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FUEL RESEARCH INSTITUTE OF SOUTH AFRICA.

TECHNICAL MEMORANDUM NO. 8 OF 1963.

A CONTRIBUTION TO THE STUDY OF THE HEAT EFFECTS
OF THE ADSORPTION OF WATER BY COAL.

By:

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The influence of moisture on the course of the oxidation or spontaneous heating of coal has been widely discussed in the literature ^{*)} but few authors have drawn definite conclusions regarding the nature and extent of such an influence.

The present paper is confined to a consideration of the heat effect of moisture adsorption which may, by raising the temperature of the coal, accelerate the oxidation reaction.

The adsorption of water vapour is of particular significance in this respect because of the high normal heat of liquefaction of water (10.5 kilo cal/mole) and its heat of adsorption which is considered to be at least as high.

It has been determined for example that under certain conditions an increase in the moisture content of a coal by 1%, may raise the temperature of the coal by more than 17°C⁴⁾.

As many factors come into play in the process of adsorption of moisture and the consequent heat evolution and temperature rise, it is advisable to consider, first of all, factors contributing to the total heat that may be evolved during the adsorption process (assessible surface, surface character and magnitude of the heat of adsorption) irrespective of any time factor.

Secondly, attention is given to factors affecting the rate of heat evolution (pore size, particle size, pressure) and finally some consideration is given to the possible temperature rise under specified conditions.

A. Factors/

*)

Literature surveys have been provided, for example, by Coward ¹⁾, Davis and Reynolds ²⁾, and Gauger ³⁾.

A FACTORS CONTRIBUTING TO THE TOTAL HEAT EVOLUTION.

1. The Pore Volume of Coals and the accessibility of Surface to Moisture.

Being a porous substance the surface area of coal is almost entirely present in pores of varying dimensions. Much of the surface area and pore volume determined by conventional methods may, however, not be accessible to water molecules and it appeared desirable to determine, at the outset what pore volume may be accessible to them.

This pore volume was determined by the method of King and Wilkins⁵⁾ i.e. the sample was soaked in water and subsequently dried until the liquid film had just disappeared from the surface of particles. The resulting moisture content - which in this paper will be referred to as "the maximum inherent moisture content" - was used to determine the pore volume.

The results obtained for a number of South African coals are given in column 3 of Table 1. The pore volume determined from mercury and helium density measurements is given in column 4 while the last column shows what percentage of the latter pore volume is accessible to water molecules. Approximate dry mineral matter free carbon and oxygen figures are given in columns 1 and 2 to characterise the coal samples. Some information on the pore size distribution (high pressure mercury method) is given in Table 2.

As expected the pore volume accessible to water molecules is much smaller than that determined by the mercury and helium density method. It is striking, however, that in some instances it represents only 18% - 20% of that volume.

2. The Effect of Rank.

(a) The accessible pore volume and surface area.

Accepting the carbon content of the coal as an indication of rank it is evident from Tables 1 and 2 that the coal becomes more "compact" with increasing rank. The results quoted in Tables 1 and 2 also suggest that the surface area accessible to water molecules will be even more drastically affected by rank than the pore volume.

(b) The combined effect of surface area and the surface character.

TABLE 1.

Values of the Pore Volume derived from Helium and Mercury Densities and from the Maximum inherent moisture content.

Coal Sample	Approx. C	D.M.M.F. O	Pore Volume according to Moisture Method and Hg-He Density Method (c.c./gram)		3 as percentage of 4.
	1	2	3	4	5
1Z	80	14	0.100	0.176	56.8
2V	79	13.5	0.092	0.160	57.5
3L	80	11	0.097	0.150	64.8
5SW	82.5	10	-	0.125	-
6A	82	11	0.057	0.132	43.2
7Co	85	8	0.04	0.121	33.1
8TN	83.5	9	0.043	0.130	33.1
9NS	84.5	8.5	0.035	0.118	29.6
10K	84	8.5	0.038	0.121	29.2
11D	85	8	0.035	0.130	26.9
12DN	85.5	6	0.026	0.124	21.0
13C	87	5	0.020	0.110	18.2
14B	88.5	3.5	0.020	0.086	23.2

TABLE 2.

Pore Size Distribution in Some Coals.

Sample	Approx. C	D.M.M.F. O	% of Pore Volume in Pores of Dia. Range				
			100A	100/500	500/1000	1000/5000	5000/5u
1Z	80	14	59	9.7	9.7	18.1	3.4
15K1	84	8.5	57	14.5	16.0	9.4	3.1
16E	89	3.5	62	22.0	5.1	9.0	1.8

Adsorption of moisture can only occur on the accessible surface if this is sufficiently hydrophyllic.

In the case of carbons, investigators such as Pierce and Smith⁶⁾ Healy, Yu and Chessick⁷⁾ and Arnell and McDermott⁸⁾ have shown that the oxygen content of the carbon and its affinity for water are closely related. Although the oxygen functions in coal may differ from those in oxidised carbon, it appears to be accepted (see e.g. van Krevelen and Schuyer, "Coal Science" Elsevier 1957 p. 126) that the hydrophyllic character of coal surfaces is largely governed by the oxygen content of the coal.

If this is correct the lower rank coals having the higher accessible surface and oxygen content should adsorb more moisture with a relatively greater total heat generation than the coals of higher rank.

This was tested by conducting heat of wetting experiments in the conventional manner but using water instead of menthanol.

The results (see Table 3) show that in fact the heat of wetting is highest for the low rank coal with the highest oxygen content.

TABLE 3.

Heat of Wetting in Water of some of the
Coals shown in Table 1.

Sample	Approximate % C.	D.M.M.F. % O	Heat of Wetting (Cal/gram of Water
1Z	80	14	665
3L	82	11.3	650
6A	82	11	651
8TN	83.5	9	640
9NS	84.5	8.5	633
12DN	85.5	6	625
14B	88.5	4	630

It must be stated, however, that the calorimetric technique used was not sufficiently accurate to record a
slow /

slow evolution of heat very accurately. Such a slow evolution of heat was more likely to occur with the higher rank (compact) coals so that the results obtained with these coals might be somewhat low.

With this proviso these results will be used to develop the following argument.

From the approximate relationship:

Heat of Wetting = Heat of adsorption - Heat of liquefaction
it follows that when heat is generated on immersion of dry or relatively dry coal in water, part at least of the water must be adsorbed with an energy release greater than the heat of liquefaction of water.

Now, assuming the amount of water taken up by the coal during the heat of wetting experiments to be equal to the "maximum inherent moisture content" one can calculate that for the coals dealt with in Table 3 the integral heats of adsorption were 75 cal/gram to 35 cal/gram higher than the normal heat of liquefaction of water, depending on the rank of the coal. Thus the effect of the greater accessible surface and of its greater hydrophyllic character is the lower rank coals is very marked and it would be of interest to determine which of the two factors is mainly responsible for the observed differences in the integral heats of adsorption between low and higher rank coals

The character of the surface will exert its influence only while the first layer of molecules is adsorbed. Information on the relative effect of the character of the surface should therefore be obtainable by comparing the heat effects during the initial phase of exposure of the clean coal surfaces to moisture with the total effect, provided that the effect of transport phenomena is negligible.

This condition can be met by sufficiently reducing the length of the path of travel of water molecules through pores i.e. by sufficient reduction of the diameter of individual coal particles.

The work of Dresel and Griffiths⁹⁾ suggests that by grinding samples to minus 240 B.B.S. the structure is destroyed/

destroyed to such an extent that the effect of relative "compactness" of coals becomes practically negligible.

From the author's own work¹⁰⁾ it was concluded that grinding to minus 60 mesh B.S.S. (such a sample contains a large proportion of much finer coal) would suffice to make the effect of transport mechanisms unimportant in the proposed study of the effect of the character of the surface.

Accordingly the following experiments were done on samples ground to pass a 60 mesh screen.

(c) The Effect of the character of the surface of the coal.

Bond et al¹¹⁾ mention heat of wetting experiments in water in which coal samples were used that had been allowed to adsorb varying quantities of water before the heat of wetting experiment was done on them.

It can be deduced from these experiments that the first quantities of water adsorbed yielded higher heat increments to the total integral heat evolvable from the coal from the dry state to that of saturation than do later quantities of moisture adsorbed.

The magnitude of these first increments varied from coal to coal being highest for the lower rank coals investigated.

Similar experiments were not done. Instead, the heat release from initially dry coal samples was studied in an isothermal calorimeter using phenol (MP 41°C) as calorimetric substance*).

The results given in Table 4 show that practically the total quantity of water adsorbed at equilibrium was adsorbed during the first hour of exposure of the sample to water vapour under given conditions of temperature and pressure. Possibly therefore any effect of transport mechanisms may be neglected.

The .../

*) This calorimeter and the general method of operation have been described elsewhere¹²⁾. For these experiments the calorimeter was used in conjunction with a volumetric adsorption system by means of which water vapour could be admitted to the coal and the changes in pressure were followed on a manometer filled with dibutylphthalate. The volume of the system was so large that the pressure drop was only a few millimeters over the first hour of adsorption. Thus the results in Table 4 were obtained at a relative pressure varying from 0.5 to 0.45.

A special container was also provided to dry the samples under vacuum before transfer (without breaking the vacuum). The drying had to be done in this way because the sample could not be heated to temperatures above 41°C in the calorimeter itself.

TABLE 4.

Heat of Adsorption of Water on Dry
Coal at 41°C and about 2.4 mm. Hg.
Water Vapour Pressure.

Period of adsorption (mins)	Cumulative Weight of water adsorbed. (grams)	Incremented heat of adsorption during period (kilo cal/mole of water)
Sample 1Z approx. D.M.M.F. % C = 80. % O = 14 Weight of water adsorbed at equilibrium by 10 grams of coal = 0.45 grams		
0 - 10	0.21	14.0
10 - 20	0.31	16.1
20 - 30	0.35	14.1
30 - 40	0.37	13.2
40 - 50	0.40	12.8
50 - 60	0.41	11.1
Sample 15 Ke approx. D.M.M.F. % C = 84, % O = 8.5 Weight of water adsorbed at equilibrium by 10 grams of coal = 0.19 grams.		
0 - 10	0.1	14.0
10 - 20	0.16	13.8
20 - 30	0.17	12.8
30 - 40	0.17	12.0
40 - 50	0.18	11.4
50 - 60	0.18	11.2
Sample 16E approx. D.M.M.F. % C = 89, % O = 3.5 Weight of water adsorbed at equilibrium by 10 grams of coal = 0.1 grams.		
0 - 10	0.08	12.1
10 - 20	0.09	11.8
20 - 30	0.095	11.5
30 - 60	Reaction too slow to obtain reasonable readings.	

The results suggest that the initial level of energy release as well as the period over which it remains at a high level depend on the rank and oxygen content of the coal.

This energy level is initially so much higher^{*)} than the normal heat of liquefaction of water that, at this stage at least, capillary condensation, if occurring at all does not appear to have any appreciable effect on the total incremental energy release.

One may, therefore, conclude that at this early stage the adsorption depends on the character of the surface and not on the accessible surface or the pore volume.

Towards the end of the experimental period the energy release decreased, approaching that of the normal heat of liquefaction of water.

During this stage where capillary condensation probably plays a part, the incremental contribution to the total heat release is comparatively small considering the quantity of water adsorbed during this period and the heat generation per mole adsorbed.

As far as heat release is concerned the hydrophyllic nature of the surface is, therefore, more important than accessible surface area or pore volume.

Bearing these facts in mind one may conclude that a higher temperature rise may result from adsorption of water vapour from the atmosphere than by complete saturation of the coal by wetting with water.

This is significant because simultaneous or subsequent oxidation reactions can only occur in the absence of saturation of the coal with water.

(d) The spacing of hydrophyllic sites.

The low rank coals have a relatively high oxygen content. Accepting the oxygen as an indication of hydrophyllic sites, the question arises whether the high oxygen content,/

*) The heat of adsorption in the first layer (Fl) may also be calculated from isotherms by applying the B.E.T. theory. Values obtained for two coals having oxygen contents of 15.8% d.a.f. and 3.8% d.a.f. were found to be 15.9 kilo cal/mole and 13.0 kilo cal/mole respectively. These values not only support those given in Table 4 but also substantiate the argument developed in this and the following paragraph of the paper.

content, or more strongly hydrophyllic nature of these coal surfaces, implies a closer spacing of hydrophyllic sites per unit of surface area accessible to water molecules.

Pierce and Smith⁶⁾ have postulated that moisture adsorption on carbon surfaces occurs by clustering on hydrophyllic sites.

If the number of sites per unit of surface area increases, i.e. the distance between sites decreases, a situation may arise where reaction between adsorbed molecules becomes large enough to be observed on adsorption isotherms.

The possibility of thus differentiating between the low and higher rank coals was investigated by studying the three coals listed in Table 2. Comparable adsorption isotherms for these samples are shown in Figure 1.

Although there is an appreciable difference in the amount of water vapour adsorbed by the three coals, the isotherms are alike in shape. There is no indication of an anomaly in the curve of the least mature coal that might be interpreted as being due to enhanced interaction between adsorbed molecules.

This range of coals is not very wide and, therefore, isotherms given in the literature^{11,13,3,5)} have been studied, but no evidence of an "interaction effect" could be found.

The less mature coals have a more open structure and at the same time higher oxygen contents than the more mature coals.

Their higher equilibrium moisture content is, therefore, not merely conditioned by the higher oxygen content, but also by the greater, easily accessible surface.

Since no anomalies occur in the isotherms, one must conclude that adsorption sites are not too closely spaced in the lower rank coals.

The higher initial heat of adsorption per mole of water adsorbed by lower rank coals must, therefore, be interpreted provisionally as an indication that in such coals the sites are more strongly hydrophyllic in character than the higher rank coals.

B. FACTORS AFFECTING THE RATE OF ADSORPTION.

The practical significance of the heat generation during adsorption of moisture will depend not only on the quantity of heat evolved, but also on the rate at which it is released .../

is released since this will largely determine the temperature to which the coal will be heated under non-adiabatic conditions.

(a) The effect of transport mechanisms and particle size.

Clearly, one of the factors that is of great practical significance in determining the rate of adsorption is the rate of penetration of water molecules to the hydrophylic sites. This will be governed by the pore sizes and the diameter of the coal particle.

Some idea of the effect of these factors may be obtained from the adsorption measurements made on various size fractions of the coals listed in Table 2.

The curves reproduced in Figure 2, (A.B.C.) demonstrate that the initial rate of adsorption is higher for coals with a large percentage of large pores (coal 1Z; 21.5% pores larger than 1000 Å; coal 16E; 10.8% pores larger than 1000 Å).

Considering a specific coal, it will be observed that while the equilibrium amount adsorbed remains practically constant, this quantity of water is adsorbed much more rapidly by the very fine coal.

Therefore, transient changes in atmospheric conditions while not appreciably affecting coarse coal may cause a considerable heat release in fine coal.

(b) The effect of pressure.

In a case where the transport of molecules may have such far reaching effects one can expect that the rate of penetration and of heat release will be affected by the force driving the adsorbate molecules to the surface viz. the relative pressure.

Changes in atmospheric conditions are accompanied by changes in the partial pressure of the moisture in the atmosphere and such changes may, therefore, enhance the rate of heat release.

The effect of changing the water vapour pressure on the rate of adsorption of moisture may be illustrated by the results/

results obtained on coal sample 1Z during gravimetric adsorption experiments using a quartz micro balance.

The samples were placed in a small aluminium foil pan attached to the quartz spiral. The spiral was suspended in a glass tube which was provided with connections to a vacuum pump and a source of water vapour.

After drying the sample under vacuum, heating the sample by radiant heat, water vapour at a predetermined constant pressure was admitted and the amount adsorbed and rate of adsorption were determined from the increase in weight of the sample.

Sulphuric acid solutions of various concentrations were used to supply water vapour at the different constant pressures required.

The rate curves obtained in the pressure range 4 mm. Hg to 22 mm. Hg. are shown in Figure 3.

It will be observed that the equilibrium amount adsorbed and the rate of adsorption are strongly dependent on the pressure even with coal samples that had been ground to pass 30 mesh B.S.S. and where, consequently, equilibrium was generally attained within about 24 hours while most of the water was adsorbed within the first hour of an experiment even at the lowest pressure used.

The effect of an increase in pressure is evident at every stage of adsorption as illustrated in Figure 4. The results on which these curves are based were obtained by allowing the coal to adsorb moisture for a given time at one constant pressure and then raising the pressure to another level. A comparatively small rise in pressure increased the rate of adsorption considerably even when equilibrium had practically been reached at the lower pressure.

C. THE TEMPERATURE RISE CAUSED BY THE ADSORPTION OF MOISTURE.

In practice coal is very seldom dried completely before stacking so that the problem of heat release and possible temperature rise may be generally formulated as follows:

A coal that has attained equilibrium conditions in contact with air of state (1) (i.e. having a temperature v_1 and a relative humidity θ_1) is brought into contact with air of state (2) (temperature v_2 and relative humidity θ_2);
how .../

how much additional moisture will be adsorbed and what temperature rise may be expected?

In this connection the following factors must be considered:

- (a) Transport phenomena may affect the rate of adsorption.
- (b) The rate of adsorption and the equilibrium amount of moisture adsorbed increases with the pressure.
- (c) The equilibrium amount adsorbed at any given water vapour pressure decreases with rising temperature.
- (d) The heat release per mole of water adsorbed decreases during the course of the adsorption.
- (e) Heat may be dissipated to the surroundings.

The problem may, therefore, be rather complex and extensive experimental work would be required to obtain all the data required for an accurate assessment of the temperature rise.

Fortunately, however, practical observations and theoretical considerations suggest simplifications whereby one can arrive at a reasonable approximation of the temperature effect and general trends without very exhaustive experimentation.

Thus the results of spontaneous heating experiments and observations, in this connection, of coal in stacks suggest that the permeability is so high, even in stacks of fine coal (minus $\frac{1}{4}$ ") that it is admissible, when seeking an approximate solution to the problem, to assume that coal situated even six to twelve inches beneath the surface of the stack will react as readily as coal at the surface of the stack to any change in the relative humidity of the atmosphere.

Considering the possible effect of heat dissipation, attention was given to the results of adsorption experiments.

It will be noted from Figure 4, (e.g. coal 1Z) that adsorption of moisture was so rapid that equilibrium was established virtually within one hour. This fact, and the general trend of the adsorption curves, suggest the application to this heat generation problem of the approach developed by van Doornum¹⁴⁾ for the spontaneous heating problem. It can thus be shown that conditions in the stack at distances greater than about 5 cm. from the surface are adiabatic to such a degree that for practical purposes, the total heat released .../

released during the adsorption of moisture by the coal in these regions may be taken into account in calculating the temperature rise.

As shown in Table 4, the incremental heat of adsorption varies during the course of adsorption, finally, approaching the heat of liquefaction of water.

Considering that in practice the coal would contain some adsorbed moisture at the outset, the initial high rate of heat release might be neglected and it is reasonable to simplify the problem by adopting an average incremental heat of adsorption value slightly in excess of the heat of liquefaction of water.

Using a figure of 600 grams cal. per gram of water adsorbed, the heat release would be 6 gram cal. for each 1% (by weight of the coal) of moisture adsorbed.

As the specific heat of coal is about 0.3 this quantity of heat would, under adiabatic conditions, cause a temperature rise of 20°C.

Adopting these simplifying assumptions, the changes occurring in fine coal of type 1Z, when exposed to air of higher humidity may be assessed by using the following simple graphical method:-

Assume coal 1Z to be equilibrium with air of state 1, 25°C, 4.7 mm. Hg. vapour pressure (or relative humidity of $\frac{4.7}{23.8} = 20.6\%$). The moisture content of the coal under these conditions is 2.5%.

The original state of the coal is indicated by the point A to Figure 5.

The curve in Figure 5, represents the adsorption isobar of coal 1Z at a water vapour pressure of 23 mm. Hg. (plotted from experimental results). Assume now that the coal is brought into contact with air of state 2, (viz. 35°C, 23 mm. Hg. vapour pressure i.e. 50% relative humidity). The coal will rapidly adsorb moisture, the change occurring as indicated by the line AB having the gradient:

$\frac{1 \text{ ordinate unit}}{20 \text{ abscissa units}}$ i.e. 20°C temperature rise for each 1% of moisture absorbed).

The .../

The immediate new equilibrium condition at 23 mm. Hg. is given by the point of intersection (B) of AB with the isobar.

The quantity of water adsorbed is: $3.7 - 2.5 = 1.2\%$
and the temperature rise therefore: 24°C .

If there is no other source of heat (e.g. oxidation) the coal would cool slowly to ambient temperature, following the isobar to point C. The rate of cooling would be slow, not only because of the reasonably adiabatic condition but also because more moisture is absorbed at lower temperature so that more heat of adsorption would be released.

The conditions assumed here may easily be met e.g. in South Africa, where rapid changes in the relative humidity from 25% to 75% and higher occur inland in one locality.

The change is very common when proceeding from the inland plateau to the coast.

Thus a temperature rise even greater than discussed here, could occur in regions of a coal stack that are also readily accessible to oxygen from the air.

By thus raising the temperature of the coal from about 25°C to 50°C or higher, the rate of oxidation would be greatly increased.

It may, therefore, be concluded that with less mature coals, at least the heat release due to the adsorption of moisture may be an important contributory factor in the occurrence of spontaneous combustion in coal.

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PRETORIA

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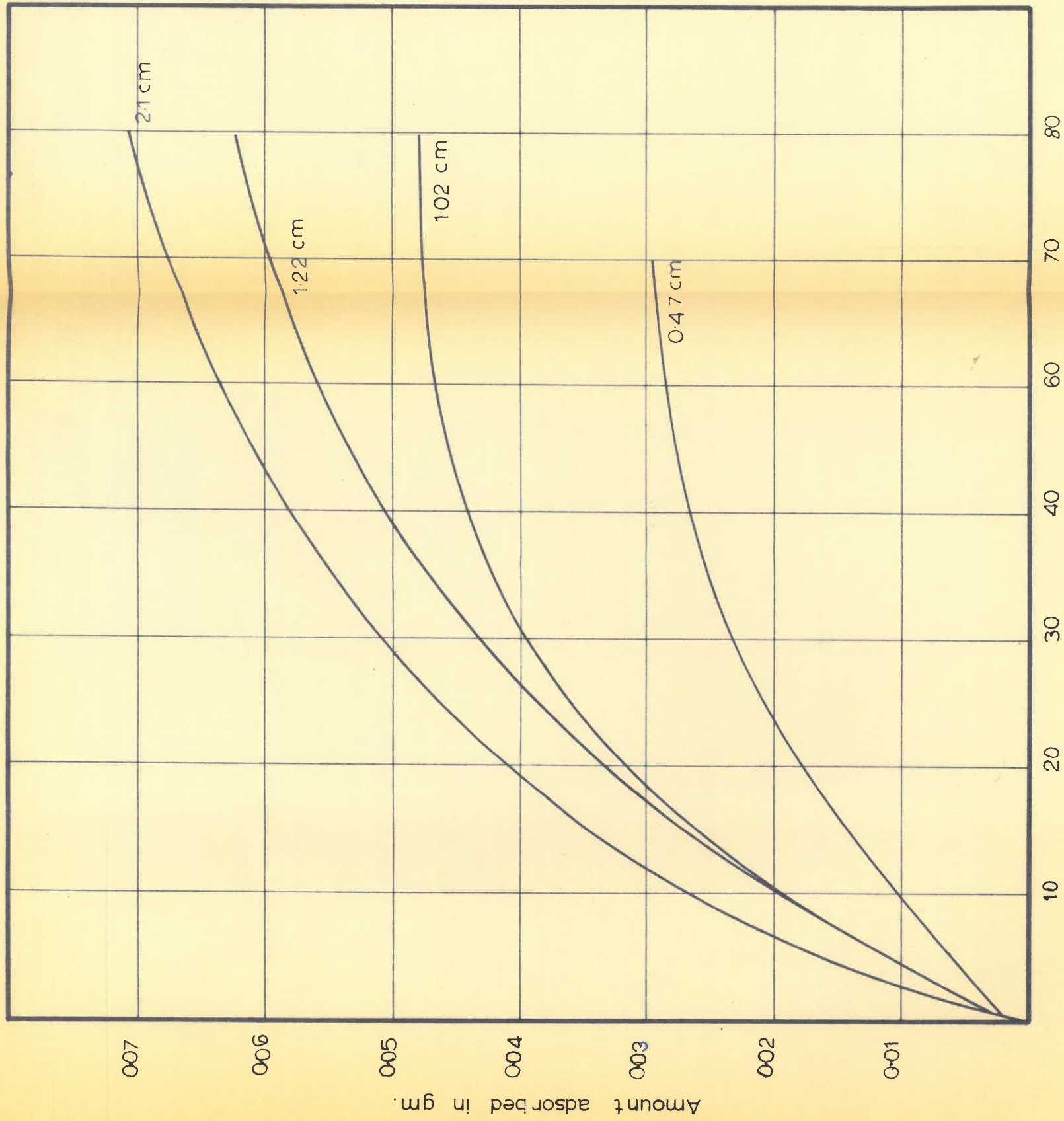
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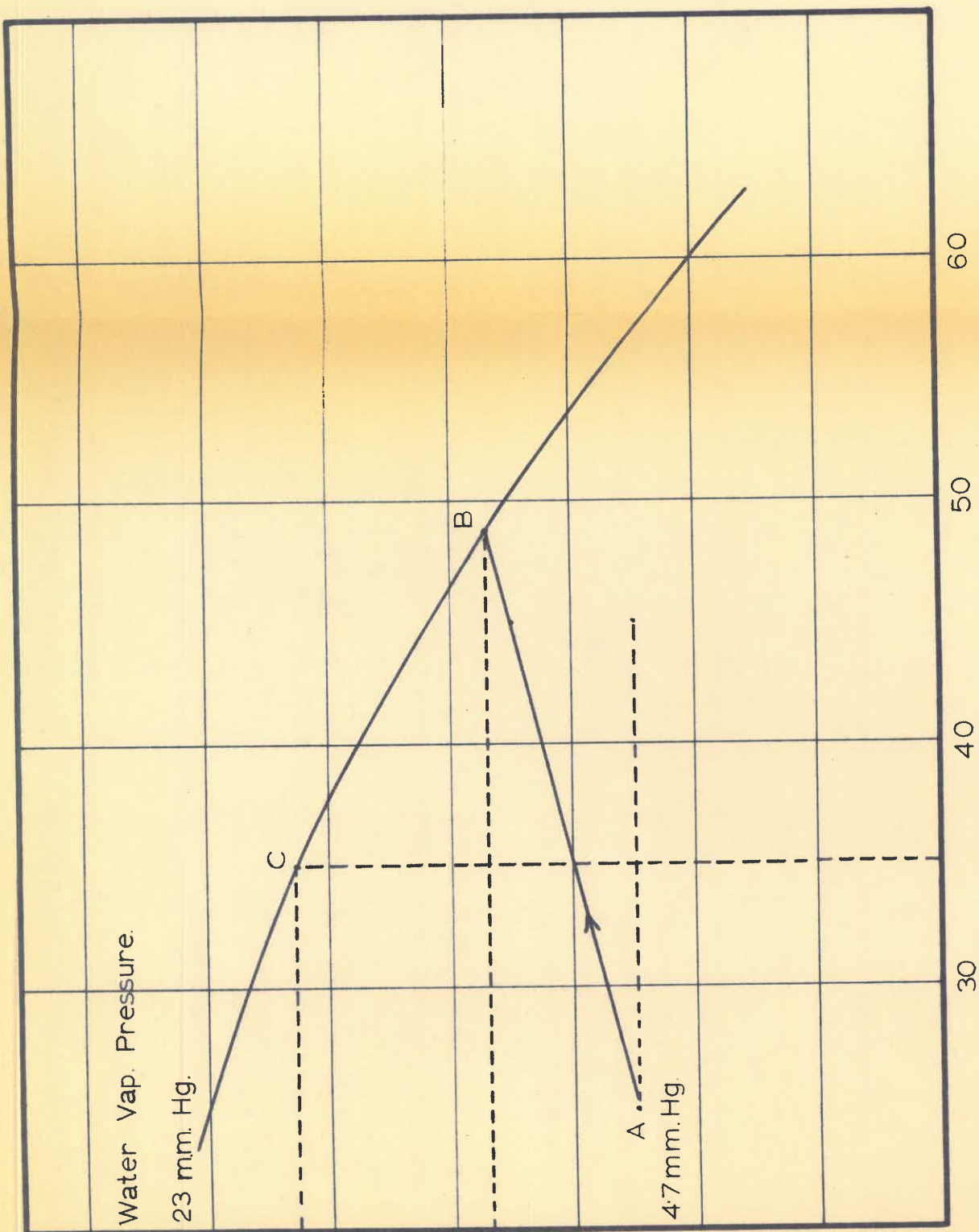
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Time in minutes.

Fig.3 The effect of pressure on the rate and amount of water vapour adsorbed by Zigma coal.

Gm. H₂O/100 g coal



Water Vap. Pressure.

23 mm. Hg.

A 4.7 mm.Hg.

Temperature in °C.

Fig. 5. Adsorption Isobar for Zigma Coal.

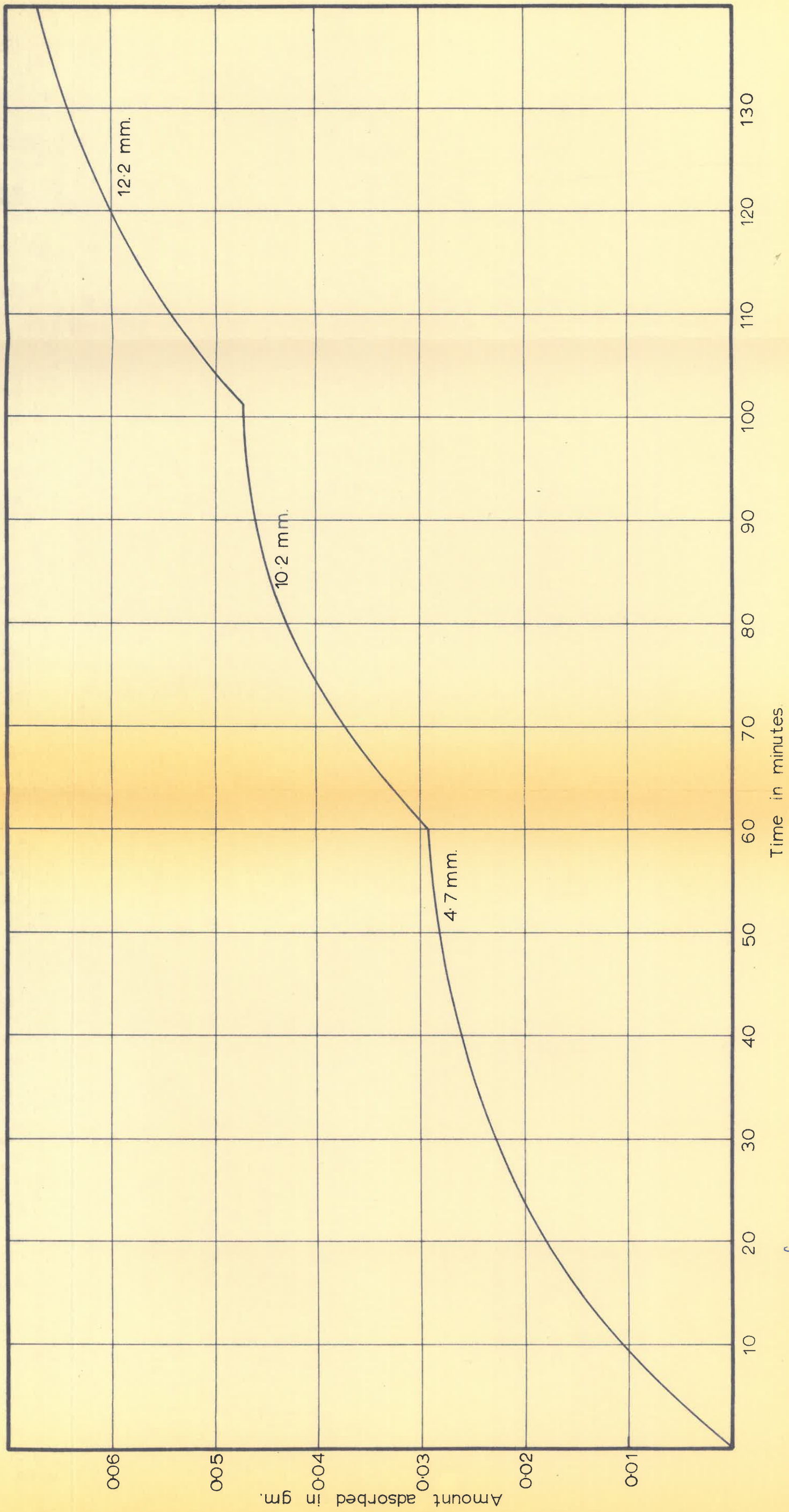


Fig. 4 Rate of adsorption at increasing pressures.

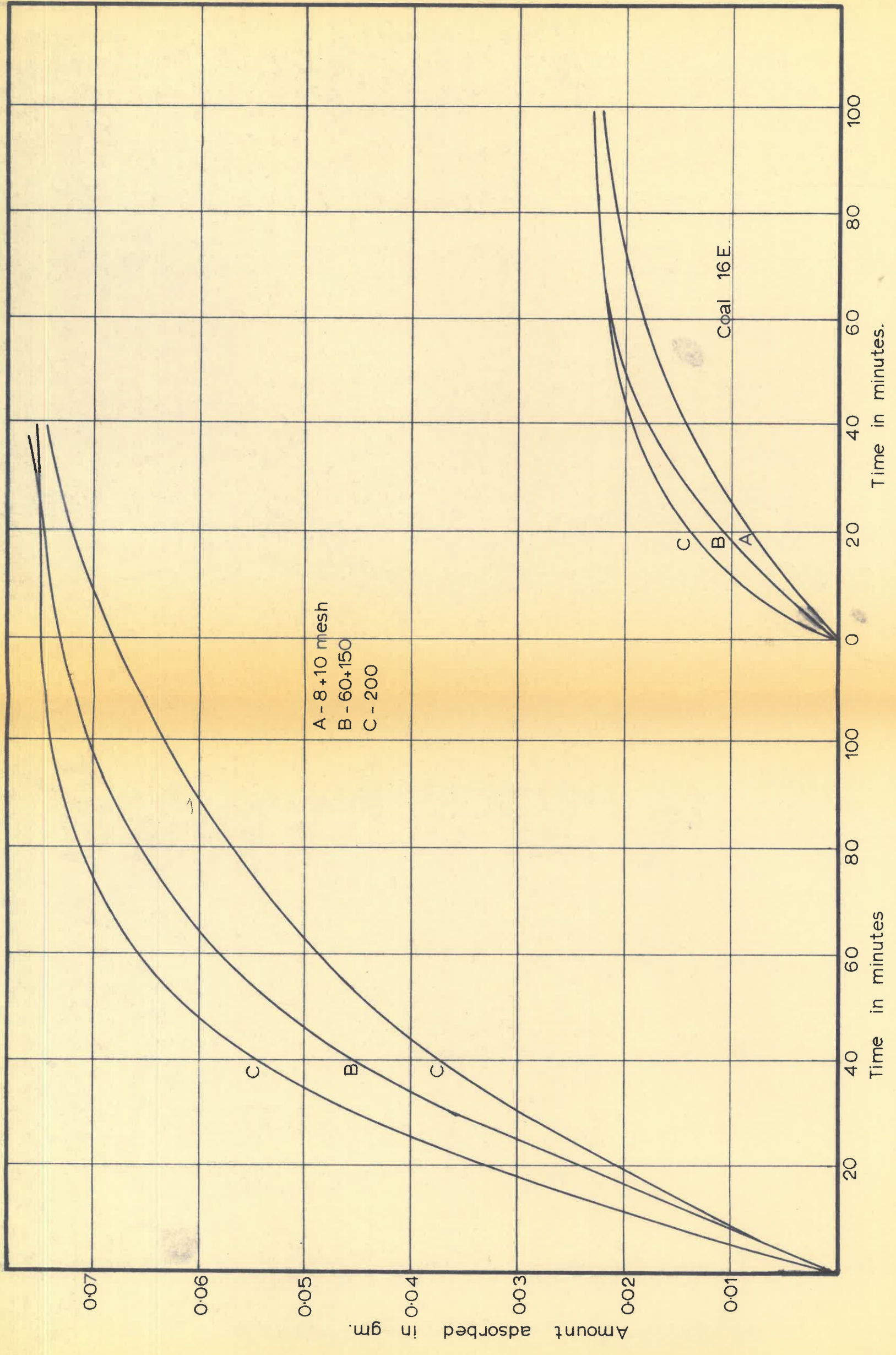


Fig. 2 The rates of adsorption of various size fractions of coal.

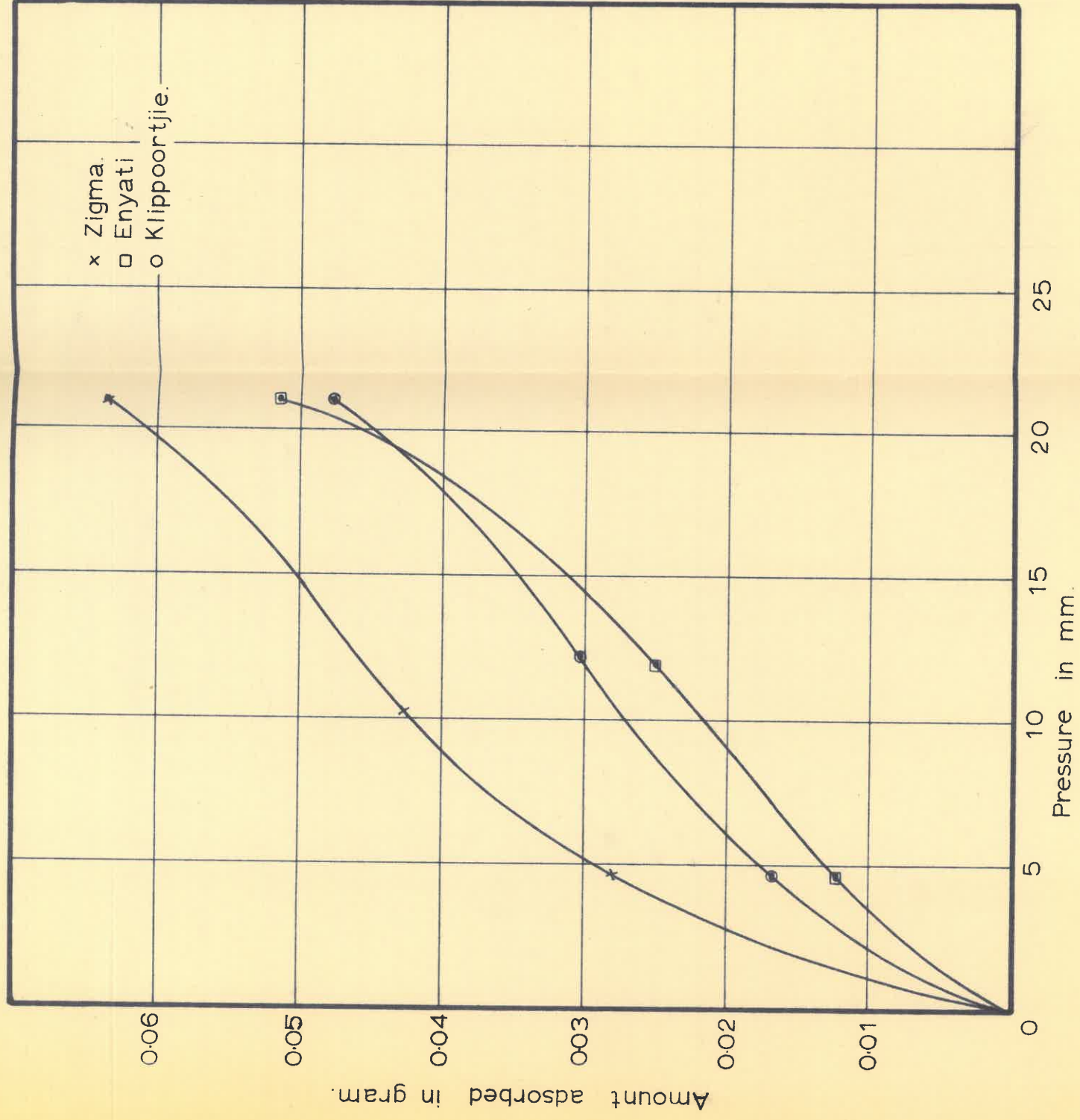


Fig.1. Adsorption Isotherms at 25° C.