APPLICATION OF ELECTRODES IN FERRO ALLOY FURNACES

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Introduction

Ferro-alloy furnaces are electrothermal in nature where heat is produced by supplying electric current through the carbonaceous electrodes to the working space of the furnace. The properties necessary for the satisfactory performance of an electrothermal electrode at elevated temperatures are (1) high electrical conductivity, (2) slow rate of oxidation (high apparent density), (3) high mechanical strength (particles well bonded together i.e. suitable aggregate having thoroughly mixed) and (4) low heat conductivity. Two types of electrodes are generally in use i.e. carbon electrodes and graphite. Carbon electrode again are of two kinds i.e. (i) soderberg electrodes of continuous and self baking type and (ii) prebaked carbon electrodes. Continuous self-baking electrodes are widely used at present. Carbon electrodes are very rarely used in the ferro-alloy industry while graphitised electrodes are used in the production of decarburised ferro-chrome, metallic manganese and crystal silicon in submerged arc furnaces (SAF). Graphite electrode find place in submerged arc furnaces of such capacities where the electrode diameter is limited to 28". The electrode size for a submerged arc furnace is selected on the current density for the operation. Economics has dictated the highest possible current density to keep capital cost to a minimum. Selecting electrodes by current density may be satisfactory, since it tends to provide good electrode performance. Ferro-alloy furnaces which are to a large extent continuously operating units need high current (upto 50000 amperes in three-phase). For the supply of high current, electrodes of a large diameter (20" to 55") are required. But the difficulties of producing quality electrodes grow with their diameter. In the ferro-alloy industry, therefore continuous self leaking electrodes are used exclusively; in the heated up condition they differ very little in their physical properties from the usual carbon electrodes. The self-baking electrodes are cheaper than the usual pre-baked carbon electrodes. They can be made on the spot and the expense in setting up a section to produce the electrode mixture is small compared with that of a carbon electrode factory. Moreover, no fuel is needed to heat the electrodes and there is no need of giant cranes to transport and screw the electrodes.

The manufacturing process of both the type of electrodes is similar which comprises of drying, crushing and grinding of the base raw materials and then mixing with a suitable binder. The paste thus formed, in the case of prebaked electrodes is extruded in the cylindrical form and baked by calcining at about 1200^{o} -1300^{o}C in reduced atmosphere. During the process a dense, fully shrunk product is obtained to give prebaked carbon electrodes. In case of continuous or self baking electrodes, the green paste is either directly placed into the furnace or moulded and kept in storage for use when needed. For graphitised electrodes, the prebaked carbon electrodes after tar impregnation and rebaking, graphitised by heating in the temperature range 2400-2600^{o}C in reducing atmosphere.

The present estimated annual requirement of soderberg paste in India is about 25,000 to 35,000 tonnes. The average consumptions (kgs) of carbon, and soderberg electrodes for various ferro-alloy production (per tonne) are given below:

Alloy	Carbon electrode	Soderberg electrode
Ferro-silicon	20-65	25-80
Ferro-chrome	30-60	40-70
Ferro-manganese	15-30	20-35
Pig iron	9-14	15-20

Production of Electrodes

The production process comprises of (i) selection of raw materials, (ii) processing and mixing of the raw materials, (iii) forming, (iv) baking

Raw materials:- In the production of electrodes, the selection of raw materials is most important. The raw materials comprise of (a) dry aggregate and (b) binder.

a) Dry aggregate:- The performance of the electrode is dependent on the proper selection of dry aggregate.

Ash content within reasonable limits i.e. 6-8% (so as not to affect the mechanical properties) is tolerable. The following base-materials are generally used as dry aggregate:

1. Calcined anthracite coal
2. Calcined petroleum coke
3. Pitch coke
4. Metallurgical coke

Amongst all these materials, calcined anthracite coal is the most desired one as it gives a paste of good mechanical strength. Generally calcined anthracite coal forms the coarse fraction of the mix (as it is massive in structure and less porous) and petroleum coke, pitch coke or metallurgical coke form the finer fractions. In India, as the availability of anthracite being almost nil, calcined petroleum coke is also used in the coarser fraction although it should not be used for such fraction because of its high porosity and thereby providing less strength and inferior properties. At National Metallurgical Laboratory, a substitute of calcined anthracite coal has been developed and named as dense carbon aggregate (DCA). It is prepared from raw petroleum coke, low ash coke and a medium soft pitch binder. It gives properties comparable with calcined anthracite. The properties of the various base materials used for electrode making are given in Table I.

Binder:- Binder also plays a very important role in the production of electrodes. The binder present in the mix after carbonization firmly cements the coke particles acting as a bridge between them and finally making the electrode mechanically strong and good conductor to electricity. In general, the coal-tar pitches are preferred as they have good binding and other properties. The main parameters that control the use of a binder in an electrode mix are (a) quality, (b) quantity

Quality of a binder mainly depends on:

i) Softening pint
ii) Coking value
iii) Coking reactions of the binder
iv) Percentage loss on distillation at low temperature
v) Free carbon and soluble resins

Softening point

The softening point of a pitch as determined by well known tests such as the Kraemer and Sarnow (K&S) or the Ring and Ball (R&B) test, is a convenient and suitable value for expressing the viscosity of the pitch which in turn controls the workability/flowability of the carbonaceous mix. Although better quality of paste is obtained by using pitch of higher softening point, medium hard pitch of softening point R&B 75-90^{o}C is preferred while considering good flowability.

Coking value

Pitches for electrode should have a high yield of coke per unit volume. Pitches from coke oven tars are most suitable as they contain less volatile oils and more carbon than the other types of pitches.

In continuous electrodes, the paste during its baking in situ, expands while loosing its plasticity and finally shrinks. This is mostly controlled by the reactions taking place in the binder in the temperature range 300-900^{o}C and making the baked mass porous to a variable extent depending on the quality of the pitch.

Loss on distillation

Presence of oils in the pitch which are distilled below 360^{o}C control the swelling of the paste while baking and finally the porosity in the binder coke. A high temperature pitch containing less of the volatile oils causes less swelling to the paste and thereby less porosity.

Free carbon and soluble resins

Free carbon which is the carbonaceous constituent of pitch, insoluble in benzene or toluene also plays a very important role in the performance of the electrode. The free-carbon is considered as high molecular weight nuclei surrounded by layers of lower-molecular weight compounds. It is mostly of colloidal dimensions and is partly soluble in solvents like pyridine and quinine, capable of forming a colloidal solution. The portion of the free-carbon which is soluble in pyridine/quinoline is responsible for giving binding strength to the baked product. In addition to free carbon, there are resins in pitch which are soluble in benzene or toluene but insoluble in light petroleum and are responsible for giving wetting and adhesion properties of the binder towards the grist particles and finally binding the particles together to form a strong compact. Some properties of the binders are given in Table II.

Quantity of Binder

The quantity of binder depends upon the raw material, the granulometry of the dry aggregate and the type of the electrode for which the mix is used. An extensive study has carried out at NML on this. In the manufacture of extruded electrode for carbon/graphite products, around 15 parts by weight of the binder for every 100 parts of the coke grist gives the maximum density whereas for the soderberg paste, the binder quantity varies from 20 to 26 parts for every 100 parts of coke. The higher binder content is required for flow properties in the paste while in use. The binder content should always be upto an optimum value.

Manufacturing Process

Manufacturing process for carbon/graphite electrodes comprises of the following:

a) Selection of proper granulometry of the grist particles
b) Mixing of the grist particles with a suitable binder in a hot mixer
c) Extrusion of the hot mix for carbon/graphite electrode or cast into suitable size for use in soderberg electrode
d) Baking in case of carbon electrodes
e) Baking followed by graphitization

A flow-sheet for the manufacture of electrode paste as well as carbon/graphite electrodes is shown in Figure 1.

In the selection of proper granulometry with a view to having the highest packing density, it is important to have various quantities of coarse, medium and fine fractions of the dry mix in right proportions. In general, the largest particle in the medium fraction must have approximately one quarter the diameter of the largest particle in the coarse range. The finer particle should be chosen such that they fill up the voids created by the mix between the coarse and medium fractions.

The dry mix having the proper granulometry and being preheated in the temperature range 130-145^{o}C is fed into a continuous/batch type sigma blade mixer through constant weight feeders and the pitch from heated pitch tank, in the molten condition after passing through a viscosity indicator, a controller and a flow meter, is injected along with the mix into the same mixer.

Mixing temperature is usually chosen 60-70^{o}C above the R&B softening point and mixing time of about 30 minutes. In case of paste for soderberg electrode, the paste is cast into blocks and sent to the customers, who break into small lumps (150 mm to 200 mm) and preheat them before charging into electrodes.

In case of pre-baked carbon/graphite electrodes, the mix being a little different in consistency but with other parameters remaining the same, the mix is extruded through an extruder capable of applying proper pressure and cut into proper length. The green electrodes are baked, in case of carbon electrodes and baked, impregnated rebaked followed by graphitisation for graphitised electrodes.

Quality Control

For smooth running as well as higher productivity of a ferro-alloy furnace using soderberg paste/carbon or graphite electrodes proper attention should be given to the quality of the paste and the electrodes as well. Quality of the paste first of all depends on the raw materials used in the carbon-mix i.e.the grist material and the binder. In case of electrodes, in addition to the properties of the mix, it also depends on the forming pressure, baking schedule of the green electrodes and finally the size control. Hence quality control of the raw materials as well as the final product are an essential part of a paste producing plant. Quality control comprises in the determination of the properties of the different raw materials required for paste production and finally of the paste also. In case of carbon/graphite electrodes it is essential to find the properties of the final product and check for the properties required in a particular case according to the pre-designed specifications.

Green Paste

If raw materials selection is proper and the dry mix having proper granulometry is fed into the hot mixing unit, the paste thus produced must have desired properties too. If a little variation in the properties of the dry aggregate takes place within limits, by slightly varying the binder percentage, desired flowability of the paste can be achieved. The flowability tests on sample cylinders are periodically done and the binder adjusted to keep the flowability within limits. It forms the routine control and is important since in the actual day to day process of manufacture, the only variable is the binder content. The apparent density of a good paste should be in the range 1.58-1.70 gm/cm^3. The green paste in the form of a test electrode is baked at 1000°C to simulate with the electrode paste baked in situ while in operation and some of the properties normally required for routine test are given below:

Electrical resistivity	60-90 ohm.cm
Crushing strength	150-250 kg/cm^2
Approx. porosity	25-35%

The above properties are used for comparison purposes of the batches processed and indicate the trend quality wise.

Some of the properties of pre-baked carbon/graphite electrode and electrode from soderberg paste are given in Table 3.

Use : Soderberg Paste

For use of electrode paste in a ferro-alloy furnace, a shell made up of 1 to 2 mm steel sheet is filled with the carbon paste in the form of lumps average size being 175 mm.

The shell acts as a casing for the electrode paste and protects it against oxidation. It also provides passage for the electric current from the electrode arm to the baked section of the electrode and intensifies heat transfer to the upper, unbaked section of the electrodes. The electrode top should be covered with a lid to avoid dust, since it may lead to a subsequent electrode breakage.

A special platform is mounted atop the furnace to facilitate electrode joint making and filling.

The heat evolving from the furnace softens the paste and enables it to fill the electrode shell compactly. Temperature for the baking of the electrodes should be such that at 110-130^{o}C the paste completely softens and form a compact cylindrical shape, at 300-350^{o}C solidification sets in and at 700-800^{o}C solidification ends with the evolution of the remaining volatile matter. Distribution of temperature in an electrode during the electrode baking procedure in large ferro-silicon furnaces is schematically shown in Figure 2.

Correct operation requires that the electrodes are not baked above the clamps, for a satisfactory "clamp-electrode" contact is obtained only when electrode clamps in a softened condition and is "moulded" by then. When the electrode begins to bake above the clamps, the operation of the open disk fan, as well as the electrode cylinder and the gland gasket should be c checked. The cooling of electrodes should be watched as carefully as that of clamps for an abnormal increase in the temperature causes premature baking of the paste.

During operation of large soderberg electrode severe difficulties which may occur are:

a) Paste flowing into the bath/furnace
b) Uneven current distribution
c) Heavy contamination of the bath

All these problems may be overcome by proper and even distribution of current, good granulometry and proper binder with the optimum flowability.

Graphitised electrodes : There are various failures leading to breakage one may encounter in working with graphitised electrodes:

1) Poor centering of electrode holders

2) Poor contact in the nipple joint which may result in sparking and local incandescence

3) Incorrect charging or negligence as a result of direct impact on the central section of the furnace when it is being cleaned or when attempting to lift an electrode frozen in the melt etc.

Summary

Use of soderberg paste in the electrodes for ferro-alloy production has been discussed. The selection of raw materials (viz grist particles and binder), their desired properties for having a good paste which performs well during operation with high productivity has also been discussed. Various means of quality control of the raw materials, paste and baked test electrode and the operation of the electrode also have been taken care of in this paper.

Use of pre-baked carbon and graphite electrodes which find a little place in the electrode usage has also been touched upon.

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TABLE I - PROPERTIES OF DIFFERENT BASE MATERIALS FOR ELECTRODE PASTE

Properties	D.C.A.	Anthracite Coke	Calcined Pet.Coke	PitchMet Coke	Coke
Ash content, %	0.4-0.5	6.50-7.50	0.28-0.30	0.215-0.35	22-25
Sulphur content, %	0.5-1.0	1.50-2.00	0.50-1.00	0.25-0.35	2.00-2.50
True Sp. Gr.	2.03-2.05	1.75-1.79	2.01-2.03	1.98-2.00	1.80-1.90
Grain Density g/cm^3	1.54-1.56	1.45-1.47	1.49-1.51	1.50-1.52	1.48-1.50
Crushability index	56	58	80	70	65
Electrical resistivity Ohm Cm	470-480	1190-1200	430-440	530-550	850-900
Microporosity, %	6-8	3-4	10-12	4-6	12-14

TABLE 2 - PROPERTIES OF BINDERS FOR ELECTRODE PASTE

Material	Softening pt °C (K&S)	Free Carbon %	Coking Value %
Coal tar	15-20	7-25	20-30
Pitch			
Soft	50-70	15-25	25-35
Medium	70-90	25-35	35-45
Hard	90-140	30-50	40-60

TABLE 3 - PROPERTIES OF SODERBERG ELECTRODE, CARBON AND GRAPHITISED ELECTRODES

Properties	Soderberg electrode (Cal.Fcl.coke based)	Carbon electrode	Graphitised electrode
Approximate porosity, %	25-35	20-25	22-25
B.D., g/cm^3	1.45-1.50	1.45-1.60	1.50-1.70
Ash content, %	0.25-0.30 (4-6)*	4-8	0.1-0.5
Sp.elect. resistance Ohm.Cm	60-90	35-55	8-12
Oxidation temp °C	425-475	400-500	600
C.C.S. kg/cm^2	150-250	200-450	200-350
M.O.R. kg/cm^2	70-80	80-175	80-100

*Anthracite based

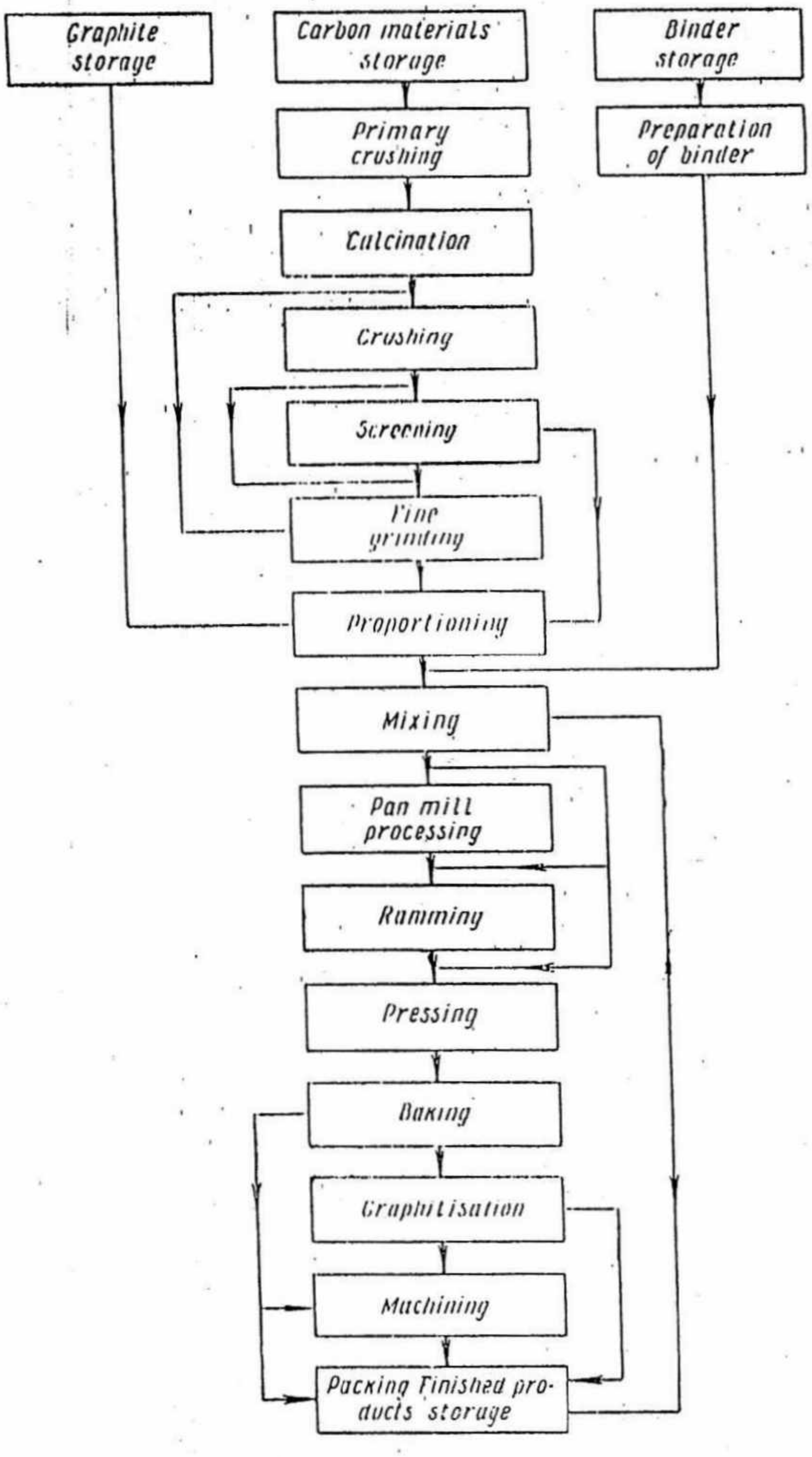

Fig. 1 Flowsheet for manufacturing electrode

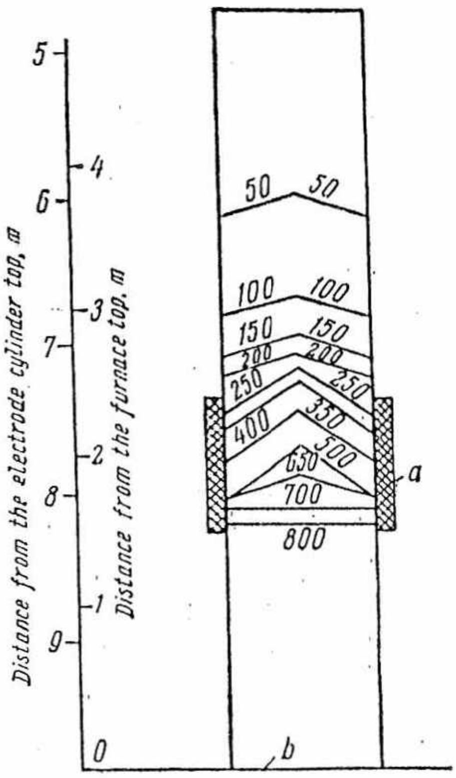

Fig. 2 Diagram of temperature zones in a self-baking electrode