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THE EFFECT OF THERMAL TREATMENT ON SOME CHARACTERISTICS OF ANIMAL CARBON

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ABSTRACT

The calcination of animal bone carbon and bone carbon waste was studied in order to characterize the processes' optima up to 1000°C. The thermal treatment in air and in vacuum, and subsequent weight loss determinations verified dehydration, dehydroxylation and decarbonization processes. The adsorption of nitrogen and water was measured to differentiate between these processes.

The calcination course showed optimum weight losses up to 500°C and the final loss was reached at 700°C. The surface area of the vacuum-treated samples attained a limiting value at 300–350°C. Below 400°C the surface area of air-treated samples increased. Above 400°C the nitrogen adsorption showed a considerable decrease in surface area, denoting solid-state sintering above 500°C. This process of sintering was characterized by an exponential function between the surface areas and temperature, i.e. $S=k\, e^{E/RT}$, from which the energies of sintering were calculated. The amount of water adsorbed and the surface area were correlated by the relation $W=kS$, i.e. the number of active sites for water chemisorption per unit area is constant. The dehydration, dehydoxylation, decarbonization and sintering processes are relatively retarded in the bone carbon waste.

INTRODUCTION

This work presents the results of a project designed to use bone ash in the production of bone china wares. This class of white wares [1] has not yet been produced or studied in Egypt.

The bone ash consists almost entirely of hydroxyapatite [$Ca_{10}(PO_4)_6 \cdot (OH)_2$]. The ash is obtained after cleaning the bones and calcination below 900°C in a stream of air sufficient to ensure complete oxidation of the remaining organic matter [2]. The residual organic matter in the bone ash after calcination is known to putrefy and the gases formed retard the maturity of the bone china body. The rate of heating during the calcination of the bone ash seems to determine the characteristic colour of the bone china. Such colour has been indicated to be not directly related to the carbon content of the ash but to the ease by which the carbon burns out. A slow heating rate during the calcination process leaves a carbon that burns out easily, whereas fast heating leaves a slow burning dangerous form of carbon (i.e. fixation of carbon) [2].

The bone carbon is usually employed for the refining process of sugar, while the bone carbon waste is produced after the refining process. Such waste is of special

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interest as it may be considered as a cheap source of bone carbon since it accumulates year after year without any possible use at present.

In view of the facts outlined above, the present work was undertaken to characterize the bone carbon and bone carbon waste in terms of weight loss, surface area and chemisorbed water.

EXPERIMENTAL

Materials

Two samples of animal bone carbon, supplied by the Sugar Refining Co. at Hawamdya, Egypt, were selected for the present study. These two samples are the fresh bone carbon (Ad) and the waste bone carbon after the refining process (Adw).

Heat treatment

In air

The two samples were heated in porcelain crucibles in an upright electrically heated furnace in the temperature range 25–1000°C at intervals of 100°C. The sample temperature was increased at a rate of 10°C min^{-1} throughout the course of heating. After reaching each desired temperature, the samples were held for 2 h and then removed from the furnace (i.e. dynamic technique). The samples were accurately weighed before and after each experiment to determine the losses due to the processes of dehydration, dehydroxylation and decarbonization.

In vacuum

Another set of Ad and Adw samples was heated in vacuum (10^{-6} Torr) up to 350°C. The weight loss after heat treatment was recorded for both samples as a result of dehydration and outgassing.

Nitrogen adsorption measurements

The surface areas of the Ad and Adw samples and also those thermally treated in air and in vacuum at various temperatures were measured from nitrogen adsorption at −196°C. The conventional type volumetric apparatus was used.

Water adsorption measurements

The chemisorbed water was determined using a microchromatographic technique for both samples and those thermally treated. Each sample (0.1 g) was charged in a silica tube connected directly to a thermal conductivity detector. A flow of helium (60 ml min^{-1}) free from oxygen and moisture was employed. Water was injected in microquantities 1, 2 and 3×10^{-3} ml at 100°C after the outgassing and removal of water from the sample at 550°C in a stream of helium. After the physisorbed water was completely desorbed at 100°C, the temperature of the sample was sharply increased up to 550°C and the amount of chemisorbed water was determined.

RESULTS AND DISCUSSION

Air thermal treatment

The results of losses upon thermal treatment of both Ad and Adw samples are graphically represented in Fig. 1. It can be seen that both samples exhibit the same behaviour in the sense that the temperature ranges up to 500°C show the maximum weight losses. These losses at each temperature range are of the same order of magnitude up to 400°C, then a considerable decrease is noticed, as given in Table 1. These results can be attributed to the destroying effect of the chemical structure of the bone.

The maximum recorded losses at 1000°C are 17.33 and 15.835% for Ad and Adw, respectively. The typical loss on ignition at 1000°C found for the dicalcium phosphate dihydrate produced from bones was indicated to be 24% [3]. The lower values obtained for the present samples (composed of hydroxy appatite as indicated by X-ray) are due to the fact that these samples are only cleaned and charred animal bone without calcination or curing. A difference in weight loss between the two samples can be observed at 150°C, where the Ad sample loses 3.25% while the Adw loses only 2.2%. This means that the water vapour and volatiles can be removed with higher rates in the Ad sample up to 150°C.

The drastic increase in the rate of loss from 200 to 400°C indicates that, in addition to water and gases, some carbon could also be removed by the combustion process. Up to this temperature (400°C) the samples are still black in colour. Further increase in temperature >400°C causes weight losses but to a lesser extent, i.e. lower

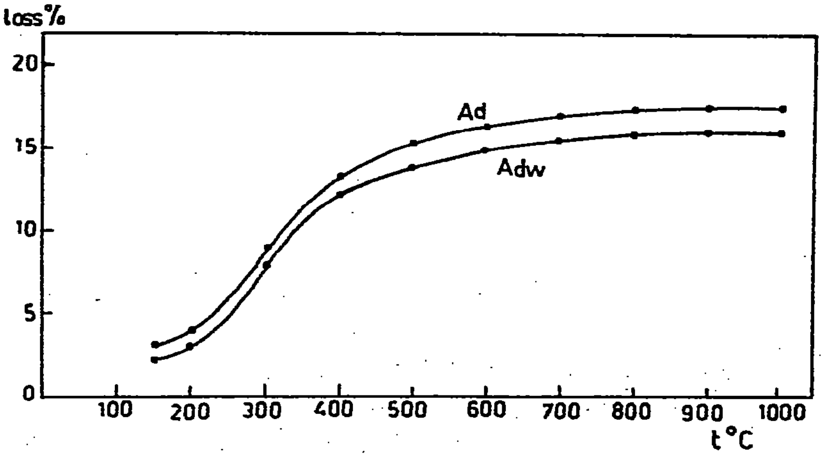

Fig. 1. % Weight loss of Ad and Adw samples as a function of temperature.

Table 1

% Weight losses in different temperature ranges

	Temperature range (°C)			
	150–200	200–300	300–400	400–500
Ad	0.7	5	4.5	2
Adw	0.7	5	4.5	1.7

rate. The colour of both samples becomes lighter and finally at ≥700°C both samples are white, proving that all the carbonaceous matter has been burned out, leaving the tricalcium phosphate.

The reactions occurring during the calcination are complex, and it has been indicated that the purified bone (dicalcium phosphate dihydrate) loses four molecules of water >150°C and one water molecule above 300°C [3]. Taylor [4] indicated that the dehydroxylation of bone ash (hydroxyapatite) starts at above 775°C according to the reaction

$$Ca_{10}(PO_4)_6(OH)_2 \overset{775°C}{>\rightarrow} 3\beta\text{-}Ca_3(PO_4)_2 + CaO + H_2O$$

The present reactions seem to be rarely complete at temperatures below 500°C, as shown by the weight loss results and confirmed by DTA of both samples using a Dupont thermal analyzer. A heating rate of 10°C min^{-1} was employed in the temperature range room temperature –1000°C. The DTA feature (Fig. 2) is a broad endothermic peak with its maximum at 220°C. This is followed directly by an exothermic one having its maximum at 380 and 410°C for Ad and Adw samples, respectively. The endothermic peak is related to the loss of all water present, while the exothermic peak is attributed to the oxidation of carbonaceous matter [5]. The absence of any other characteristic peaks proves the completion of such reactions below 550°C.

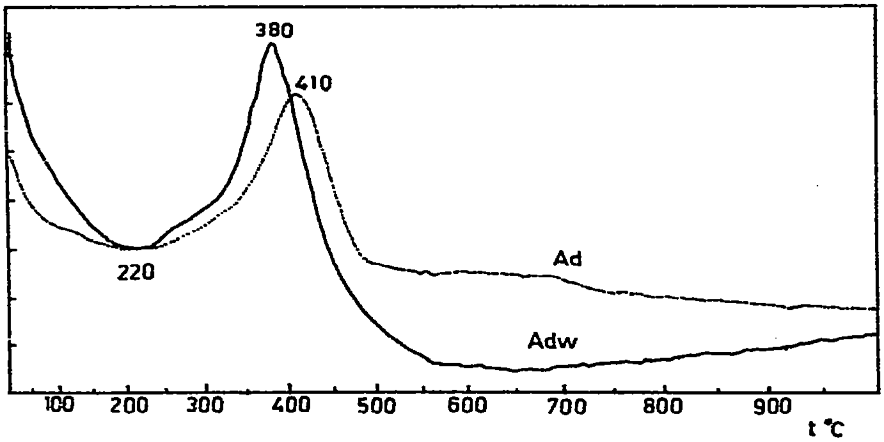

Fig. 2. Differential thermal analysis of Ad and Adw samples.

Vacuum thermal treatment

The results of losses of both Ad and Adw samples heated in vacuum are graphically represented in Fig. 3 from which it can be observed that increasing the temperature is accompanied by an increase in the weight loss of the samples. The maximum recorded losses are 5.5% for Ad and 3% for Adw, obtained at 350°C, and represent the water and gases only as there is no oxygen available for the combustion of the carbonaceous matter.

The weight loss values achieved up to 200°C in vacuum which vary from 4.9 to 2.1% for Ad and Adw samples and at complete dehydration at 350°C the values of 5.5 and 3.0%, suggest that the reactions proceed as a result of the formation of nuclei at certain localized spots in the reactants followed by a relatively rapid growth of these nuclei. This together with the decreasing surface area values are in a good agreement with Mample's theory [6] which states that the dehydroxylation process of solids obeys the equation of phase boundary controlled reactions for a sphere reacting from the surface inwards. Thus, the contracting envelope suggested by Mample [6] and applied by many investigators in the dehydration and dehydroxylation of solids [7,8] could be satisfactorily applied to the present data.

Comparing and contrasting the results of losses obtained from the thermal treatment of both samples in air and in vacuum (Table 2), it is clear that the differences in losses are 11.83 and 12.835% for Ad and Adw, respectively. This proves that the Adw sample contains ~ 1% more carbonaceous matter gained during the refining process.

Nitrogen adsorption

The results of the surface area measurements of the original samples (Ad and Adw) and those thermally treated in vacuum and in air are cited in Table 3. The surface areas of all samples are calculated by applying the BET equation [9]. It can be seen from Table 3 that the Ad samples either the original or that heated in air or

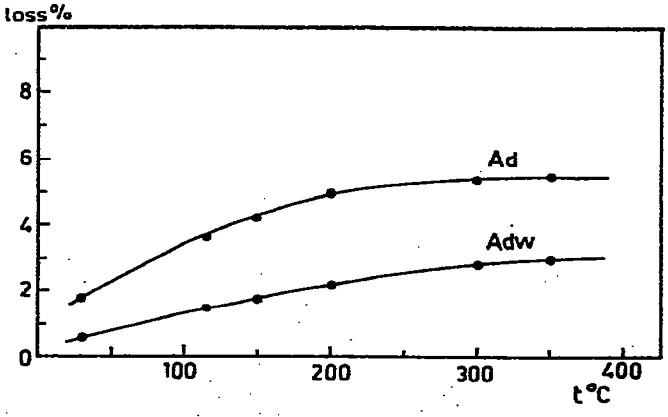

Fig. 3. % Weight loss of Ad and Adw samples heated in vacuum.

Table 2

The weight losses of Ad and Adw in vacuum and in air at different temperatures

Temperature (°C)	Ad Vacuum	Ad Air	Ad Diff.	Adw Vacuum	Adw Air	Adw Diff.
150	4.1	4.1	0.0	1.7	2.2	0.5
200	4.9	5.0	0.1	2.1	3.9	1.8
250	5.2	7.0	1.8	2.5	5.0	2.5
300	5.4	10.0	4.6	2.8	8.0	5.2
350	5.5	13.3	7.8	3.0	10.7	7.7
1000	(5.5)[a]	17.33	11.83	(3.0)[a]	15.835	12.835

[a] These represent the limiting values obtained at 350°C.

in vacuum, possess higher surface area values than their Adw sample analogues. This may be attributed to the fact that the Adw contains another carbonaceous matter which covered the surface of the Adw sample and also due to the higher rate of loss in the Ad sample than the Adw.

The surface areas of both samples are found to increase upon increasing the temperature up to 400°C. Such pronounced increase may be attributed to the dehydration, outgassing, as well as decarbonization processes that lead to a more accessible surface for adsorption. The higher value achieved at 150°C for the Ad sample when heated in air coincides with the weight loss values. The differences in the surface area values of both samples when heated in air and in vacuum are related to the oxidation of some of the surface carbon leaving a more porous structure. The limiting surface areas reached at 300–350°C for both specimens heated in vacuum indicate the complete loss of the total water content and some of the volatile organic matter.

Further increase in the heating temperature in air >400°C causes a significant drop in the surface area of both samples, proving the occurrence of the sintering phenomenon. The surface area temperature curves (Fig. 4) are characterized by two stages. The first continues up to 400°C and is characterized by the marked increase in the surface area. The second begins at a temperature >400°C and is characterized by a decrease in the surface area denoting solid-state sintering and

TABLE 3

The surface areas of Ad and Adw samples and their thermally treated derivatives

	Treatment temperature (°C) 100	150	200	300	350	400	450	500	550	600
Ad (air)	112	145	111	132	140	156	90	64	22.2	8.7
Ad (vacuum)	92	125	118	110	100					
Adw (air)	66	63	63	118	120	132	79	55	46	35
Adw (vacuum)	58	58	73	69	66					

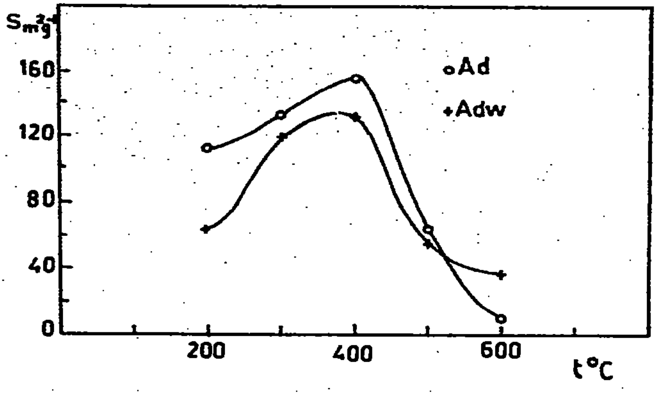

Fig. 4. Surface area variation of Ad and Adw samples with temperature.

resembles the first stages of the sintering of oxide ceramics [10–12]. Physical and mineralogical changes are also taking place [13].

From the above results it can be observed that the relation between surface area and temperature is an exponential function, then

$$S = A\,e^{E/RT}$$

or

$$\ln S = \ln A + E/RT$$

where S is the surface area in $m^2\,g^{-1}$, T is the absolute temperature at which the sample was treated, E is the energy of sintering, and A is a constant.

A plot of ln S (surface area) vs. $1/T$ for both samples (400–600°C) (Fig. 5) confirms two reaction courses. The first proceeds, in both samples, with an energy of 8 kcal $mole^{-1}$ (up to 500°C in the case of Ad). The other course is more obviously shown in the Ad sample at >500°C with an energy of 26.5 kcal $mole^{-1}$. However,

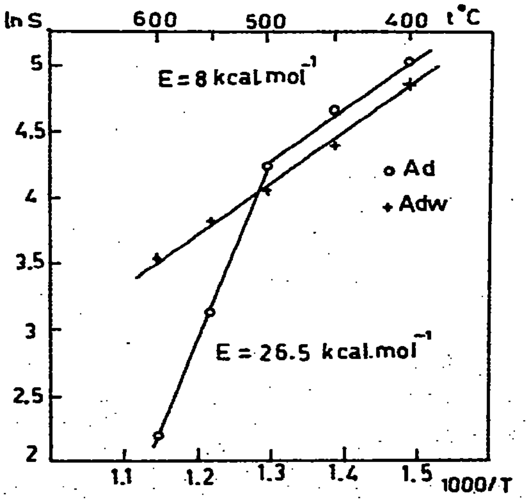

Fig. 5. Plots of ln S (surface area) vs. $1/T$ (absolute temperature) for Ad and Adw samples.

the only one straight line obtained for the Adw sample indicates that both courses overlap and the second course may be detected only at temperatures higher than 600°C. This is confirmed by the weight loss values denoting the presence of 1% more carbonaceous matter in the Adw sample when heated at 1000°C for 2 h. The presence of such matters retards, to a certain extent, the sintering of the Adw sample.

Water adsorption

The results of the chemisorbed water, ash content, and BET surface areas for both samples at each treatment temperature are included in Table 4. The peak areas corresponding to the chemisorbed water for each sample are independent of the amount of water injected.

From Table 4 it can be seen that the samples having high surface areas adsorb more water molecules chemically and vice versa. At a temperature $\geqslant 500$°C the pronounced decrease in the chemisorbed water on the samples coincides with the drop in their surface areas. This proves that a certain correlation can be established between the amount of water adsorbed and the surface area available of the solid under investigation: then w is proportional to S or

$$w = k'S$$

Taking into consideration that pure carbon is hydrophobic, any chemisorbed water should be due to the presence of ash or any functional groups associated with the carbon. These groups could be removed at temperatures above 500°C. Consequently, the chemisorbed water in this system is mainly dependent on the ash content. Then

$$w/a = kS$$

where a = ash content, or

$$W = kS$$

TABLE 4

The dependence of the adsorptive capacities of the samples on the ash content and the surface area

Treatment temperature (°C)	Ad sample				Adw sample			
	a	S	c.w.	W	a	S	c.w.	W
Original	0.8113	112	3.816	4.704	0.8324	66	2.307	2.772
200	0.8540	111	3.981	4.662	0.8486	63	2.249	2.646
300	0.9014	132	4.997	5.544	0.8956	118	4.438	4.956
400	0.9540	156	6.283	6.552	0.9406	132	5.215	5.544
500	0.9705	64	2.609	2.688	0.9550	55	2.206	2.310
600	0.9870	8.7	0.360	0.365	0.9581	35	1.408	1.470

a=Ash (g/g carbon); c.w.=chemisorbed water (μl/g carbon); S=surface area (m^2/g); W=cw/a= chemisorbed water/g ash.

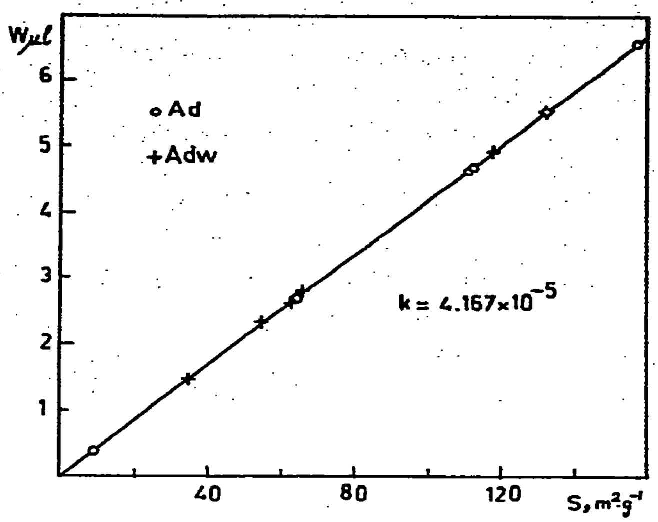

Fig. 6. The relation between surface area and chemisorbed water.

TABLE 5

The number of active sites for water chemisorption

Temperature t (°C)	S_{BET} (m^2 g^{-1})		No. of active sites $\times 10^{-20}$ [a]	
	Ad	Adw	Ad	Adw
Original	112	66	15.68	9.24
200	111	63	15.54	8.82
300	132	118	18.48	16.52
400	156	132	21.84	18.48
500	64	55	8.96	7.7
600	8.7	35	1.22	4.9

[a] No. of active sites $=0.14\times 10^{20}\times S$ (S=surface area).

The constant k is defined as the amount of water adsorbed per unit area.

A plot of W vs. S gives a straight line passing through the origin (Fig. 6) which proves the validity of this equation for the correlation of the chemisorbed water and the BET surface area. From Fig. 6 the value of k is found to be 4.167×10^{-5}, and corresponds to 0.14×10^{20} water molecules per unit area. If we consider that for each active site on the surface only one water molecule is adsorbed, then the number of active sites for water chemisorption can be calculated for each sample. The results of these calculations are listed in Table 5.

CONCLUSIONS

From the results obtained in this investigation the following conclusions are drawn:

(1) The thermal treatment of animal carbon and the waste animal carbon showed

nearly the same tendency for weight loss;

(2) Thermal treatment in air up to 600°C was accompanied by dehydration, dehydroxylation and decarbonization (including outgassing);

(3) Thermal treatment in vacuum was accompanied only by dehydration and dehydroxylation and a limiting loss was attained at 300–350°C;

(4) The surface area of the air thermally treated samples increased up to 400°C, above which the decreased surface area denotes solid-state sintering. The difference in the values of energy of sintering was attributed to the impurities captured during the refining process by the carbon waste;

(5) A direct relationship is established between the amount of water adsorbed, ash content and the surface area. Accordingly, the number of active sites for water chemisorption was calculated.

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