A STUDY OF THE PRODUCTION OF SOEDERBERG PASTE FROM INDIAN RAW MATERIALS

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CONTINUOUS self-baking electrodes of the Soederberg type are used in electrolytic extraction of metals such as aluminium and in electric smelting of pig iron and certain ferro-alloys. These electrodes are made of carbon paste tamped in situ in hollow sheet metal columns that travel downward as the electrodes get consumed in the furnace. The descending paste gets baked by heat of the furnace and thereby becomes a fairly rigid and dense conductor when it contacts the electric bus-bars. Below this point there is virtually no difference between this and prebaked amorphous carbon electrodes.

In India, the main consumers of Soederberg paste are aluminium, iron and ferro-alloy smelting plants. At present the aluminium units are producing their own paste from petroleum coke obtained from Digboi refinery. Most of the paste for electric ferro-manganese furnaces is imported. Aluminium industry, it is gathered, is not fully satisfied with the quality of its paste as their electrodes usually suffer from susceptibility to cracking. Research and development work at the National Metallurgical Laboratory has been aimed at exploring possible indigenous raw materials for making optimum quality paste for Soederberg electrodes at the instance chiefly of the industry.

Basically Soederberg paste consists essentially of carbon particles and a binder. This mixture has to possess certain green and baked characteristics in order to give satisfactory electrodes. Following the pastes' flow in chronological order, it must be easily flowable and at the same time give a dense closely packed matrix. As it travels down the column with increase in superincumbent load and temperature, it must carbonise without shrinking or cracking. When fully baked, its conductivity must be uniform not only over its cross section but also along its length of descent. It must be very dense, capable of bearing high current surges without shattering, and resistant to oxidation and possible alkali attack in the furnace.

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Literature available on this subject is rather scanty though some excellent studies[1,2,3,4,5] have appeared in recent years. The general concensus of opinion appears to be that the initial density of the grist, its size distribution and its bulk porosity affect the electrode shrinkage while the viscosity, degree of swelling and subsequent shrinkage of the binder, act as contributory factors. The grist must also be preshrunk to the maximum by adequate calcination.

The maximum particle size of grist is another important point on which there seems to be general agreement. In a study[6] on the formation of cracks in the Soederberg anodes of aluminium cells, it has been shown that the shrinkage responsible for cracking increases with increasing ratio of finer fraction and with decreasing ratio of coarse fraction to medium fraction and smaller maximum size of coarse fraction. The coarse and medium fractions used in these experiments support the conclusion of other workers, that the dry aggregate acts as a reinforcement in the electrode counteracting the shrinkage of the binder coke. This reinforcement becomes greater, higher the coarse fraction contained in the paste and possibly closer the packing of the dry aggregate particles. The paste manufacturers are conscious of the importance of granulometric composition of the carbon grist. Table I gives the granulometric compositions of some pastes.

Another important constituent of the paste, the binder, has also received due attention. The workability of the paste or in other words, the ease with which a paste will flow efficiently into the container as well as the mechanical strength of the baked paste are mainly dependent on the binder and the nature of residue it leaves on coking. Of the various types of pitches available in the market, those made from tars of high temperature carbonisation are preferred. Aluminium producers in different countries are in good agreement as to the required properties of the pitches for such use as binders. Pitches with softening points between 70–85 K and S are said to be satisfactory for this purpose, apart from possessing high density and give a high yield of coke per unit volume. Amongst the individual constituents of the pitch, pyridine soluble C_2 fraction is known to influence viscosity and binding strength while the C_3 or gamma

TABLE I

Granulometric compositions of carbon grist used in Soederberg pastes.

1		2		3		4	
Size of particles mm	Per cent of grist	Size of particles mm	Per cent of grist	Size of particles mm	Per cent of grist	Size of particles mm	Per cent of grist
3–5	1·7	3·33 –2·76	7	25·4 –11·9	6	6·73–4·76	16·6
2–3	1·8	2·76 –1·77	9	11·9 – 5·5	7		
1–0·2	8·2	1·77 –0·76	16	5·54– 2·67	17	4·76–2·00	21·4
0·2 –1	31·2	0·76 –0·29	15	2·67– 1·77	5	2·0 –0·5	14·3
0·075–0·2	10·5	0·29 –0·16	13	1·77– 0·99	4	0·5 –0·15	17·0
0·0 –0·075	46·6	0·16 –0·075	17	0·99– 0·45	4	0·15	31·0
		0·075–0	23	0·45– 0·19	8		
				0·19– 0·09	22		
				0.09– 0	27		

Nos. 1, 2 and 3 are from German patents. 4 is from an imported Norwegian paste (sieve analysis by authors).

resins influence the wetting and adhesion characteristics. There is also experimental evidence that susceptibility of viscosity to change with temperature is dependent on the C_3 compounds. In general, a pitch may beneficially contain 30–35% of free carbon. European manufacturers specify a minimum of 20% of benzene insoluble/anthracene or quinoline soluble resins. Given a pitch with a correct percentage of free carbon and a correct grading of grist, a Soederberg paste can be obtained, the flowability of which changes little at temperatures between 140°C–220°C. This is accompanied by decreased tendency of the binder to segregate and to be drawn away. Free carbon has no wetting properties and to ensure adequate wetting properties, it is customary to specify that the coking-value per cent minus the free carbon per cent should not be less than 20. If the pitch is about 55% in coking value, the free carbon is therefore limited to 35%.

Scope of present study : Carbon for Soederberg paste should not only be as free from ash as possible (the permissible ash contents vary from industry to industry) but must be capable of yielding hard dense particles of size up to $\frac{1}{2}''$ and above, that do not shrink during baking or service. Similarly the pitch or tar binder used in minimum optimum proportions should render the paste flowable and possess low-temperature co-efficient of viscosity, should not start distilling below 300°C and also leave a strong and coherent residue in adequate quantity.

In India, the material used at present for Soederberg electrodes is petroleum coke. The report that some imported low ash anthracite is also employed is yet unconfirmed. The supply of petroleum coke however falls far short of the existing demands. With setting up of special type of cracking plants at Gauhati and Barauni, the supply position may be easier. Petroleum coke is low in ash and becomes a good conductor when calcined ; it is however very cavitatious as obtained from the still and becomes more so when calcined in the usual manner, rendering it particularly difficult to obtain hard dense grains of sizes larger than approximately 3 mesh, from it. Under India's conditions, a point of considerable importance is to obtain a carbonaceous material from which a grist of acceptable density, strength and conductivity could be made. The second point is the type of binders available in the country. The coal tar industry is largely geared to the production of tars and pitches conforming to high-way specifications. Except for one pitch which is said to be specially meant for anode paste, there has been no practical effort on actually tailoring the production of such pitches for binding carbon grist. This aspect, however, is basically essential if any progress is to be made in anode paste production. The problem, therefore, resolves itself into two broad aspects : first, examining possibilities of converting readily available carbonaceous materials into suitable base materials for anode pastes and secondly, possible improvement in tar and pitch quality for binders. The first of these has been pursued in some detail at the National Metallurgical Laboratory and the results thereof are presented below.

Materials

The raw materials available in India for this purpose are the high volatile non-coking coals of the Ranigunj area, the high volatile coals of Assam, the lignites of the Neyveli, Rajasthan and Kashmir areas and petroleum coke which has already been mentioned. Of these, the Assam coals are particularly low in ash and need no beneficiation. Coals from some seams of Ranigunj area need to be washed as their ash content is very high and yield of low ash coal may not be very cheap. However, there are several coals in this area which have 10–11% ash and by blending with other low ash materials, it is possible to bring the ash low enough for use in anode paste for ferro-alloy smelting furnaces.

The materials used in this investigation were petroleum coke, low ash coal obtained from Central Fuel

Research Institute, Jealgora, Road Tar No. 3, electrode pitch, soft medium pitch, and hard pitch. The proximate analyses of the petroleum coke and low ash coal are given in Table II.

TABLE II

Material	Ash%	V.M.%	Fixed carbon%
Petroleum coke ...	0·25	11·7	88·1
Low ash coal ...	5·5	29·6	64·9

Experimental

The raw material such as petroleum coke or low ash coal was crushed to desired fineness in jaw and roll crushers.

(*a*) *Mixing and briquetting:* The carbonaceous raw materials were mixed with a binder such as suitable coal tars in a laboratory sigma blade mixer designed for this purpose at predetermined temperature. Both the carbon raw material and the binder were heated to predetermined temperatures and mixed hot. The temperature of mixing was controlled. Briquettes were made in steel dies on hydraulic press at various suitable pressures.

(*b*) *Carbonisation of briquettes:* The briquettes were placed in saggers, covered with coke powder to prevent oxidation and were heated to maximum temperature of carbonisation according to predetermined temperature schedules.

(*c*) *Packing densities of carbon aggregates:* The carbonised briquettes were crushed in jaw and roll crushers to the desired degree and the crushed product was graded into coarse and medium fractions taking into consideration the maximum size of the particle in the crushed product. The coarse and medium fractions were blended with fines in variable proportions and the packing densities of the resultant carbon mixes were determined in a modified type of Westmann's packing density apparatus. A sketch of the apparatus is given in Fig. 1. It consists essentially of a polished hollow wooden cylinder in which the powder is packed by its own weight under the influence of regular bumping motion generated by a cam rotated by a motor. An easily sliding wooden disc was used to prevent the material from scattering while bumping.

To determine the packing density, a known weight of the material was placed in the hollow cylinder and was levelled. The wooden dise was slid into the cylinder so that it rested on the material. The whole apparatus was fixed on the cam whose bumping motion was continued till there was no more shrinkage in the height of the material as measured on a scale attached vertically to the wooden disc. The final free height of the material was measured correct to a millimetre. Difference between the original height of the empty cylinder and the final free height gave the height of the compact. As the diameter of the cylinder was known, volume of the compact and hence its density was calculated.

(*d*) *Thermogravimetric studies on coal pyrolysis:* The apparatus and the method adopted for this purpose are described elsewhere[7]. Fig. 2 is a photograph of

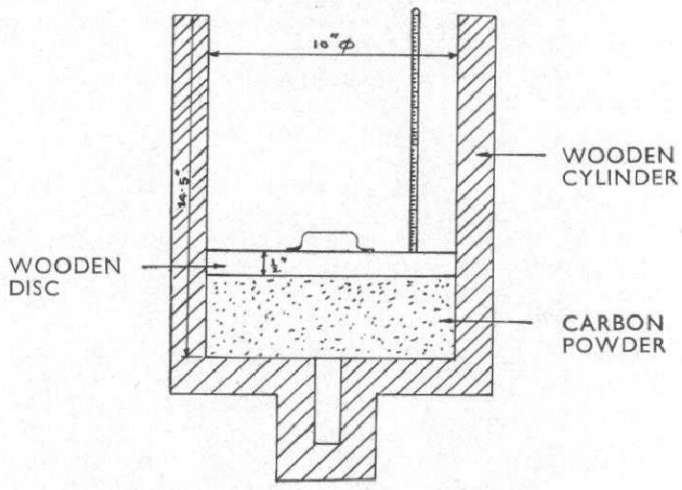

Fig. 1.
Packing density apparatus.

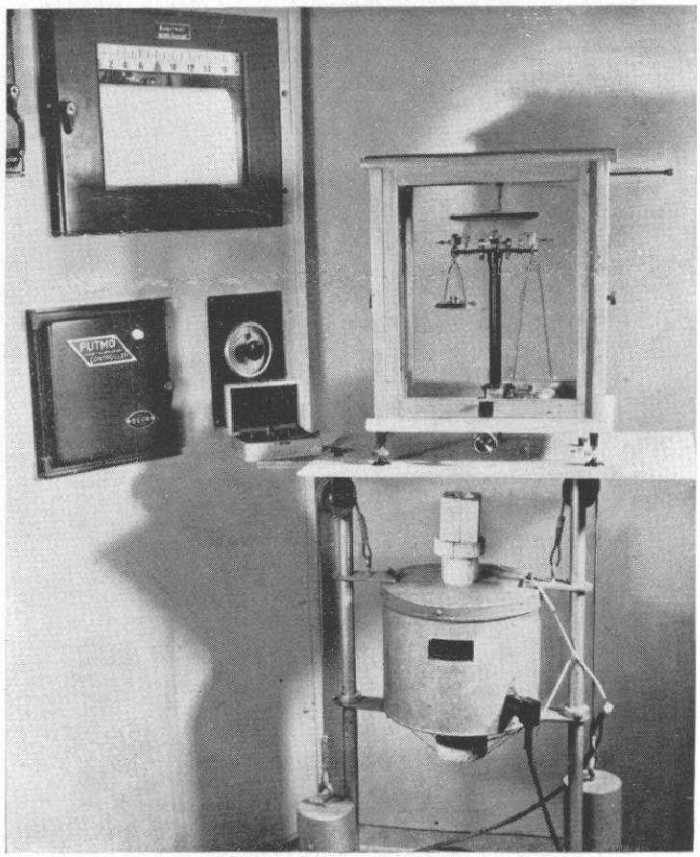

Fig. 2.
Thermal balance set-up.

the set-up. The apparatus consisted of a manually operated thermal balance and the experiments were conducted in an atmosphere of nitrogen, free from oxygen.

(*e*) *Preparation of carbon paste compositions:* For this purpose, the carbon aggregates of different size distribution were mixed in predetermined proportions. The material was mixed hot with a suitable binder in certain proportions at predetermined temperatures in a sigma blade mixer. The resultant mix was tamped in a steel mould whilst hot, by means of a compressed air rammer.

(f) Methods of testing the paste compositions: For testing the green and fired properties of the paste, the tamped paste was hardened by immersing it in ice-cold water and specimens were cut from it under running ice cold water. The green bending strength was determined on 6″ long specimens by an apparatus fabricated at the National Metallurgical Laboratory, according to specifications[8] laid down by the Standards Committee of the American Ceramic Society. For determining the fired properties of the paste, the samples were heat treated as described in section (*b*). The bending strength of the calcined paste was determined on 6″ long specimens and the compressive strength and porosities were determined on 2″ square samples.

The electrical resistivity of the calcined paste was determined on 6″ long specimens having 2 square inches area of cross section by means of Kelvin's bridge, using a sample holder with adjustable length between the contactors as shown in Fig. 3.

Results and discussion

Production of dense carbon aggregates: Carbon is the end product in the pyrolysis of carbonaceous materials; its coherency, density and strength vary with the nature of the starting material, the atmosphere, the temperature and time factors of the pyrolitic process. Thus depending on the nature of the starting material, it is possible to control the characteristic of the residual carbon within a fairly wide range.

In this investigation, the variables studied included (*i*) briquetting pressure, (*ii*) thermal gradient with respect to time and (*iii*) final temperature of pyrolysis. Each of these factors has been studied in some detail and the quantitative deductions form the subject matter of our patent[9]. In general, it can be concluded from these studies that it is possible to produce hard dense carbon from many coals (including suitable low ash non-coking coals) and petroleum cokes provided certain incorporations are made; the solid materials are

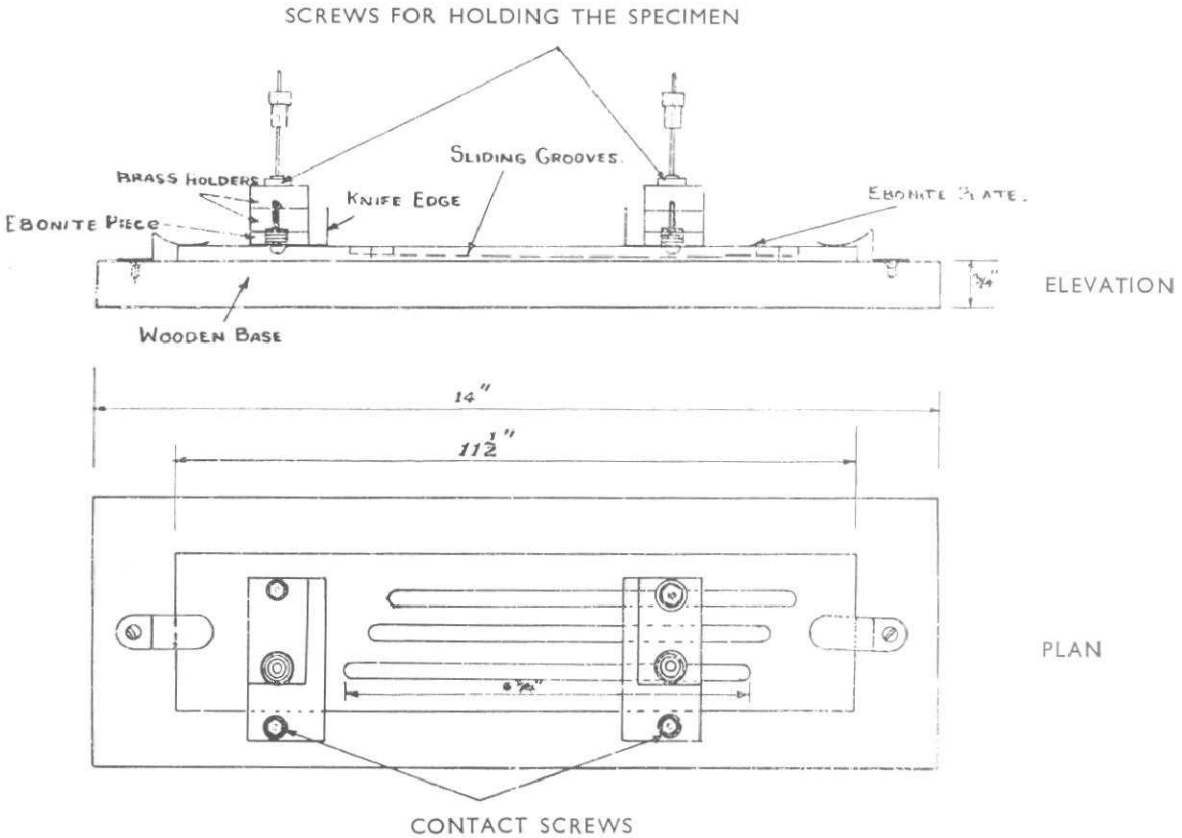

Fig. 3.
Specimen holder for electrical resistivity measurements.

crushed to optimum size and briquetted under suitable values of pressure. The most important factor which needed considerable experimentation and control is the time versus temperature schedule of pyrolysis and the maximum temperature attained. Table II gives the physical properties of dense briquettes made with raw petroleum coke under different sets of conditions.

Considerations in the production of dense aggregates from bituminous coals: Experiments on the production of dense carbon from bituminous coal/binder compacts revealed that the total volatile content of the briquettes should be within optimum limits. Therefore, in the utilisation of high volatile coals particularly of the type obtained from Ranigunj coal fields, additions of cokes or low volatile char become necessary. Such additions would preferably be of low temperature chars of the same coal as they would have the same shrinkage and other characteristics as those of the parent coal at high temperatures. Therefore, for preparing a low temperature char having a definite volatile content, thermal decomposition studies of coal in the temperature 410-456°C were carried out. The experimental percentage loss/time curves of the thermal

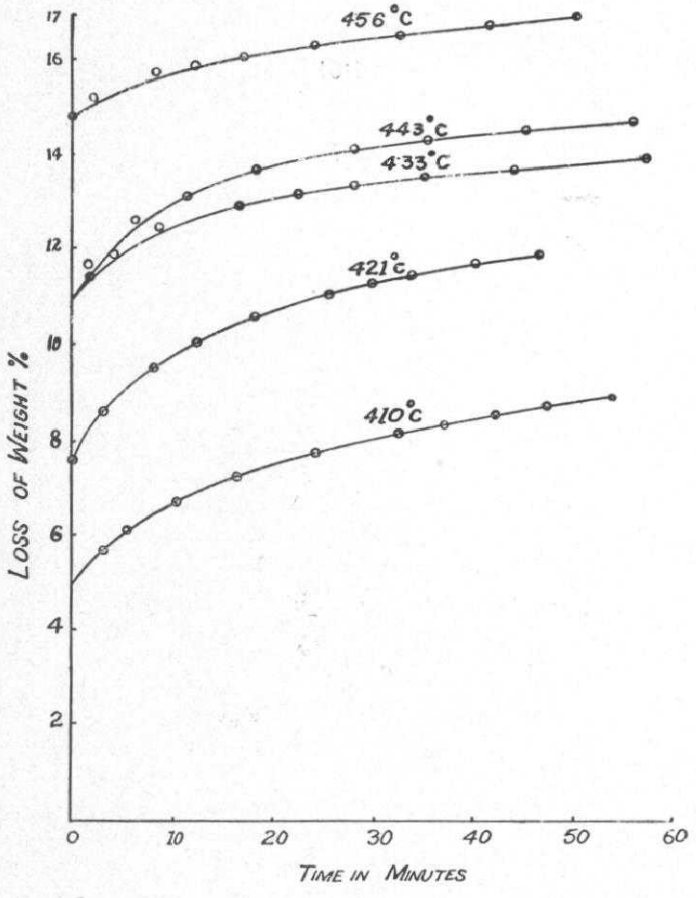

Fig. 4.
Experimental integral curves of thermal decomposition of coal at various temperatures.

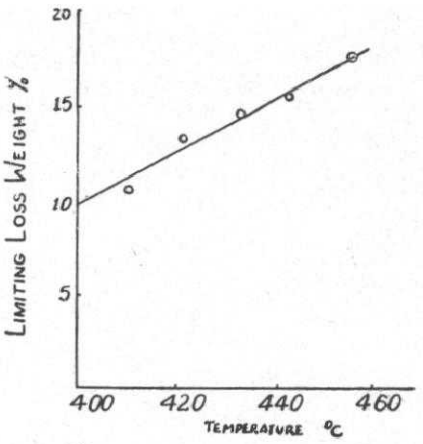

Fig. 5.
Plot of limiting loss vs. temperature°C.

decomposition of coal at temperatures in the above range are shown in Fig. 4. In all these cases, the time at which the reaction temperature was attained was reckoned as zero time even though varying amounts of loss had taken place by the time the reaction temperatures were reached. As the initial decomposition was very rapid, it was not possible to realise experimentally the exact zero time. All these curves follow relationship of the type $y = \frac{x}{a+bx} + c$ throughout the range of study, where y = the percentage loss, x = the time from the assumed zero, c = the intercept on the y axis at the assumed zero time and "a" and "b" are constants.

The horizontal asymptote of a curve having the above equation is $y = \frac{1}{b} + c$ where y, b and c have the same significance as those in the above equation. The limiting loss as calculated from the equation of the asymptote is the theoretical maximum loss that can occur at a particular temperature for which the curve stands.

In Fig. 5 the calculated limiting losses were plotted against temperature and the plot thus obtained is a straight line which follows a relationship $L = 0{\cdot}14t - 46{\cdot}2$, where L is the limiting loss and t the temperature in degrees, centigrade. From this equation, the loss at any intermediate temperature within the experimental range can be calculated by interpolation. This method of examination gives a workable idea for preparing low temperature chars of definite volatile contents from bituminous coals.

Preparing high density carbon mix: In view of the importance of the high packing density of carbon aggregate mix, experiments were carried out on the packing densities of various proportions of coarse, medium and fine fractions of aggregate powders. In order to obtain a high packing density powder mix (a high packing density carbon powder mix is one

TABLE II

Properties of dense carbon briquettes made of petroleum coke and a coal tar binder, formed under various pressures and subjected to different pyrolytic schedules.

Sl. No.	Forming pressure P. S. I.	Heating schedule	Apparent porosity per cent	Compressive strength P. S. I.	Bulk density gms/cc	Remarks
1	A	A	22·15	800	n.d.	The remaining specimens of the batch were all cracked.
2	A	A	22·14	896	n.d.	
1	B	B	21·25	1,420	n.d.	The remaining specimens of the batch were all cracked.
1	A	C	34·2	1,600	n.d.	All the specimens of the batch were completely free from visible flaws.
2	,,	,,	31·0	1,500		
3	,,	,,	30·0	1,500		
4	,,	,,	30·0	1,450		
5	,,	,,	31·0	1,400		
1	A	D	17·4	7,940	1·63	All the specimens of the batch were completely free from flaws.
2	,,	,,	16·8	4,210	1·64	
3	,,	,,	18·4	6,776	1·61	
4	,,	,,	17·5	8,170	1·61	
5	,,	,,	17·7	6,425	1·63	
6	,,	,,	18·7	7,026	1·61	
7	,,	,,	18·6	5,260	1·60	
8	B	,,	17·4	6,210	1·65	
9	C	,,	19·4	4,833	1·59	

which has a bulk density of the order of 1·3 gms/cc) it is necessary to classify the crushed aggregate powder into two fractions designated as coarse and medium respectively. The largest particle in the medium range must have approximately quarter the diameter (in practice this is taken equivalent to the length of the aperture of the standard sieve on which the particle is just retained) of the largest particle in the coarse range. A third fraction, called the fine fraction, consists of particles that are much finer than those in the other two fractions. When these fractions are blended in certain well defined proportions, high packing density mixtures result and the authors' experiments have shown that these mixtures occupy a definite area in the triaxial packing density versus composition diagram as shown in Fig. 6 and it is evident from the graph that all the high packing density mixes have a density of the order of 1·3 gm per cc.

Comparison of imported pastes and experimental compositions: Testing of the green and fired properties of the experimental compositions and the imported pastes under identical conditions has revealed that the authors' compositions[10] are well comparable to those of French and Norwegian pastes in their green, fired and electrical properties. Table III gives the various properties tested.

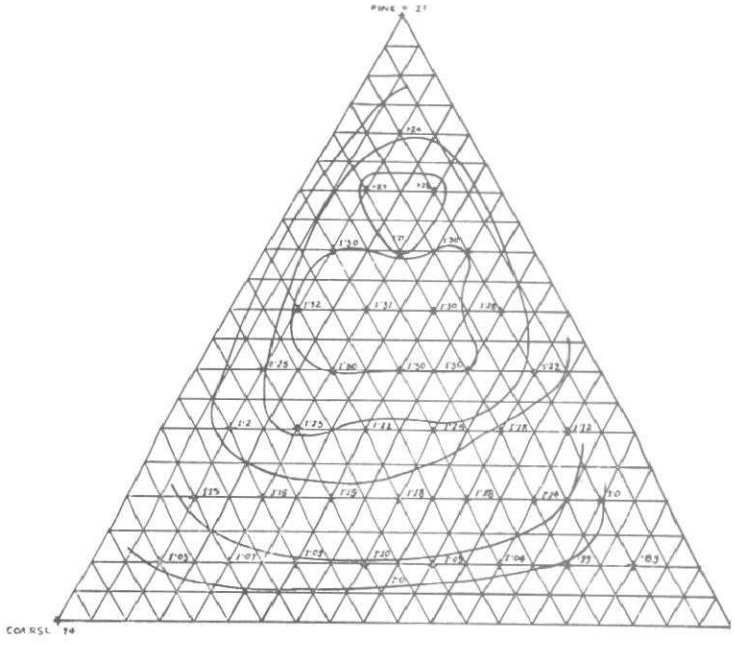

Fig. 6.
Packing densities of three component powder mixes.

Conclusions

The work so far done indicates that while calcined petroleum coke is being used for production of this paste, converting it into dense aggregate even at the expense of somewhat higher cost involved, imparts to the material uniform density and conductivity and the electrodes are consequently expected to be stronger, more wear resistant and better conductors. Conversion of bituminous coals into dense aggregates will involve addition of low temperature chars. Related Kinetic studies undertaken at the National Metallurgical Laboratory have indicated that it is possible to conduct low temperature carbonisation such that a predetermined quantity of residual volatiles remain in the char. Conversion of bituminous coals into dense aggregate is a prerequisite for their utilisation as raw materials for Soederberg pastes.

Laboratory scale experiments have revealed that it is possible to obtain hard dense briquettes from petroleum coke or low ash coal, which can be used as carbon grist in the Soederberg pastes after crushing, grading and mixing.

Results indicate that the paste compositions made out of these carbon aggregates are comparable to imported pastes as shown in Tables III and IV.

TABLE III

Comparison between the green and fired properties of the imported electrode pastes and the authors' compositions.

Sample	Bending strength of the green paste kg/cm	Physical characteristics of tamped paste fired to 1200°C		
		Compressive strength lb/sq inch	Apparent porosity %	Bulk density gms/cc
French paste	24·20	1,650	22–25	1·4
Norwegian paste	22·4	2,000	22–24	1·5
Authors' compositions :				
1.	20·0	2,400	22–25	1·5
2.	14·0	1,500	22–24	1·5

TABLE IV

Electrical resistivities of the authors' compositions and French paste calcined at 1200°C.

Sample	Binder composition	Electrical resistivity ohms mm^2/m
French paste		175·0
Authors' compositions :		
1.	Electrode pitch and tar	37·0
2.	Hard pitch and tar	113·0

Acknowledgements

The authors' thanks are due to Dr. B. R. Nijhawan, Director, National Metallurgical Laboratory, for his keen interest in the investigation and permission to publish the paper. Thanks are also due to Mr. H. V. Bhaskar Rao, Assistant Director of Refractories Division for his valuable and critical comments, Mr. A. K. Sinha for his assistance and Dr. A. Lahiri, Director, Central Fuel Research Institute, Jealgora for very kindly furnishing the coal sample and its plastometric data.

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