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SINTERING CHARACTERISTICS OF COAL ASHES BY SIMULTANEOUS DILATOMETRY-ELECTRICAL CONDUCTANCE MEASUREMENTS

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Two different experimental procedures were used to investigate the sintering characteristics of coal ashes on heating. First, the Leitz heating microscope was used to record the shrinkage of an ash pellet and the electrical conductance was measured by inserting two platinum wire electrodes into the sample carrier. Another furnace assembly was also constructed where the shrinkage of the ash compact was monitored by a linear displacement transducer, and the conductance of the sample was measured between two platinum disc electrodes. Usually the results are consistent with a sintering model based on the precept that the development of a sinter bond between the particles is accompanied by the external shrinkage of the ash compact and by the increase of the conductance.

Recently there has been renewed interest in utilizing coal for electricity generation and a number of countries, including Great Britain, are currently planning to exploit new coal-fields. This has given a fresh impetus to research on the problems caused by coal mineral impurities in large boilers. Boiler slagging is one problem which has been subject to much research and many different ways of assessing the slagging characteristics of coal ash have been proposed.

There is no single laboratory test which gives a good indication of the tendency of a coal to boiler slagging. There are two aspects of this: the fast melting of particles in the flame and zones of high radiation, and slow sintering of agglomerated particles at lower temperatures. This work concerns the latter phenomenon. The well-known ash fusion test [1] for testing this slow sintering property of a coal mineral tends to be rather imprecise and subjective while ash viscosity measurements [2–4] although more precise require complex equipment and are not really suitable for routine testing.

The object of this work was to develop a method which could be used for laboratory studies of the coalescence of hot ash particles as a routine test of slagging characteristics. Measurement of the electrical conductance of ash pellets in the temperature range (800 to 1600 K) appeared to be the most promising technique to use.

Viscosity and conductance models in particle coalescence

The majority of the mineral particles in pulverized coal are transformed to spherical shapes in a boiler flame [5]. Particles deposited on boiler tubes will coalesce when there is a significant mass transfer at the contact points. The driving force for this viscous flow is the surface tension and the rate of change is controlled by the viscosity of the glassy material,

$$f = \eta \varepsilon \tag{1}$$

where f is the acting stress, η is the viscosity coefficient and ε is the strain rate.

Frenkel [6] has developed a simple model for bonding of spherical particles by viscous flow,

$$x^2 = \frac{3r\Phi t}{2\eta} \tag{2}$$

where x is the radius of neck, Φ is the coefficient of surface tension, r is the radius of particle, t is the time and η is the coefficient of viscosity.

The Frenkel equation predicts that the initial shrinkage of a compact of spherical particles will be linear with time as shown by Cutler and Henrichsen [7]

$$\frac{l_0 - l}{l_0} = \frac{\Phi t}{2r\eta} \tag{3}$$

where l_0 is the initial length of the pellet, l is the length at time t, and Φ, r and η are as defined for equation (2).

Cutler and Henrichsen have also shown that sintering rates of powdered glass compacts of uniform size can be determined by the shrinkage measurements. Earlier Smith [8] had used the shrinkage technique to determine the sinter point temperature of ash pellets. The shrinkage measurements can give useful information on the ash sintering characteristics. However, with some ashes anomalous results can be obtained, which show that a significant degree of sintering can occur without any shrinkage. This deviation in the sintering behaviour from the Frenkel model makes it necessary to measure another parameter relating to the process of particle coalescence. Viscosity is an obvious choice, but Gibb [4] has shown that viscosity measurements of coal ash slags are difficult to carry out, and several different techniques would be required to cover the necessary range. The rod penetration technique is capable of measuring the viscosity in the range of 10^3 to 10^7 N s m^{-2}, but a significant rate of sintering can occur well above this viscosity range [3].

Instead of measuring the viscosity, the rate of sintering by viscous flow can be deduced from the electrical conductance measurements. Ramanan and Chaklader [9] have developed a mathematical expression which relates the electrical conductance measurement to the density changes of powder compacts on heating, when sintering takes place,

$$\Lambda = C\Lambda_0[(D/D_0)^{2/3} - 1]\exp(-E/RT) \quad (4)$$

where Λ is the conductance when the sample density is D, D_0 is the initial density, C is a constant, Λ_0 is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the temperature.

Equation (4) predicts that on heating a powder compact, the conductance would increase rapidly after the initial contact between the particles has occurred. To test the conductivity model for coal ash sintering two different measuring arrangements were used.

Experimental

Conductance measurements in heating microscope

A Leitz heating microscope was used for the initial measurements of electrical conductance of small ash pellets subjected to heating. The usual sample carrier was replaced by a 4-bore alumina rod to take a Pt/13% Rh–Pt thermocouple and two platinum wires, 0.2 mm thick, which were connected to an AC-bridge. The bare ends of the wires at the hot end of the carrier rod were doubled back on the top side of the rod and kept 1.0 mm apart. An ash pellet of 3.0 mm cube was placed on the wires as shown in Fig. 1, and then pushed into the furnace. The sample was heated in air at a rate of 10 K per minute. The change in the shape of the pellet was recorded photographically in the usual manner.

The output signal from the AC-bridge, operating at a frequency of 1592 Hz, was rectified and then recorded. Conductance values were expressed in S. I. units, in milli-Siemens (mS) or in micro-Siemens (μS).

Simultaneous shrinkage and conductance measurements

The furnace assembly for measuring shrinkage and electrical conductance simultaneously is shown in Fig. 2. All support tubes and platinum wire sheaths, as well as the sample crucible were made from high grade alumina. A linear displacement transducer resting on an alumina tube was used to record the linear displacement to an accuracy of ± 0.01 mm. The apparatus had a near linear thermal expansion of 1.5 μm K^{-1}. For conductance measurements the AC-bridge was used as before.

An alumina crucible with a flat base, 8 mm internal diameter and 14 mm high was used to contain the ash sample. The ash in the crucible was loosely compacted to give a bulk density of 750 kg m^{-3}, and it was then heated in air at a rate of 5 K min^{-1}. Care was taken to stop heating when the sample had decreased in size by about 30 per cent. A cut-out device, activated by the D. C. signal from the displacement transducer can be used to reverse the furnace from heating to cooling when the shrinkage of the sample has reached a pre-set value.

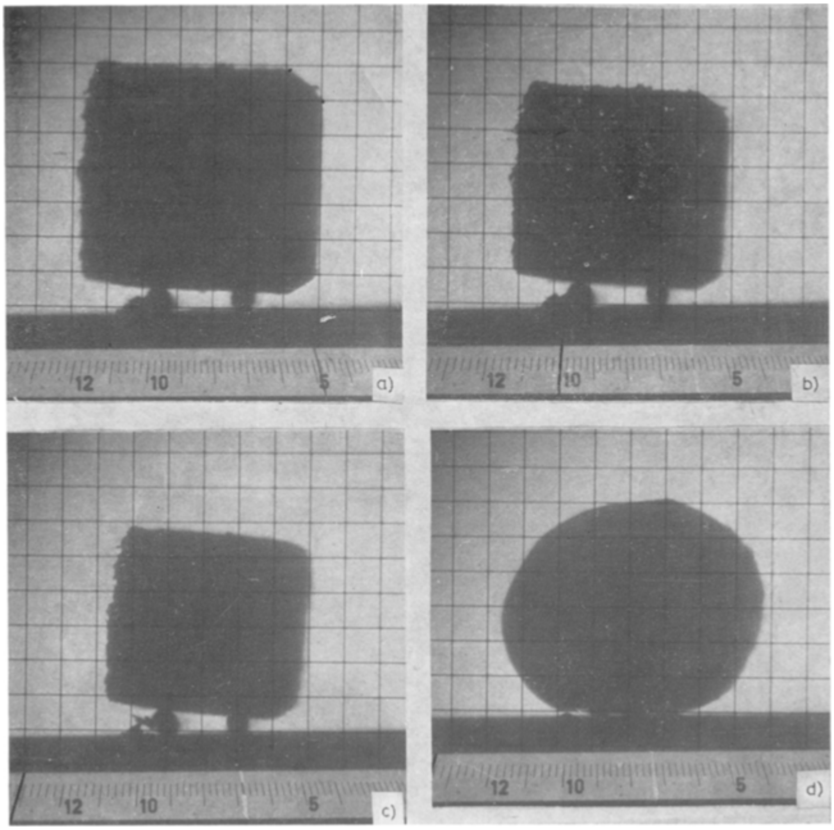

Fig. 1. Deformation and electrical conductance of Pye-Hill ash in Leitz heating microscope: (a) Original sample, conductance 1.0 μs, (b) Initial shrinkage at 1275 K, conductance 8,5 μs, (c) Initial deformation at 1575 K, conductance 40.5 μs, (d) Half sphere at 1630 K, conductance 2400 μs

Results

Conductance of ash pellets measured in the heating microscope

The plots of conductance as a function of temperature in Fig. 3 show that there was a large hysteresis effect in the conductance values when a small pellet of ash on the platinum wires was first heated to 1650 K (curve *A*) and then allowed to cool (curve *B*). On reheating, curve *C* closely follows the cooling curve. This behaviour is in accord with the sintering model as described in Section 2 and defined by equation (4).

There are two simultaneous effects which cause the conductance to increase sharply with temperature. First, the contact area between particles increases as the temperature rises and secondly, there is the usual exponential dependence of

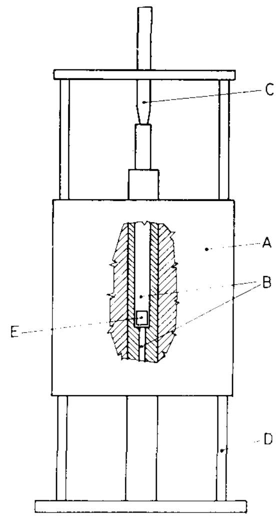

Fig. 2. Furnace assembly for ash shrinkage and conductance measurements: A Furnace; B Conductance leads and thermocouple; C Displacement probe; D Furnace has balanced lowering and raising action; E Sample

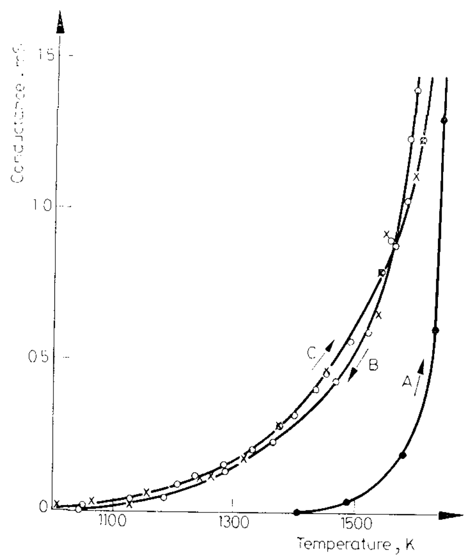

Fig. 3. Conductance measurement in heating microscope — Pye-Hill ash: A — First heating; B — Cooling; C — Reheating

conductance on temperature. On cooling and reheating, the process of particle coalescence is "frozen" and the conductance change is governed only by the exponential rate law.

A number of ashes from British coals were tested and similar hysteresis curves of conductance were obtained. The next state of the work will be to obtain possible correlations between the conductance values and the conventional ash fusion tests.

The ash of Australian brown coal (Leigh Creek) was also tested and showed an unusual feature on reheating (Fig. 4). Following the initial increase, the conduc-

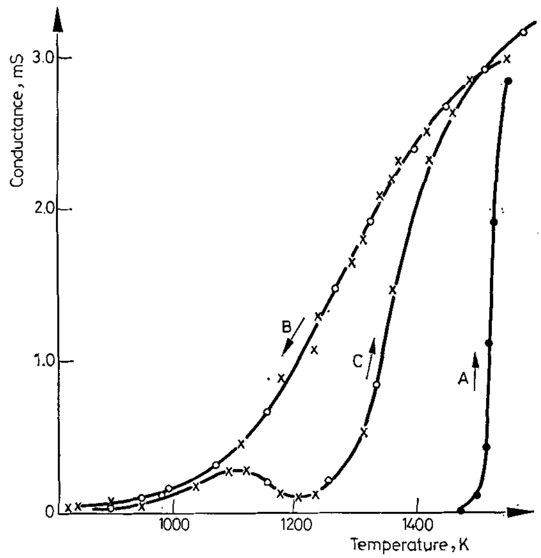

Fig. 4. Conductance measurement in heating microscope — Leigh Creek ash: A — First heating; B — Cooling; C — Reheating

tance decreased to a minimum at 1200 K, after which, it increased rapidly with temperature. The ash contained unusually high amounts of alumina (41.5 per cent by weight) and sodium oxide (6.3 per cent) and it is likely that some sodium aluminate had crystallized between 1100 and 1200 K, resulting in a reduction of sodium ion mobility in the sinter matrix.

The few examples of the results referred to above demonstrate that the method of measuring electrical conductance of ash pellets, detailed in the Experimental Section, is capable of yielding interesting data. However, care must be exercised in placing the pellets on the conductance wires in order to obtain consistent results. Further, since the geometry of the conductance cell could not be defined, another furnace assembly was designed and constructed which enabled both the conductance and shrinkage of an ash pellet to be measured precisely.

Simultaneous shrinkage and conductance measurements

The results of the simultaneous shrinkage and conductance measurements for a soda-glass of known viscosity, the latter measure by Napolitano and Hawkins [10] are shown in Fig. 5. In dilatometric experiments it is usual to define the sinter temperature as the point at which the thermal expansion of the apparatus is equal to the shrinkage of the sample. This is defined by the point of intersection of curves A, and A_1 on Fig. 5. It is interesting to note that the conductance curve (B) starts at exactly the same point as predicted by equation (4). At this temperature 875 K the soda-glass has a viscosity value of 10^{10} N s m^{-2}.

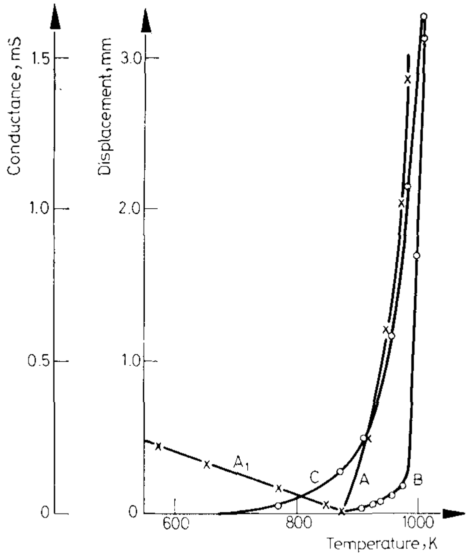

Fig. 5. Simultaneous shrinkage and conductance measurement of soda-glass: A_1 — Thermal expansion; A — Shrinkage; B — Conductance on heating; C — Conductance on cooling

A comparison of the changes in the logarithms of viscosity and conductance with inverse of temperature is shown in Fig. 6. It shows that the conductance measurements were made over a temperature range where the viscosity changes from 10^{11} to 10^6 N s m^{-2}. It was suggested earlier by Raask [3] that this is the important viscosity range in defining the rates of build-up of deposit in pulverized coal fired boilers. That is, at the top of this viscosity range a sinter bond between the ash particles occurs only after several hours, whereas at the lower range, only a few seconds are required for the same degree of bonding.

The results shown in Fig. 7 indicate that both the shrinkage curve (A) and the conductance curve (B) for a typical British coal ash start at the same temperature

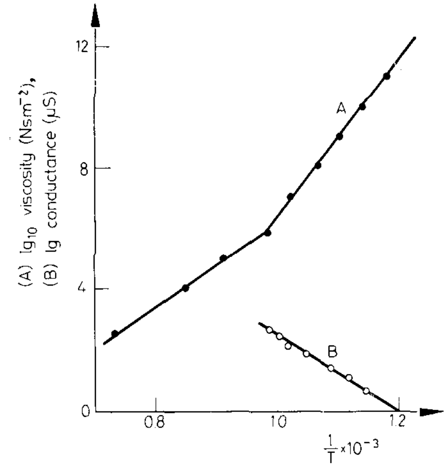

Fig. 6. Arrhenius plots of: A. Viscosity (Napolitano and Hawkins, 1962); B. Conductance of soda-glass

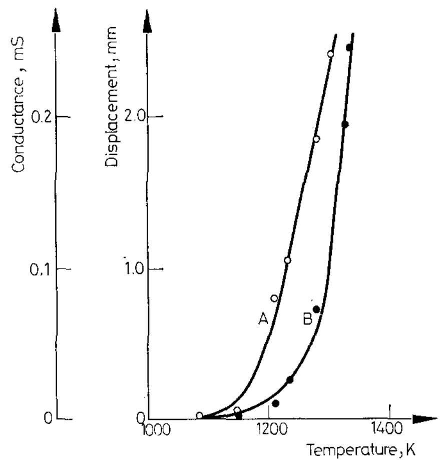

Fig. 7. Simultaneous shrinkage and conductance measurements — Pye-Hill ash: A. Shrinkage; B. Conductance

of 1100 K. The conductance curve shows the highest rate of change around 1250 K and this temperature was chosen for an isothermal test with the same coal ash (Fig. 8). In the initial stage of sintering, the conductance was proportional to the reciprocal of pellet length raised to the power 0.67 as shown in Fig. 9. At this stage the density of the pellet was approximately proportional to the reciprocal of its length since the pellet contracted more along its length under the applied load than it did along its diameter. Thus, it was confirmed that equation (4) defines fairly accurately the process of the initial coalescence of ash particles.

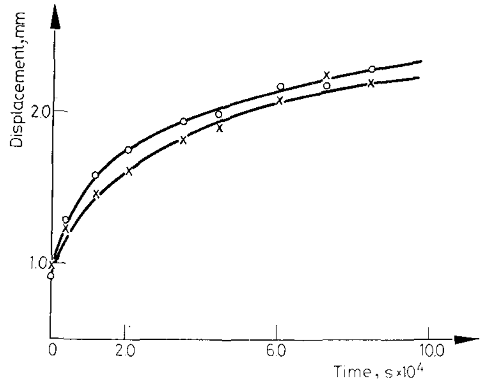

Fig. 8. Shrinkage (A) and conductance (B) at 1250 K — Pye-Hill ash

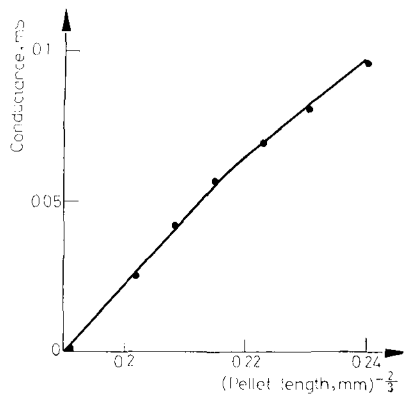

Fig. 9. The relationship between shrinkage and conductance, Pye-Hill ash at 1250 K

The preliminary results of the isothermal runs at 1250 K suggest that these are useful for testing coal ashes and their slagging potential. Pye-Hill coal ash had a conductance value of 50 μS after three hours (Fig. 8) and it has a marginal tendency for fouling when burnt in a typical pulverized coal-fired boiler. A number of other coals which are known to be non-slagging gave insignificant conductance readings of less that 5 μS after three hours at 1250 K.

For the majority of coals the shrinkage measurements can be used equally well to predict the slagging behaviour of coals. However, marked deviations from the shrinkage conductance model can occur as shown in Fig. 10. Leigh Creek ash (Australian coal) required heating to 1350 K before any shrinkage occurred (curve *A*). Meanwhile, the conductance curve (*B*) showed a marked abnormality. The curve starts at 1100 K, has a maximum at 1260 K, then a minimum around 1300 K, and finally, the conductance increased rapidly with temperature. In this

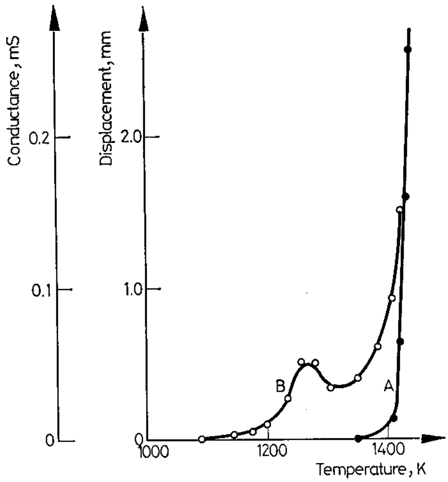

Fig. 10. Simultaneous shrinkage and conductance measurements — Leigh Creek ash. A. Shrinkage; B. Conductance

case the shrinkage curve and also the conventional ash fusion tests give erroneous assessment of the sintering and slagging behaviour of the coal ash.

The conductance changes (curve *B*, Fig. 10) suggest that there was a significant degree of sintering in the temperature range of 1200 to 1250 K, whereas the shrinkage curve does not indicate any activity at these temperatures. Our results are in agreement with those of Gibb [4] who found that compacted pellets of the ash developed a high strength at these temperatures.

Discussion

The measurement of the electrical conductance and shrinkage of ash compacts has shown that these techniques could have a potential for the development of more scientific laboratory tests of the slagging characteristics of coal ashes than are now in practice. The mathematical model in Section 2 defines closely the process of coalescence of ash particles for the majority of coals and the rate of development of sinter bond can be monitored by conductance and shrinkage measurements. Deviations from the model do occur, but these can be defined and appropriate tests could be developed for such ashes.

It is not claimed here that the test conditions as described in Section 3 are the optimum. Ash compacts of a density of 750 kg m^{-3} were chosen to be approximately equal to the density of ash landing on boiler tubes. The specific gravity of ash material is around 2300 kg m^{-3}. That is, the ratio of the volume occupied by ash particles to that of voids was 1 : 2. Also, a loading of 150 kN m^{-2} on the ash pellet, made up by the weight of the top contact rod (Fig. 2) and the force of the transducer spring, was used to ensure an electrical contact between the platinum plates and the ash sample. It may be possible to reduce the loading and thus further simulate the conditions of mechanically unstressed ash deposit on boiler tubes.

Further work on assessing the slagging characteristics of different coal ashes using the dilatometric and conductance techniques will be carried out in close cooperation with the boiler operation staff at large coal-fired power stations. The object of the work will be first to identify slagging coals, and then to assess how far the slagging characteristics of these ashes will respond to changes in boiler operation.

The measurements of the shrinkage and the electrical conductance would be useful also in other fields of powder technology. For example, the knowledge of the rates of sintering of powdered glasses and metals is essential in the manufacture of sintered, porous materials. The methods are in keeping with modern trends where experimental data are required with a minimum of labour. The equipment described in Section 2 could be readily programmed so that after initial placing of the powder compact in the furnace no further supervision would be required.

Conclusions

1. The rate of coalescence of ash particles (sintering) on boiler tubes after deposition from the hot flue gas is dependent on the viscous flow at the contact points of spherical particles. Accurate measurements of the viscosity of coal ashes in the relevant range, 10^6 to 10^{12} N s m^{-2}, are difficult, but the rate of sintering at different temperatures can be determined by measurement of the electrical conductance. This sintering model utilizes previous findings that both the viscosity and the conductance of silicate glasses and slags change exponentially with temperature.

2. Measurement of the electrical conductance of 3 mm cube pellets of ash can be made in a Leitz heating microscope. Each ash has its own characteristic conductance/temperature curves arising from heating at a rate of 5 K/min^{-1} from 1000 K to 1600 K and cooling at the same rate. The preliminary results suggest that the curves will define the sintering behaviour of different ashes more scientifically than the visual observation in the Leitz heating microscope.

3. The furnace assembly described can be used for simultaneous measurements of the linear shrinkage and the electrical conductance of coal ash compacts. The measurements can be made either by a constant rate of heating, conveniently at 5 K min^{-1}, up to the limiting temperature of the platinum furnace, 1800 K, or isothermally at any chosen temperature.

4. Usually the shrinkage and the conductance changes follow the sintering model defined by equation (4). That is, the curves for shrinkage/temperature and for conductance/temperature start at the same temperature and also the relative values of the two parameters at higher temperatures are as predicted by the equation. However, with some ashes marked deviation from the predicted model occurs

and a high degree of sintering takes place before there is any measureable shrinkage of the ash pellet. In this case the conductance measurements give a better guidance of the sintering behaviour of the ash.

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The work was carried out at the Central Electricity Research Laboratories and the paper is published by permission of the Central Electricity Generating Board.

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Résumé — Deux procédés expérimentaux différents ont été utilisés pour étudier les caractéristiques du frittage des cendres de charbon lors du chauffage. En premier lieu, un microscope à platine chauffante Leitz a été utilisé afin de suivre la contraction d'un comprimé de cendres et la conductibilité électrique a été mesurée en introduisant deux électrodes de fil de platine dans le porte-échantillon. Un autre dispositif de chauffage a également été réalisé pour suivre la contraction du comprimé de cendres à l'aide d'un capteur de déplacement linéaire; la conductibilité de l'échantillon a été mesurée par deux électrodes en platine en forme de disques. Les résultats se sont généralement montrés en accord avec un modèle de frittage reposant sur le principe du développement d'une liaison par frittage entre les particules accompagné de la contraction extérieure du comprimé de cendres et de l'augmentation de la conductibilité.

Zusammenfassung — Zwei verschiedene Versuchsverfahren wurden zur Untersuchung der Sintereigenschaften von Kohlenaschen beim Heizen eingesetzt. Zuerst wurde das Leitz'sche Heizmikroskop zur Aufzeichnung der Schrumpfung eines Asche-Pellets angewandt und die elektrische Leitfähigkeit durch Einlassen zweier Platindrahtelektroden in den Probenbehälter gemessen. Eine andere Ofenvorrichtung wurde konstruiert, in welcher das Schrumpfen der komprimierten Asche durch einen linearen Verschiebungsanzeiger verfolgt, und die Leitfähigkeit der Probe zwischen zwei Platinscheibenelektroden gemessen wurde. Gewöhnlich sind die Ergebnisse mit einem Sinterungsmodell in Übereinstimmung, das auf dem Konzept beruht, nach dem die Entwicklung einer Sinterbindung zwischen den Teilchen durch die äußere Schrumpfung der komprimierten Asche und den Anstieg der Leitfähigkeit begleitet wird.

Резюме — Для исследования характеристик спекания угольной золы в процессе нагревания, были использованы две различные экспериментальные методики. В первой методике был использован нагревательный микроскоп Лейца для регистрации усадки зольных гранул и была измерена электропроводность путем присоединения двух платиновых проволочных электродов к носителю образца. Во второй методике была построена нагревательная установка, в которой усадка плотной золы контролировалась линейно смещаемым датчиком, а электропроводность образца измерялась между двумя платиновыми дисковыми электродами. Результаты согласуются с моделью спекания, основанной на представлении, что развитие спекания между частицами сопровождается усадкой плотной золы и увеличением электропроводности.