

PROPERTIES AND BEHAVIOUR OF GREEN ANODES

S. Wilkening
 Leichtmetall-Forschungsinstitut
 der Vereinigte Aluminium-Werke AG
 Bonn

It has been tried to pursue the process of carbon anode manufacture from the green mixture to the stage of solidification, and to sketch the particular problems in this section of anode production with respect to the materials and intermediate products involved. Examples are given for the analysis of composition, apparent density, real density and porosity of green anodes. Some measurements have been carried out on thermal expansion, volume changes, thermal conductivity, softening behaviour and evolution of volatile matter.

Introduction

Quality control of green anodes is commonly restricted to the determination of the green apparent density, at least in routine work. From the fact that other characteristic properties of green anodes have been much less investigated and discussed it may be concluded that there is no real need for additional information on green anodes. We believe, however, that more knowledge about properties and behaviour of green anodes helps a lot to take favourable measures in anode production and to trace back deficiencies occurring in baked anodes.

A short survey on the determinable properties of green anodes is given in Table I. The points listed there will be treated in more detail in the following chapters.

Table I. Main Properties of Green Carbon Anodes

GROUP	No.	PROPERTY
I	1	Composition :
		a) Pitch content b) Granulometry
II	2	Green apparent density
	3	Real density
	4	Total porosity
III	5	Thermal expansion
	6	Thermal conductivity
IV	7	Compressive strength
	8	Flexural strength
	9	Modulus of elasticity
V	10	Softening behaviour
	11	Distillation behaviour
	12	Coking behaviour

Composition

One should think that the composition of a green anode is well known from its formulation or recipe. But, when comparing the particle size distribution of the filler material in its original state with that in the green mix, it is noticed that an after-crushing or diminution of particles takes place during the mixing procedure. Usually a substantial loss of coarse particles is observed. This loss predominates above a particle size of 2 mm and leads to an equivalent increase of smaller particles below 2 mm. The shift from coarse to fine in the granulometry of the aggregate depends on several factors:

- particle strength of the petroleum coke,
- type of mixer or kneader,
- free space between the mixing blades and the shell of the mixer or between the mixing tools,
- operating conditions of the mixer such as temperature, mixing time and exposure of the mix to strong shear forces.

The particle size spectrum of the original dry filler can either be obtained from the screen analysis of the individual particle fractions and their percentage in the filler or from the screen analysis of a representative sample of the blend.

For determining the particle size distribution in the green mix we take a 500 g sample from the green mix or from the moulded green anode and extract this with 1000 g of anthracene oil at 180°C. The hot mixture is filtered on a flat 185 mm-diameter filter paper in a preheated Büchner funnel. The residue is washed with toluene, dried at 140°C, and then submitted to sieving. A 100 g pitch sample is treated with anthracene oil in the same manner as the green mix. The anthracene insoluble matter of the pure pitch is taken into consideration to calculate the precise pitch content of the mix and the quantity of carbon dust remaining in the filler material from the pitch. The sieve fractions in the fine powdery range of the filler material is normally found too low after extraction, because some of the fine dust is deposited in the open pores of the coarser particles. No definite correction can be made for this phenomenon.

A schedule for analyzing the composition of green anodes is outlined in Table II.

Table II. Analysis of Composition of Green Anodes

① Each PARTICLE FRACTION of Filler Material, ABOUT 5kg	S A M P L I N G		③ PITCH, 2x100g
	② GREEN MIX, 3 x 500g OR 3 CORE SAMPLES, 70φ x 80mm		
SIEVE ANALYSIS OF THE FILLER FRACTIONS SIEVING ON A SELECTED SET OF TEST SIEVES	EXTRACTION ADDITION OF 1000g OF ANTHRACENE OIL TO EACH SAMPLE, 180°C, DISSOLUTION OVER NIGHT		
PARTICLE SIZE DISTRIBUTION OF FILLER MATERIAL CALCULATED BY USING THE SIEVING RESULTS AND PROPORTION OF FILLER FRACTIONS	FILTRATION AND WASHING BÜCHNER FUNNEL, φ 195mm, PREHEATED TO APPROX. 150°C. FILTER PAPER, φ 185mm WASHING: 1x500ml HOT ANTHRACENE OIL, 4x500ml TOLUENE		
	DRYING AT 140°C		
	WEIGHING OF RESIDUE WEIGHT LOSS = SOLUBLE PORTION OF PITCH RESIDUE = ANTHRACENE OIL INSOLUBLE MATTER		
	CALCULATION OF PITCH CONTENT		
	SIEVE ANALYSIS OF RESIDUE SIEVING ON A SELECTED TEST OF TEST SIEVES		
COMPARISON OF PARTICLE SIZE DISTRIBUTION OF FILLER MATERIAL BEFORE AND AFTER MIXING			

According to our tests the extraction and sieve analysis of green anodes have revealed remarkable changes of the filler during mixing.

Density and Porosity

Green Apparent Density

The expression apparent density designates here the ratio of the mass of a body to its outer volume. Sometimes this ratio is defined as bulk density, particularly in the refractory and ceramic industry.

In anode production the first decisive mark is set by the green apparent density. It is related to the baked apparent density and consequently to other properties. Beyond the processing step of moulding all those blocks having an insufficient apparent density may be sorted out to prevent them from travelling the costly long way through baking, rodding and less efficient performance in the potroom.

The apparent density can be determined on the whole block or on core samples taken from the block. The determination on the whole anode block requires special equipment for weighing the block in air and in water, if the buoyancy method is applied. The calculation of the block volume from the block dimensions is not as accurate as the displacement method in water. A crane balance is a very useful means of carrying out the density determination of the whole block which is suspended by an appropriate holding device. The block is first weighed in air, then immersed in a water tank, and weighed again. Such a procedure cannot be recommended for routine control, but it is advisable to make the test once to establish the exact relationship between volume and height of the block or to check the apparent density occasionally.

If the relationship between block volume and block height is known and the side faces of the blocks are rather plane, it is reasonable to install an automatic gauge of length for measuring the block height. By using the charging weight of the block from the hopper scale above the moulding station it is possible to record the green apparent density of all anode blocks produced.

Core samples which may be bored from the top side of the anodes allow a greater variety of tests. We prefer core samples with a diameter of 50 mm and a length of about 120 mm, from which two isometric specimens of 50 mm φ x 50 mm with ground circular faces are prepared. Green core samples must be bored under cool water in order to avoid sticking of the hollow borer to the green block. The cooling path of the anodes after the forming station seems to be a convenient place to drill the cores. Details of the apparent density determination can be omitted here since extraordinary problems do not exist. The volume determination can be achieved either by measuring the dimensions of the specimen with a slide gauge or by the water displacement method. The scheme in Table III illustrates how to proceed in determining the green apparent density.

Pitches show a remarkable change of density with the temperature. Our results of density measurements on pitches as a function of temperature are plotted in Fig. 1. The temperature dependence of high-softening pitches can be expressed over the temperature range from 25 to 300°C by the formula $d_t = d_{25} [1 + 0.00044 (t - 25)] \text{ g/cm}^3$, where d_{25} is the density of pitch at 25°C. The thermal volume change of petroleum coke is about 50 times smaller than that of electrode pitch. It is difficult to compute the volume increase of the green anode from its components, i.e. from the volume proportions of

petroleum coke and pitch. If the apparent density is measured immediately after releasing the block from the mould, the values will be approximately 0.02 g/cm³ lower than at room temperature.

Table III. Determination of Density and Porosity of Green Anodes

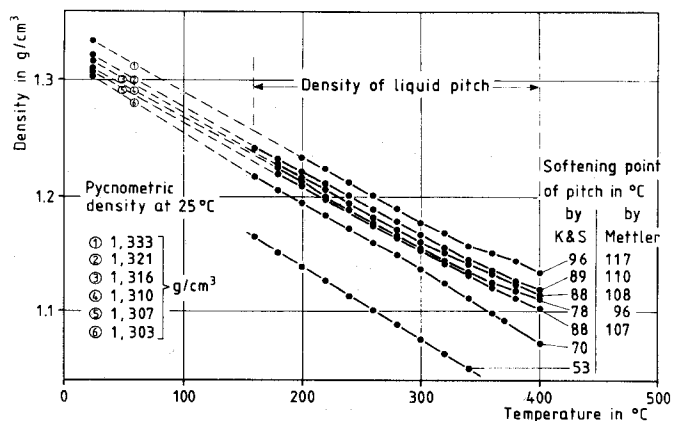
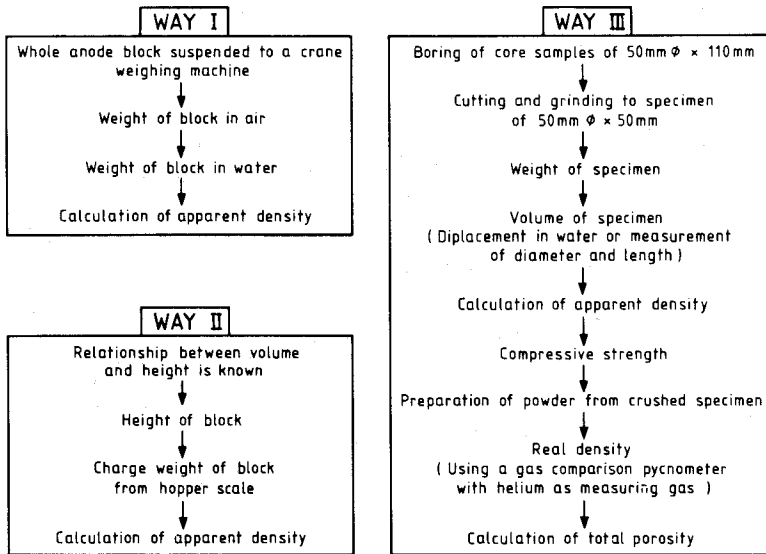


Fig. 1 - Density of electrode pitches in dependence of temperature

Although green anodes look quite dense from the outside they can be impregnated with water under vacuum up to about 10 %. Water impregnation should precede reliable volume determinations by the buoyancy method. When we tried to measure the apparent density decrease of green anodes at rising temperatures in water we noticed that the green test bodies absorbed appreciable amounts of water. The absorption of water increased with temperature and immersion time. This experiment proves that green anodes may take up moisture when stored outdoors. We were not very successful in measuring the change of the green apparent density with temperature.

Real Density

Standardized methods are available to determine the real density of coke and pitch. The real density of coke is generally determined by a pycnometric method for which a fine powder <0.063 μm and xylene as a dispersing liquid are used. A similar method is applied for pitches but it differs from the fore-going one by the use of grains of 0.5 to 1 mm and of water to which a surfactant is added. The temperature is normally kept at 25°C.

With respect to density determinations of green anodes the pycnometric method with xylene has to be discarded because xylene dissolves pitch. On applying the pycnometric method with water difficulties may arise from insufficient wetting of the finely pulverized green anode sample. The best solution to this problem is offered by the application of a gas comparison pycnometer using helium as the measuring gas. The German working group carbon has elaborated and tested this method to achieve a precision to the third decimal.

Total Porosity

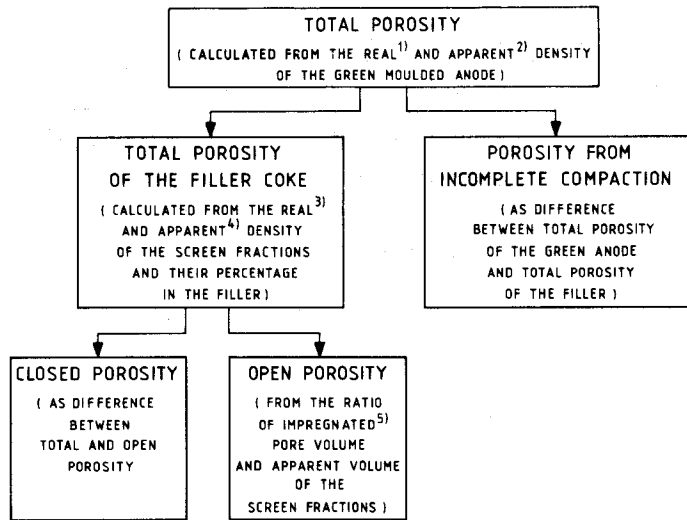
The total porosity of a green carbon anode is easily calculated from the apparent and real density (see Table IV).

In the formulation and compaction of green anodes it is an interesting aspect to know the three proportions of total porosity which originate from pores in the coke, from poor packing of the mixture and from incomplete compaction.

One approach to the division of total porosity is the exclusion of incomplete compaction. We take a test portion from the green anode mix of the plant and subject it to a moulding test on a laboratory vibrating table under very effective conditions, i.e. low vacuum pressure, strong impacts and optimum forming temperature. If compaction is conducted at increasing temperature a maximum is attained where densification levels off and where thermal volume expansion reduces the apparent density in the hot state (see Fig. 2). If the assumption can be made that the interstices between the granular structure are fully filled with a homogeneous mixture of pitch and coke fines the total porosity is equal to the residual porosity of the filler coke.

The problem of classifying the total porosity of the green anode can also be tackled directly from the coke side. We have developed a method to determine the total porosity of coke particles. A detailed description of the method will not be presented in this paper. To evaluate the total porosity of the filler material we take a representative sample from the filler coke and sieve off the dust below 0.125 mm (<115 mesh). The coarse fraction above 0.125 mm is used for the determination of the apparent particle density under water. In addition a powder sample is prepared for the deter-

Table IV. Types and Determination of Porosity in Green Anodes



- Determination of volume :
- 1) By means of helium comparison pycnometer
 - 2) By water displacement method or from dimensions of specimen
 - 3) By pycnometer method with xylene
 - 4) By water displacement in a 500ml pycnometer, own special method
 - 5) By impregnation of particles with water under vacuum and vibration

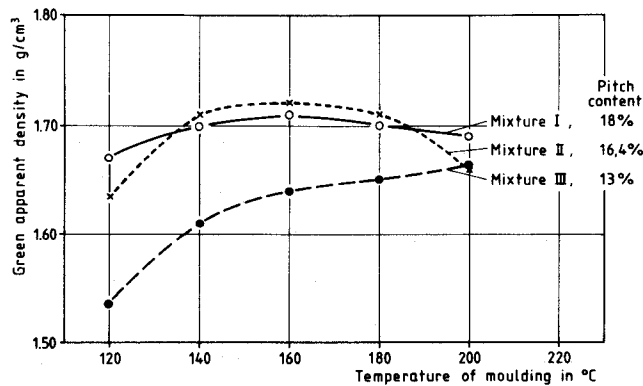


Fig. 2 - Green apparent density of vibration-moulded anode mixtures in dependence of moulding temperature

mination of the true density which is necessary to calculate the total porosity. The average porosity of the filler material is then compared with the total porosity of the moulded green carbon anode.

A little bit more complicated method to get a relevant figure for the apparent density of the filler coke shall be briefly reported here. A 100 g sample of the coke fractions without the dust is placed in a 500 ml calibrated pycnometer (see Fig. 3). A weighed quantity of electrode pitch is added to the filler sample and melted down in the pycnometer at 200°C. After cooling to room temperature the pycnometer is filled up with water to the mark, equilibrated at 25°C and weighed. The apparent volume of the filler coke particles can be calculated by using the known real density of the electrode pitch. We believe that the pitch melting method yields results that are closer to practice. A series of porosity determinations by the pitch method are plotted in Fig. 4.

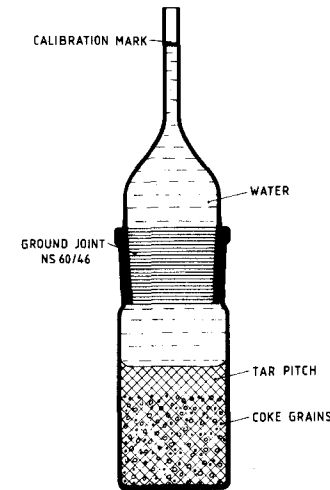


Fig. 3 - Pycnometer of 500 ml for the apparent density determination of coke grains under pitch

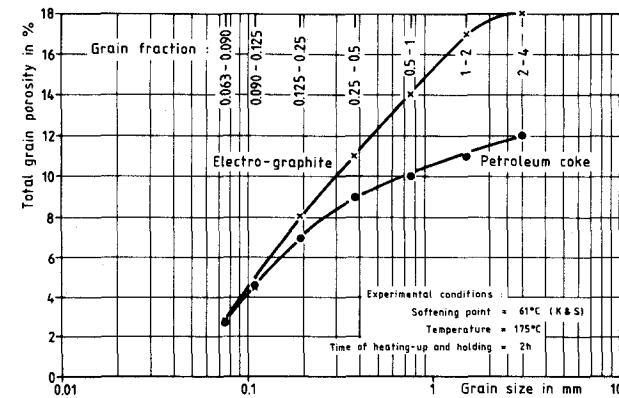


Fig. 4 - Total grain porosity vs. grain size, determination under pitch

Thermal Expansion

The coefficient of linear thermal expansion (CTE) of pitches should be one third of the temperature coefficient of volume expansion or density change. We have carried out a few dilatometric measurements on pitches from room temperature up to around 50°C. The results obtained were not in full agreement with the extrapolated slope of the thermal density change.

Fig. 5 demonstrates the significant differences between the thermal expansion of coke, green anodes and pure pitch. A green anode with, for instance, a pitch content of 15 % by weight contains approximately 22 % pitch by volume. The comparatively high CTE of green anodes makes them sensitive to thermal shock at low temperatures where the hard pitches are brittle. Rapid cooling of warm anode blocks in a cold water bath may cause shrinking cracks at the surface due to tensile stresses. The fissures are mostly invisible after equalization of the block temperature but may show up again after baking. When during the winter fairly cold green anode blocks are placed in the still warm chambers of a baking furnace it may also happen that the blocks are cracked or disrupted.

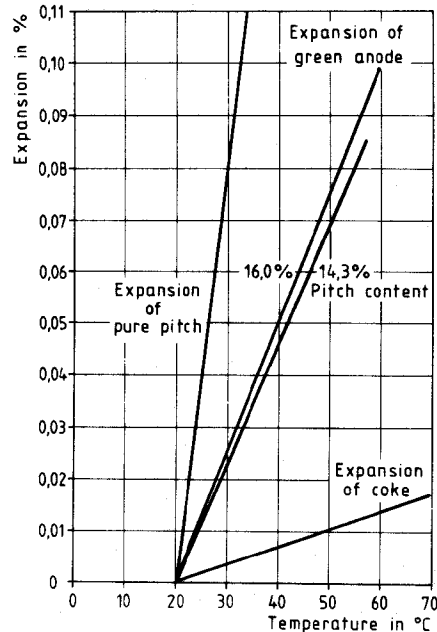


Fig. 5 - Thermal expansion of green anodes below the softening point of the pitch

Thermal Conductivity

The literature about heat conductance of pitches and green anodes is scarce. We have measured the thermal conductivity of a binder pitch (Mettler softening point 110°C) in the solid state at 45°C and arrived at a value of 0.23 W/m.K. Conductivity data from the literature (1,2) are 0.15 and 0.17 W/m.K. The thermal conductivity of green anodes, which has been measured by ourselves, ranges from 2.5 to 3 W/m.K at an average temperature of 100°C. These values are not so low as one should expect from the small thermal conductivities of the pitch and the filler coke, and if they are compared with baked anodes exhibiting conductivities of about 4 W/m.K. The property of thermal conductance is of importance when the thermal shock behaviour or the heating-up of green anodes in the baking furnace is considered.

Strength

We have tested the compressive strength of green anode specimens (Ø 50 x 50 mm) at 25°C to see whether it may have any significance. Fig. 6 shows the variation of compressive strength with the green apparent density. From this diagram it can be seen that the green apparent density has an appreciable effect on the crushing strength which varies more steeply than it is known from baked products. Hence, the testing of green compressive strength gives an excellent indication of successful formulation of the green mixture and its degree of compaction.

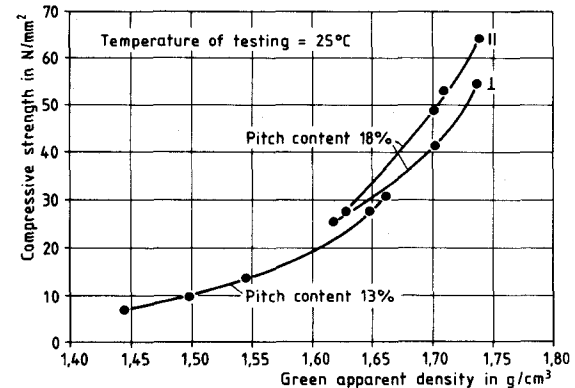


Fig. 6 - Dependence of compressive strength on green apparent density

Regarding the mechanical properties of green composites much can be learned from the testing of road paving materials where asphaltic or bituminous binders are used. In this field of industry many methods of test (3) have been introduced to characterize bitumens and paving mixtures, and to guarantee high performance of road layers.

Behaviour at Elevated Temperatures

Softening Behaviour

On heating up green anodes they have to pass a crucial range of softening and plasticity. For this reason green anode blocks have to be supported by a coke packing material in the phase of weak coherence. For testing of Soderberg pastes for electric arc furnaces we apply a method which is called "Determination of the deformation point". The apparatus of this method is depicted in Fig. 7. We have adopted this method to get an idea of the deformation behaviour of moulded green anodes. The specimen (Ø 35 x 100 mm) stands under the load of a steel piston and is heated up in an oil bath with a rate of 1°C per minute. The specific pressure exerted by the steel piston is 0.25 N/mm² for Soderberg pastes but several of our green anodes withstood this load up to nearly 200°C without any sign of failure. Then we increased the weight of the piston to reach a specific load of 0.75 N/mm² which corresponds to a 5 m stack of green anode blocks in the baking chamber. Soderberg pastes show a flowage, that means a continuous deformation with increasing temperature. Green vibratory-moulded anodes do not deform significantly, i.e. less than 2 %, until they undergo a sudden fracture at a certain temperature. Most of the green anodes bonded by a pitch of 110°C softening

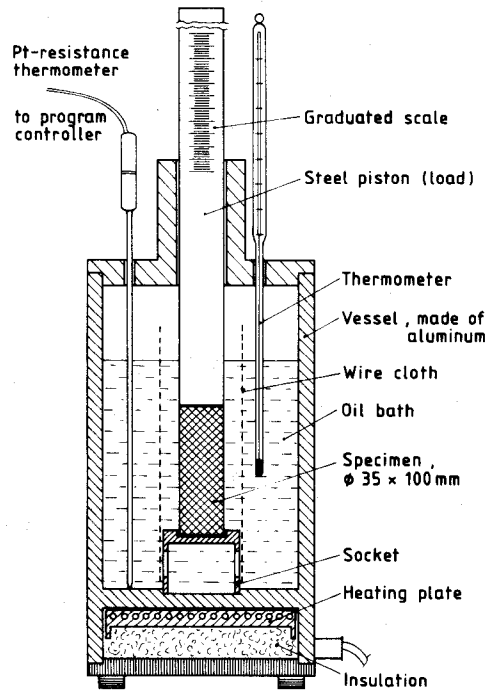


Fig. 7 - Apparatus for the determination of the deformation point

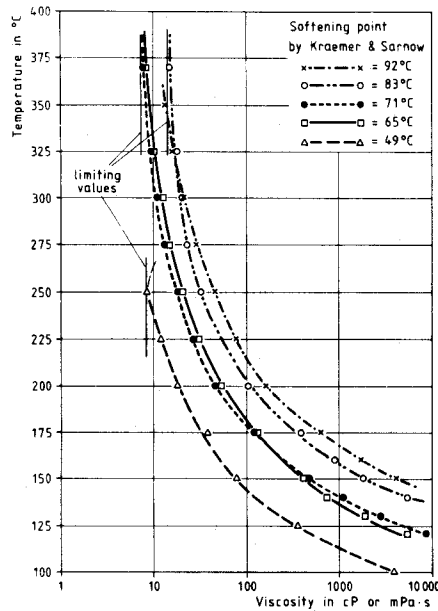


Fig. 8 - Viscosity measurements on pitches up to high temperatures

point by Mettler (about 90°C by K&S) broke down between temperatures of 135 and 155°C. The consistence of a green anode is characterized by a rather stable structure of interlocking coke grains with very little flow properties. The cohesive forces of the pitch bond are linked to the viscosity of the pitch. High-softening pitches do not surpass a lower limit of viscosity as it is obvious from the curves in Fig. 8. During heating-up the minimum viscosity may not be reached because above 200°C distillation starts causing a decrease of fluidity by the loss of light pitch constituents.

Distillation Behaviour

Distillation behaviour of pitches as well as of green anode samples can be investigated by means of a thermo-balance. Our set-up consists of an analytical electronical balance connected to a recorder and a tube furnace combined with a program controller (see Fig. 9). For distilling pitches we use a sample weight of 5 g, for green anodes a ring-shaped specimen of approximately 25 g. From the distillation curves of pitches in Fig. 10 it can be inferred that the cumulative distillation losses move to lower temperatures, are constricted to shorter ranges and remain at lower finishing levels if the heating rates become slower. A similar prediction can be made from the distillation curves of green anode specimens. The evolution of volatiles from the green anode in the plastic region implies the great risk that they may be expanded or deformed by the vapour pressure of the volatiles. Therefore two important things are diminished by slow heating: firstly, the temperature range of a weak and breakable bond in the green carbon body between the points of softening and minimum viscosity of the pitch, and secondly, the danger of deformation or even bursting by the liberation of volatile substances.

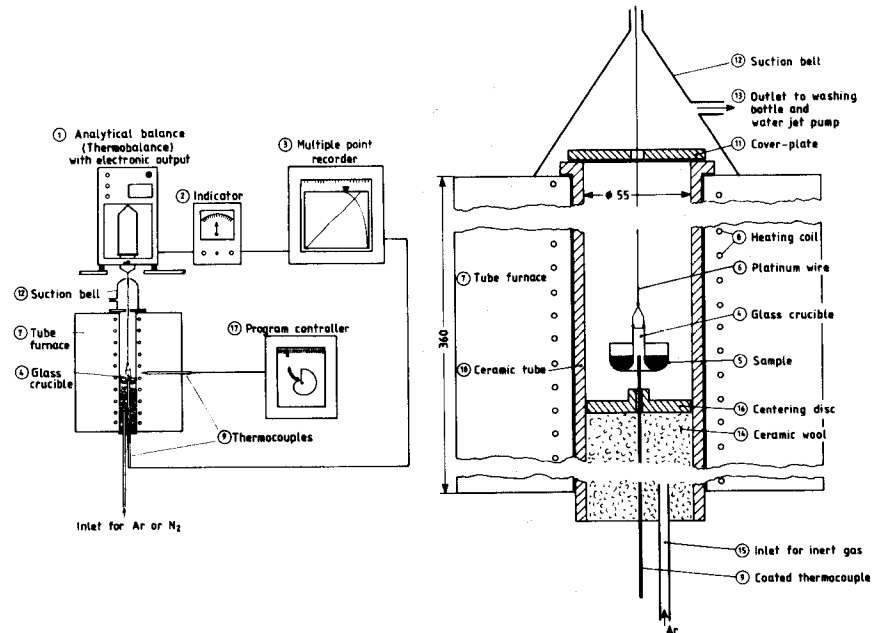


Fig. 9 - Apparatus for thermogravimetric distillation

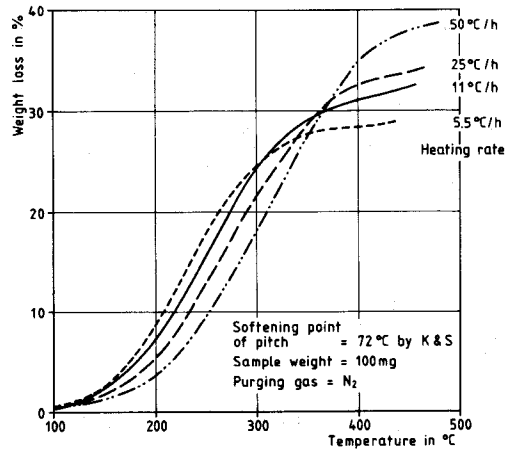


Fig. 10 - Distillation loss of a pitch at different heating rates (thermogravimetric study)

Coking Behaviour

The term coking is often applied to cover the whole process of transforming a green carbon anode into a baked one. Coking is confined here to the principal stage of coke formation and distinguished from the stages of mere softening and distillation. The coking process in the strict sense is accompanied by strong changes in volume and density of the pitch binder and ends with a solidified product. During the period of coking the anode blocks tend to form cracks of shrinkage. Fig. 11 and Fig. 12 represent some of the physical changes occurring in the coking range.

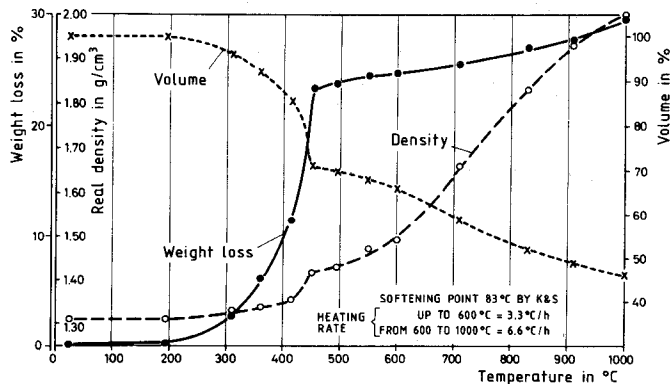


Fig. 11 - Changes of a pitch during coking

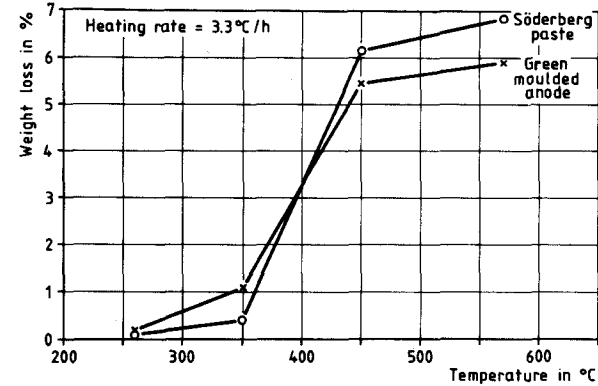


Fig. 12 - Weight loss of green electrodes in the coking range

Conclusions

The analysis of green anodes as outlined in this paper is one of the early measures to secure adequate physical properties of baked carbon anodes. It clearly indicates what has been achieved in the processing steps of mixing and forming. Investigations on the softening, distillation and coking behaviour of green anodes are very useful to understand and evaluate the initial period of baking.

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