel (to increase carbon levels), carbon refractory bricks for blast furnace, baking media for anode baking furnaces and material for cathodic protection of pipelines, [1, 3].

Experimental

1- Types of Petroleum Coke

Two types of petroleum coke are used in our calcination process, all the tests on the two types of petroleum coke were done in Al-Basil Company. These types include the following:

1-Petroleum coke form Indian source whose properties are shown in table (1).

Table (1): Physical Characteristics of Particles size of needle Petroleum coke (Indian source)

Material	Characteristics	Material	Characteristics
Volatile	4.3 %	Ash content	0.45 %
Fixed carbon	93.94	Moisture	0.263 %
Sulfur content	1.05 %	Real density 25˚C g/cm^3	1.80

2-Petroleum coke from local source (Al-Gayara Refinery),where properties are shown in table (2).

Table (2): Physical Characteristics of Sponge Petroleum Coke (Al-Gayara refinery)

Material	Characteristics
Volatile content	8.2%
Fixed carbon	85.7%
Sulfur content	5.2 %
Ash content	0.34 %
Moisture	0.5 %
Real density 25 ˚C gm/cm^3	1.60

2- Calcination process

The process was done with two types of petroleum coke, the first is a needle type and the other is sponge type.

The following are the operation steps of the furnace for any type of coke:

1- The used petroleum coke was crashed by using a hammer type crasher and a sieve of about (12.5mm and less) particle size , this value is related to our local manufactured furnace and was found experimentally .
2- A (15 kg) of the crashed coke was weighted.
3- The discharge valve was closed and the coke was fed from the top of the furnace.
4- The thermocouple was seated in its place in the furnace.
5- The electricity was turned on for the blower and the electric panel to be ready to measure the temperature.
6- The main fuel valve and the burner fuel valve were turned on and the fuel was ignited.
7- The fuel ratio from the burner fuel valve was increased.
8- Heating up to 1300 ˚C was gradually continued by 100 ˚C/hr, after the furnace temperature reached 1250 ˚C the quantity of coke against the chamber room was held there for half an hour.
9- The discharge valve was opened in order to obtain (2 kg) of the coke.
10-The obtained coke was collected with ladle, which can hold (2 kg) when it is full with the coke.

11-The ladle and the coke were taken away from the bottom of the furnace and the coke was cooled with a light stream of water in order to reach 50˚C and less.
12- The coke was returned into the furnace by the tool.
13-After half an hour, steps (9-12) were repeated.
14-After half an hour, the calcined coke reached down and was collected by the tool, so in the last one hour, the calcined coke passed through the cooling zone in the first third part of the furnace to decrease its high temperature to 500 ˚C to become easy to collect.
15-Sample of calcined coke (or a sample of coke in any temperature), was taken after cooling the coke to 50˚C or less.
16-The remaining coke was returned to the furnace.
17- After all the operation was done, the furnace was turned off by closing the burner only gradually to cool the furnace to 500˚C and less by repeating steps (9-12).
18- The electricity of the panel and blower was turned off.
19- The charge was downloaded and weighted with the samples in the next day.

3- Calcination process tests

Table (3) shows two types of coke samples in different temperatures.

Table (3): Samples taken from the two types of petroleum coke

A- Petroleum Coke (foreign source)			**B-Petroleum Coke (local source)**		
Seq.	Sample symbol	Temperature	Seq.	Sample symbol	Temperature
1	A1	500˚C	1	B1	500˚C
2	A2	750 ˚C	2	B2	750 ˚C
3	A3	1000˚C	3	B3	1000˚C
4	A4	1050˚C	4	B4	1150˚C
5	A5	1150 ˚C	5	B5	1250 ˚C
6	A6	1250 ˚C	6	B6	1296 ˚C
7	A7	1300˚C	7	B7	1300˚C

All the tests that were carried out on the raw materials were also done for the product materials after calcination. That includes moisture test, volatile, sulfur and ash tests. Electrical resistivity test was carried out to determine the degree of calcination.This is done under pressure of 150 psi loaded by using ceramic cylinder tube packed with particle size 4.33*65 mesh. This particle size was obtained by hand grinding and sieving. Silver-platted brass rams was used on either ends of cylinders. Petroleum coke actually changes from an insulating material into a conductor upon calcination. All these tests were carried out in Al-BASIL Company.

Results

Experiment results are as followis :

1- Results of Calcination of Petroleum Cokes

Calcination was applied at 1250 ˚C in the shaft furnace for 30 minutes. The results of the tests before and after calcination for the two types of petroleum coke that were calcined in our local manufactured shaft furnace are shown in tables (4) and (5). The properties of petroleum coke from foreign source are given in table (4) .

Table (4): The properties of needle petroleum coke (Indian source)

Materials	Characteristics	
	Before calcination	After calcination
Volatile	4.3 %	0.5%
Fixed carbon	92.74%	95.54%
Sulfur content	1.05 %	1.08 %
Ash content	0.45 %	0.39 %
Moisture	0.263 %	0.171 %
Real density 25 ˚C g/cm^3	1.80	2.13
Others (nickel, iron, etc.)	1.2	2.319

Table (5): The properties of sponge petroleum coke (local source)

Materials	Characteristics	
	Before calcination	After calcination
Volatile content	8.2%	0.5%
Fixed carbon	85.7%	94.7%
Sulfur content	5.2%	3.7%
Ash content	0.34%	0.57%
Real density 25 ˚C	1.6%	1.8%
Bulk density gm/cm^3	1.56	2.07
Others	0.56	0.53

Discussion

1- Effect of Heat on Calcination

It was found that there is no effect of heat on calcination process below 1000 ˚C. Heat has more effect in temperature range of 1000-1250 ˚C . It was found experimentally that 30 minute is the proper time to reach the ratio of 0.5% of the remaining volatile matter which is necessary to ensure that the calcination process has been completed .The effect of temperature and calcination time on the change in volatile matter between 500-1250 ˚C for the two types of cokes is shown in Figure (1). Kirk [1, 2]and spiropoules [9] had reached similar conclusion and he indicated that devolatilization occurs mostly at 1000-1250 ˚C. Ellis et. al. [3] said that devolatilization occurs mostly at 500-1000 ˚C in calcining zone and further desulfurization and coke shrinkage (densification) takes place in calcined coke zone at 1200-1400 C.

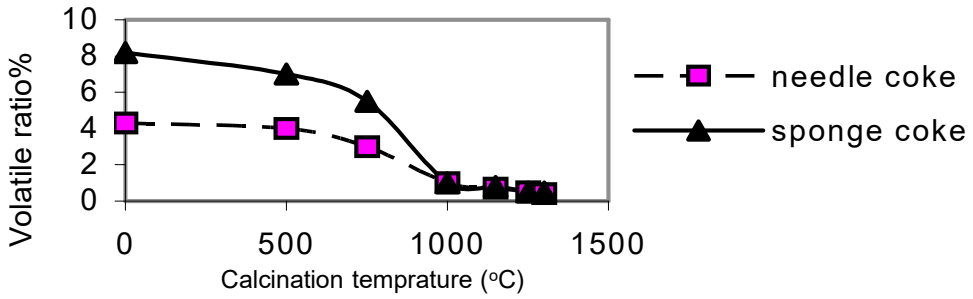


Fig. (1): The effect of temperature on the volatile matter for the two Types of petroleum coke

2- Sulfur Ratio in the Coke

Calcination to 1250 ˚C for several hours produces gases and vapors. From these gases, sulfur can be recognized by its yellow- green vapors and strong smell. It is clear that the more sulfur content in the coke, the more sulfur gases are vaporized. The Iraqi coke contains sulfur as shown in table (5), so it is not suitable for making carbon electrodes that are used in electrical arc furnaces. The needle petroleum coke (Indian source) contains about 1% as shown in table (4).

This type of coke is suitable for making carbon electrodes. The typical sulfur content for a coke suitable for making carbon electrodes is 1% or less. The result agrees with the work of Ellis et. al [3], who indicated that sulfur must not be more than 1% in the coke and also agrees with Kirk [1], and Christopheret et. al. [10] who illustrated that the coke before calcination process must have 1% sulfur ratio or less.

3- Loss in Coke's Weight

As a result of calcination process, it is clear that there is some loss in the weight of the coke, which can be illustrated as follows:

A- For local source coke
1- A weight loss in volatile matters by 8% from the weight.
2-Loss in weight due to the reduction in sulfur content by 1.5%.
3- Loss in weight due to reduction in humidity by 0.5%.
4- Loss in weight due to oxidation process by 20-25% .

Therefore, the total losses in coke weight in calcination process for Iraqi coke reach 1:3 of the original weight. This weight loss is calculated as a result of solid and volatile materials.

This is called the shrinkage in coke which happens due to calcination process. This causes the increase in carbon ratio, the electrical resistivity, and the real density for the coke to be a suitable material for carbon and graphite electrode production.

B- For Indian source coke
1- Loss in volatile by 3.6% from the weight.
2- Loss in weight due to the reduction in humidity by 0.1%.
3- Loss in weight due to oxidation process by 15%.

So, the total loss in coke weight reaches 1:5 of the original weight. This result for the two types of coke is compatible with the principles of calcination procedures. The loss in the local coke (sponge type) results agrees with that of Kirk [1,2] who indicated that the loss in the coke in shaft furnace is between 25-30%.

The lower ratio in the Indian coke (needle type) is due to its type and specifications which contain some degree of calcination in the coke before its delivery to the factory .

4- Coke Size

During calcination process, it was found for our local manufactured furnace that best coke size is 12.5 mm and less with a ratio of

12.5 mm –5 mm	33.5%
less than 5 mm	66.5%

This is related to the dimensions of the furnace. If all the particle sizes are with 12.5 mm diameter, this will cause over burning, and if we use all the particle sizes with less than 5 mm, this will not cause draft on the coke column .

5- Metals in the Raw Coke

Metals in the raw coke normally increase upon calcination process due to the weight loss from evolution of the volatile matter, hydrogen, sulfur, and nitrogen. This result agrees with works of Kirk [1,2] and Paul [3].

Conclusions

From this paper, the following conclusions are drawn:

1-Calcination temperature used is 1250 ˚C.
2-The best calcinations results were observed for Indian coke source which indicates the best filler material is needle type petroleum coke.
3-Sulfur ratio in the filler material for making carbon electrodes should be about1%.
4-Volatile matter after calcination is 0.5% and less.

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