Developments in the production of soderberg paste for electrodes in ferro alloy furnaces

B. Chatterjee
M. C. Kundra
K. R. K. Rao
M. R. K. Rao*

ABSTRACT

Using raw petroleum coke as raw-material, NML has developed a dense carbon aggregate as a substitute for gas calcined anthracite. This dense carbon aggregate has been used for making soderberg paste, the properties of which have been studied and compared with a Norwegian and two indigenous pastes. The suitability of this material has been tested on a commercial scale in ferro alloy and pig iron furnaces.

Attempts also have been made to produce dense carbon aggregate by partial replacement of petroleum coke with low ash coal and the study of its properties have been described in this paper.

Introduction

Carbon electrodes play a very important role in the production of ferro-alloys viz. ferro-chrome, ferro-manganese, ferro-silicon etc. The quality of the smelted products i. e. ferro-alloys and the performance of the ferro-alloy furnace are essentially affected by the physical and chemical properties of the electrodes used.

Continuous self baking electrodes now-a-days have replaced the carbon electrode almost every where because of many reasons which include the possibilty of manufacturing in situ large diameter electrodes, their low cost, the possibility of adding joints without the interruption of power input Electrodes should possess low electrical resistivity, adequate mechanical strength, high oxidation resistance, low disintegration capacity with lower cost. In India, the present demand[1] of soderberg paste for ferro-alloy industry is of the order of 20,000 M. T. per annum which is expected to reach 25,000 M. T./ annum at the end of this decade.

Anthracite is considered to be the basic component (coarse fraction) of anode paste for self baking electrodes. It has a high carbon content, high mechanical strength, considerably low ash content and low volatile matter. However in India suitable anthracite deposits have not yet been found. Therefore, in search of a suitable substitute for Anthracite, work was undertaken at NML and a dense carbon aggregate primarily based on raw petroleum coke was developed.

This dense carbon aggregate has good bulk

* Authors are Scientists with the
National Metallurgical Laboratory, Jamshedpur.

TABLE — 1
Properties of grist materials

	D. C. A.	Blended carbon aggregate Calcination temp.°C 1300	1400	1500	Anthra-cite coke	Petro-leum coke
Ash content%	0.44	3.00	3.00	3.00	6.60	0.27
True Sp.gr	2.05	1.93	1.97	1.98	1.78	2.03
Grain density 9m/cm^3	1.55	1.48	1.50	1.52	1.46	1.5
Crushability index	56	60	55	56	58	80
Electrical resistivity Pressure Ohm - cm 40.10 Kg/cm^2	475	675	620	597	1200	435

density, high strength, high electrical conductivity etc. thus fulfilling all requirements in its use for soderberg electrode for ferro-alloy furnace and thus replacing gas-calcined anthracite. After finding suitability of soderberg paste made from NML dense aggregate as compared to an imported Norwegian paste and two indigenous pastes, attempts were made to make further improvements in the properties as well as to reduce the cost, keeping in view of the continuously heavy rise of petroleum coke price. In this attempt, semi-coking coal from Bhowrah with 10-12% ash has been tried as a blending tool with raw petroleum coke. As this blend has a little higher electrical resistivity, graphite addition was made to improve this property. Graphite addition has also been experimented in studying the change in the properties of the green as well as baked paste.

Materials and methods

A dense carbon aggregate prepared by briquetting uncalcined petroleum coke followed by thermal treatment was used as one of the grists now. Another aggregate based on a suitable blending of raw petroleum coke and a semi coking coal from Bhowrah colliery was also used. The properties of these aggregate along with those of Anthracite coke (regular ash) from M/s. Great Lakes Carbon Corporation, U S.A. are given in Table 1.

Electrode graphite tailings is used as an additive. An imported paste (Norwegian) and two indigenous pastes from two leading manufacturers are also used for comparison with NML paste and other experimental pastes. Run of still pitch from Bhilai steel plant was used as the binder.

It had the following properties :—

Moisture	...	0 9%
Volatile matter	...	51.6%
Ash	...	0.24%
Fixed carbon	.	47.26%
R & B softening point	...	77°C
Benzene insoluble	...	26.58%

and distillation loss upto 350°C....12%

Preparation of the material

The dense carbon aggregate[2] was crushed, graded and blended to give a three-component powder mix (coarse, medium and fine in the ratio 2:1:2) having a maximum packing density.

The pitch used had a tendency to froth when heated and thereby it was kept at 180°C±10°C for about 1 hour to remove all the frothing constituents before its temperature was brought down to add to the mixer.

Preparation of the pastes composition

Paste compositions were prepared in 3 Kg lots in a 8 litre sigma blade electrically heated mixer. In each case, the grist particles were maintained at 130°C±5°C in the mixer itself for about 3 hours, before, the binder pitch was added. Weighed quantity of de-frothed pitch at 130°C±5°C was introduced into the mixture and the mixing was allowed to continue at a temperature of 130±5°C for a period of 30 minutes. The pastes thus produced were pressed into specimens of 2in. dia x 2in. height at 3000 lbs/sq.in. pressure for the determination of flowability in the green condition and other physical properties after baking. Bars of 1" x 1" x 6" dia were also pressed at 3000 lbs/sq.in. for the determination of modulus of rupture (bending strength) and electrical resistivity after the baking of the specimens.

EXPERIMENTAL

Tests on dry aggregate

True specific gravity and grain densities were determined according to ASTM standard for refractory materials. The methods used for the determination of crushability index and Electrical resistivity of grist particles are given below :—

Crushability index

100 g of single sieve fraction (—3+4 Tyler) of grist particle was introduced into a 2" dia steel mould with a plunger at the bottom A second plunger was kept into the mould from the top on the grist material. The whole assembly was placed under a hydraulic press (30 ton cap) and a pressure of 700 Kg/cm^2 was applied on the specimen. The pressed material after removal from the mould was sieved through 8 mesh Tyler in a 'Rotap' sieve shaker as per ASTM standard The percentage of the material passing through the 8 mesh sieve was a measure of the crushability index.

Electrical resistivity

This is determined by a method based on M/s. Electrokemisk of Norway and modified at N. M. L. The apparatus consists of an ebonite cell (30 mm dia x 50 mm height) tightly fitted in a brass cylinder, as the specimen holder, a load cell of 1 tonne capacity, a. d. c. source (rectifier) and a senior Kelvin bridge with a spot galvanometer for resistance measurement. Weighed quantity of powdered sample (—44+60 mesh B. S. S.) dried at 120°C was packed into the ebonite cell so as to attain a height of approx. 25 mm. A load was applied to the top plunger introduced into the cell amounting to 40 kg/cm^2. The exact height of the particle bed was measured with a depth gauge reading upto 0.0002 cm. Current of 5 amp was passed through the bed by means of brass electrodes placed co-axially. The resistance of the bed was measured with an accuracy of 1 x 10^{-4} Ohm.

Tests on green paste

Plasticity index was delermined according to a method as described earlier[3].

Baked properties

Pressed specimens after weighing were placed in graphite crucibles covered with coke dust. The crucibles were heated in a gas-fired down draft kiln upto 1000°C as per the schedule below :—

Room temp-500°C @ 50°C/hr	...	10 hr
500°C - 700°C	...	2 hr
700°C - 1000°C	...	2 hr
Soaking at 1000°C	...	6 hr

Bulk density, apparent porosity and apparent specific gravity were determined by standard ASTM methods. Cold crushing strength was determined on the two inch dia buttons and bending strength (M.O.R.) on bars using Avery universal testing machine and Riehle testing machine respectively.

Electrical resistivity[4] was measured on the bars keeping a gauge length of 2".

Results and Discussion

Table 1 shows the properties of Dense carbon aggregate based on Raw petroleum coke and Raw petroleum coke/coal blend calcined at 1300°C, 1400°C and 1500°C along with Anthracite coke (regular ash). True sp. gravity of Anthracite is quite low as compared with the other materials The blended aggregate is found to have a low specific gravity as expected due to the coal addition which goes on increasing with increased calcination temperature. Grain densities of the blended aggregate are also found to increase with the increase in temperature of calcination. Crushability indices of the blended aggregate are comparably good with reference to petroleum coke based dense carbon aggregate as well as Anthracite coke. Only drawback of the blended aggregate is higher electrical resistivity as compared with dense carbon aggregate (pet. coke) but still lower than anthracite coke.

Table - 2 (A & B) shows the comparative statement of NML paste (Pet. coke based) with imported and indigenous pastes. As regards the plasticity and bulk density of green pastes, NML paste is quite comparable with the other pastes.

In case of baked pastes, B. D., App. porosity, C.C.S. and M.O.R. values for NML paste are higher than all the other pastes. Electrical resistivity although near to the imported paste but is still lower than it. For the indigenous pastes App. porosity is quite high and the strength is also very poor.

TABLE — 2 - A

Comparative statement of NML paste with imported and indigenous pastes

	NML paste	Imported	Indigenous I	Indigenous II
Green paste				
Plasticity index	21	24	14	22
Bulk density gm/cm³	1.71	1.62	1.65	1.69

TABLE — 2 - B

Baked at 1000°C	NML paste	Imported	Indigenous I	Indigenous II
B D gm/cm³	1.49	1.37	1.35	1.34
App porosity	23	24	31	33
CCS kg/cm²	250-280	180-210	70-75	80-85
Modulus of rupture kg/cm²	75-80	40-45	20-25	25-30
Electrical resistivity Ohm. cm	80-85	85-90	110-115	80-85

Industrial evaluation of the NML paste (Pet Coke base)

As the NML paste was quite comparable with imported and indigenous paste, tonnage lots of this paste prepared at the pilot plant of National Metallurgical Laboratory underwent plant trials in M/s Ferro Alloys Corporation Limited, Shreeramnagar & M/s. VISL, Bhadravati in an open furnace for ferro-silicon production and for electric pig iron respectively. At FACOR the paste performance was comparably satisfactory with the indigenous pastes whereas at VISL[5] compared with the imported paste the NML paste was found superior.

To improve the properties of the paste based on dense carbon aggregate and to cut down the costs several measures were taken[4] As a first measure, graphite tailings (Table 3)

TABLE — 3

Sieve analysis of Dense carbon aggregate and graphite fines (tailings)

	D C A fine %	Graphite tailings %
+ 44	10	15
— 44 + 72	25	25
— 72 + 100	10	9
— 100 + 150	11	7
— 150 + 240	9	8
— 240 + 350	16	9
Pan	29	27

TABLE — 4

Properties of different paste composition on Dense Carbon Aggregate

Batch No.	Composition	Green paste: Plasticity Index	Green paste: Bulk density gm/cm^3	Baked at 1000°C: Elect resistivity Ohm $cm \times 10^{-4}$	CCS kg/cm^2	MOR kg/wt	BD gm/cm^3	App. porosity%	App. Sp Gr
A	DCA + 33% pitch	20	1.64	76	200	60	1.43	23	1.85
B	DCA + 10% graphite + 33% pitch	17	1.67	54	162	50	1.44	24	1.89
C	DCA + 20% graphite + 33% pitch	15	1.69	52	214	40	1.47	22	1.89
D	DCA + 30% graphite + 33% pitch	14	1.69	44	195	46	1.45	21	1.87
E	DCA + 40% graphite + 33% pitch	7	1.69	40	153	42	1.52	22	1.94
F	DCA + 36% pitch	34	1.66	79	102	37	1.40	26	1.90
G	DCA + 10% graphite + 36% pitch	40	1.66	77	121	53	1.42	25	1.88
H	DCA + 40% graphite + 37% pitch	11	1.69	41	136	54	1.47	26	1.99

were added to the mix in different quantities (10% to 40%) replacing the fine fraction of dense carbon aggregate. Addition of graphite was justified due to its low electrical resistivity and high resistance to oxidation[6] as well as the enhancement of plastic properties[7] of the paste.

The properties of the different composition of dense carbon aggregate (pet. coke base) and blended carbon aggregate with and without graphite addition are given in Table 4 & 5.

From Table 4 it is observed that with the increased percentage of graphite the plasticity index decreases. This may be due to the dispersion of the graphite fines without being covered by the pitch droplets and thus enhancing the viscosity of the paste. However with higher pitch content, graphite addition enhances the plasticity. In case of bulk density there is not much appreciable increase due to graphite addition. Electrical resistivity values gradually decrease with the increasing quantity of graphite content. This was according to the expectation as graphite has a very low resistivity as compared to other carbons. Cold crushing strength initially decreases but after a rise at 20% graphite, it again decreases. The rise at 20% graphite may be due to proper distribution of the graphite in the carbon matrix. There is an appreciable rise in bulk density values due to graphite addition. Porosities also vary within limits. From the above it is therefore apprehended that graphite addition around 20% to the dense aggregate makes improvement in all the properties with some decrease in M.O.R. but still comparable with the imported paste (Table 2B).

From Table - 5 we see the possibility of making paste from blended carbon. Blended carbon without any addition has a low green and baked bulk density, a little high electrical resistivity. On addition of graphite to an extent of 10%, although there is an improvement in all

TABLE — 5

Properties of paste composition on blended carbon aggregate

Batch No.	Composition	Green paste: Plasticity Index	Green paste: Bulk density gm/cm³	Baked at 1000°C: Elect. resistivity Ohm cmx10⁻⁴	CCS kg/cm²	MOR kg/cm²	BD g/cm³	App. porosity	App. Sp Gr
A	Blended carbon aggregate + 28% pitch	15	1.59	95	94	39	1.36	22	1.75
B	Blended carbon aggregate + 30% pitch	30	1.60	101	57	30	1.32	24	1.75
C	Blended Carbon aggregate + 10% graphite + 28% pitch	5	1.59	73	200	80	1.45	23	1.88
D	DCA + Blended carbon aggregate 20% fines + 20% graphite + 33% pitch	14	1.66	58	129	46	1.43	28	1.97

the properties, the plasticity decreases. This may be again due to the insufficient pitch content in the mix. It is expected that to maintain the plasticity index in the range of 15 to 20, an increase in the pitch content by about 1 to 2% may be necessary. From this table, we therefore, find that the properties of the paste made from blended coke with a little graphite addition may be successfully used in the ferro-alloy production. Use of high volatile high sulphur (3 to 4%) but with low ash (6 to 8%) is also being tried.

Conclusions

1) NML dense carbon aggregate is very dense and hard and it is stronger than anthracite and petroleum coke.

2) The properties of NML paste are quite comparable to that of imported Norwegian paste and are better than the indigenous paste.

3) The service performence of NML paste at FACOR and VISL was very satisfactory.

4) Addition of graphite around 20% to dense carbon aggregate improves the properties with prospects of still better performance with higher output in production.

5) Blended carbon aggregates without any addition, although give a little higher electrical resistivity on addition of a small quantity of graphite (around 10%) give very good properties comparable to Norwegian paste and better than the indigenously made petroleum coke based paste.

Acknowledgement

The authors wish to express their gratitude to Prof. V. A. Altekar, Director, National Metallurgical Laboratory, for his keen interest in this investigation, his encouragement and kind permission to publish the paper.

References

1. D.G.T.D. Sub-committee panel report of raw material committee of the Carbon & Graphite Panel, Feb 1977.

2. Murthy H. P. S. and Chatterjee B. "Certain factors influencing the production of Dense carbon aggregate from Low and high

volatile carbonaceous substances", Proceedings of the Seminar on Carbon and Carbon Products at N. P. L., Part - I, New Delhi, Nov. 1963.

3. Murthy H. P. S., Chatterjee B., Sarkar N. B. and Mitra B. K., Quantity of Binder as a factor affecting the properties of carbon pastes. Indian journal of technology, Vol. 15, Oct 1977, pp. 439-445.

4. Prabhakaram P. & Murthy H. P. S., Symposium on Light Metal Industry in India, National Metallurgical Laboratory, Jamshedpur, 14-17 Feb. 1961. P. 107.

5. Vernekar G. V., Improved performance of 'Soderberg Electrodes' at VISL, Bhadravati. Proceeding of the All India Seminar on Carbon Technology, organised by BALCO, Korba & I. I. M., Korba Chapter. 4-5 March 1978, pp. 57-64.

6. Chatterjee Bimal Sarkar N. B. & Murthy H. P. S., A comparative study of some technological properties of Raw materials used in the manufacture of carbon products Transaction of the Indian Ceramic Society, Vol. XXXV (4) July-August, 1976.

7. Khodorovsky M., Riss Y., Production of Ferro-alloys, 1967, pp. 36-101.

Discussion

Y P Rao, Nav Bharat Ferro Alloys, Hyderabad

Q. What is the role of plasticity of soderberg electrode paste ?

A. Different manufacturers are giving different plasticity number varying from 25 to 45 which is the most suitable number in case of Ferro Silicon production. The role of plasticity in case of continuous type of soderberg electrode paste is to keep the paste continuously flowing in a smooth manner. The most desirable plasticity is 15-25 in Ferro-silicon production. If it is lower than from 15 i. e. if it is too low then the flow of the paste will not be smooth thus the property of the baked paste will not be suitable for the production of ferro alloys and lot of problems will arise. If the plasticity goes too high say above 25 then the flow will be very rapid and will lead to segregation of coarser particles from the finer ones.

S Basu, M N Dastur & Co., Calcutta

Q. How does the prices compare amongst the Norwegian paste, indigenous paste and NML paste ?

A. I am not aware of the present price of the Norwegian electrode paste but indigenous paste if I am not wrong it may be of the order of Rs. 6500-7000 per M. T. and NML paste based on petroleum coke - dense carbon aggregate will be little higher may be around Rs. 7500 or 8000 per M. T. because of double operations involved. If petroleum coke is replaced by coal then the price will go down to a great extent.

M N Ramachandra, Sandur Manganese, Karnataka

Q. What was the quantity of paste produced ? FACOR tried the paste in which furnace ? Produced what product, for how many days it was tried and whether 100% NML paste was used or was it used in blend ?

A. For industrial trials we made 50 tonnes of paste. Out of which, 10 tonnes went to VISL for electric pig iron production and 40 tonnes went to FACOR, out of which 10 tonnes the first trial was used in their open furnace for ferro silicon production and 30 tonnes were used as a trial for ferro manganese production in their closed furnace. Actually no blend was used. 100% NML paste was used.

V N Babu, Nav Bharat Ferro Alloys, Hyderabad

Q. What is the maximum current density achieved on the electrode as some of the alloys required more than 6 Amps per centimetre square ?

A. We have not measured any current density. Only suitability in regard to the electrical resistivity of the paste was ascertained.

M Nawaz, IMFA, Bhubaneswar

Q. We use electrode paste from supplier 'A', we tried electrode paste from supplier 'B'. We had many electrode breakags. During discussion the supplier 'A' says that we are using the same material with granulometry and same binder contents as supplier 'B'. In your opinion what may be wrong with the paste 'B' ?

A. In my opinion apart from the granulometry and pitch of the material and, quantity of pitch, another important operation is mixing. If the mixing is not proper then there is no uniformity and there is every possibility of the development of hot spots while using the paste and breakages may occur.

S K Patnaik, IMFA, Bhubaneswar

Q. May I know the cost of production per tonne of the paste, developed by NML ?

A The cost of production is around Rs. 7,000/-

Q. Is NML still having further trials by more ferro alloy producers ?

A. No. At the moment we are not making any further trials.