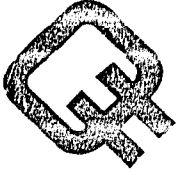
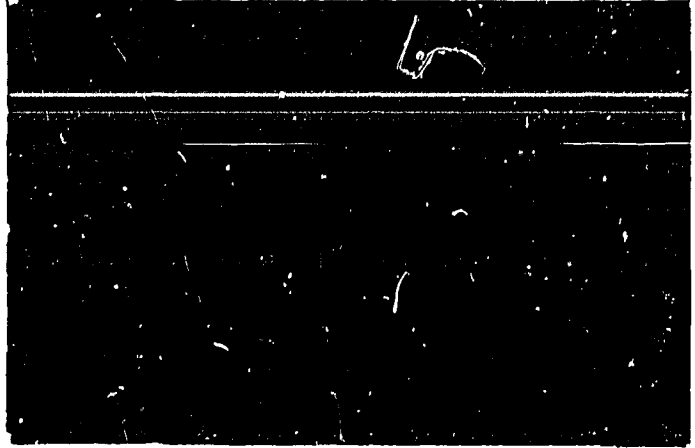
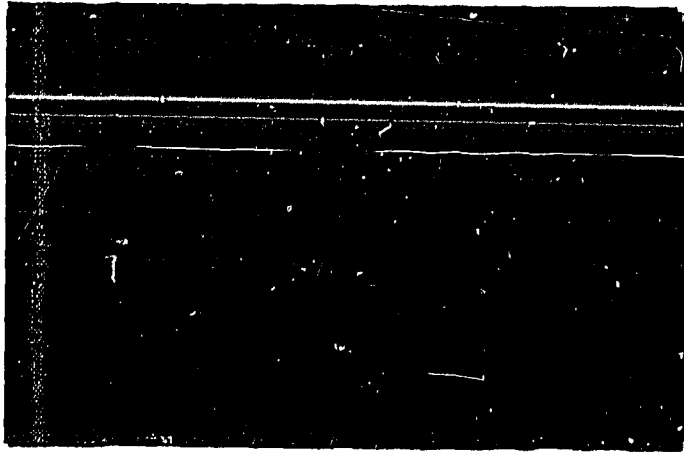


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Fuels Technology
Project*





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Adsorption of Moisture
on Molecular Sieve
Adsorbents at Low Humidity

Report # F84026

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1.0 ABSTRACT

This report summarizes the results and conclusions of a contractor's study (attached) on the performance of 4A molecular sieve under very low humidity conditions, eg, as expected in fusion reactor plants. The results suggest that:

- (a) Very efficient regeneration of the sieve to low residual moisture contents (<~2 g/100 g sieve) is necessary to ensure adequate performance with exit dew points of -60°C or less.
- (b) Based on equilibrium data, there is no significant isotopic effect at water vapor concentrations above about 100 µL/L ie, molecular sieve driers for this condition can be designed for the adsorption of DTO/HTO using easily obtainable data for the H₂O/4A sieve system.

2.0 BACKGROUND

Current design concepts for tritium control in fusion reactor tritium handling systems emphasize the use of molecular sieves for adsorption of the oxidized forms of tritium both for glove box clean-up as well as for the much larger ventilation and emergency tritium clean-up systems. Molecular sieve adsorption systems have been in use for many years at CANDU stations as part of the D₂O vapour recovery systems since there is not only a radiological need to remove tritium but also a strong economic concern because of the high cost of D₂O associated with the tritium.

The major difference between the application of molecular sieves to CANDU and fusion reactor tritium control systems is that some fusion reactor systems are likely to have lower inlet humidities and much higher tritium activity levels requiring very high decontamination factors (~1000). At very low water vapour concentration, the available information on adsorbent performance is fragmentary and comparison is difficult because of differing adsorbent activation

conditions. In a previous study/1/, it was found that the capacity of the molecular sieve adsorbents was lower than predicted from manufacturer's equilibrium capacity data. A limited study was therefore contracted out to Dr. D.M. Ruthven at the University of New Brunswick (UNB). The main objectives of this study were:

1. To measure accurately the equilibrium isotherms for water on 4A sieve and to account for anomalies observed at very low water vapour concentrations.
2. To compare adsorption capacity for light and heavy water, and
3. To obtain data for the prediction of full scale adsorber performance.

This report summarizes the results and conclusions and the full report and two addenda from UNB are included in Appendix A and B.

3.0 SUMMARY OF RESULTS OF UNB STUDY

3.1 Isotopic Effect

Determination of static equilibrium isotherms (amount of water adsorbed as a function of water vapour pressure at a given temperature) was facilitated with a readily available gravimetric balance. Static isotherms were measured for both H₂O and D₂O at 30 and 250°C. At water vapor concentrations above about 100 µL/L, there was no significant difference between the isotherms for D₂O and H₂O (some scatter in the data occurred at about 10 to 100 µL/L where the adsorption and desorption rates are slow and additional data in this range are required). It is therefore likely that the isotherms will be similar for HTO and DTO and an adsorber bed design based on equilibrium capacity data obtained with H₂O will be valid for all isotopic forms of water. However, kinetic effects were not investigated.

3.2 Dynamic Capacity

Dynamic capacity measurements were carried out on small 2.5 and 7.5 cm long columns and with two sizes of 4A molecular sieve (1.59 and 3.18 mm dia pellets) using a breakthrough point of 10 $\mu\text{L H}_2\text{O/L}$ (10 ppm, -60°C dew point/2/). The length of unused bed was found to be quite small and similar to the values found previously/1/ under high humidity conditions. Simulation of full scale adsorber performance where operation is adiabatic indicated that allowance of 7 to 10 cm for the length of unused bed (LUB) would be adequate.

At about 10 $\mu\text{LH}_2\text{O/L}$, the equilibrium capacity of the molecular sieve pellets consisting of crystals and a 20% by weight clay binder was reduced by the presence of the binder to about 80% of the capacity of an equal weight of crystals. However, at about 1000 $\mu\text{LH}_2\text{O/L}$ (-2°C dew point) the capacity of the sieve was increased by as much as 30% over the capacity of the crystals due to the highly adsorptive properties of the binder at this humidity level.

The capacity of the sieves was found to be very dependent on regeneration conditions and could be significantly greater than predicted from most isotherms for the H_2O -4A system under the presently used rigorous dehydration conditions of 400°C and 1.3×10^{-3} Pa for 72 h. For example after 72 h, the maximum capacity for a -18°C dew point entering airstream/2/ is 31 g $\text{H}_2\text{O}/100$ g sieve and about 29 g $\text{H}_2\text{O}/100$ g sieve based on 400 and 350°C regeneration temperatures, respectively. Working capacity is significantly less with lower regeneration temperatures and times and depends on residual moisture after regeneration. However, as discussed below, the residual moisture must be reduced below the equilibrium capacity value for any desired exit dew point.

3.3 Regeneration Requirements

Regeneration of the 4A molecular sieve to moisture levels of less than about 2 g/100 g sieve is required for operation at very low humidities (-60°C dew point). The amount of purge air required for regeneration based on mass transfer considerations is estimated in the addenda to the UNB report (see

Appendix B). Regeneration with pre-dried air (dew point lower than -2°C) at a temperature between 350 and 400°C was recommended to reduce the purge air volume requirement to less than 1400 bed volumes (≈ 2 h at 0.15 m/s for a 0.75 m long bed). At a lower regeneration air temperature of 300°C , the regeneration time is increased to about ten hours.

3.4 5A Sieve Performance

Limited tests were also carried out with 5A sieve because it has a potential capacity advantage for low humidity applications. However, regeneration temperatures greater than 400°C are required and this may not be economically feasible.

4.0 RECOMMENDATIONS

It is recommended that a limited experimental study be carried out to confirm (i) similar static isotherms for H_2O and D_2O in the range 10 to 100 $\mu\text{L/L}$ since slow adsorption and desorption rates produced significant scatter in the present data and (ii) the theoretical indication of similar lengths of unused beds for adsorption of H_2O and D_2O vapor from mixtures in air under flow conditions.

It is also recommended that the equilibrium isotherms be determined at 300 , 350 and 400°C for 4A pellets rather than for crystals used in the present work and which do not include the binder. These isotherms are required for evaluation of the high temperature regeneration option thereby producing low exit dew points and reducing the amount of water swamping required for a given decontamination factor. The same recommendation applies for 5A pellets which show potential for very low exit dew points and for which equilibrium isotherms at regeneration temperatures above 250°C are not available. In addition, extended aging tests are required since exposure of both 4A and 5A sieve to cycling between ambient

and higher regeneration temperatures could cause an increase in aging of the sieves with a resultant loss in dynamic capacity and crush strength.

Purge air volumes required during regeneration were presently estimated based on mass transfer considerations. However, heat transfer may be the limiting factor in determining purge air volumes required and it is therefore recommended that calculations based on both heat and mass transfer be done.

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2. Scott, F.R., Defreece, D.A., Wagoner, L.M., Zukerman, D.S. "Assessment of Technical Risks and R&D Requirements for a Magnetic Confinement Fusion System". EPRI Report AP-3283. November 1983.

APPENDIX A AND B

ADSORPTION OF MOISTURE ON MOLECULAR
SIEVE ADSORBENTS AT LOW HUMIDITY

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APPENDIX A
UNB FINAL REPORT

ADSORPTION OF MOISTURE ON MOLECULAR
SIEVE ADSORBENTS AT LOW HUMIDITIES

A.1 INTRODUCTION

The present investigation was undertaken as part of a larger research program, carried out by Ontario Hydro, and aimed at the development of an efficient system for clean-up and recovery of tritium containing gas streams. In order to facilitate efficient recovery, the tritium containing gas is to be oxidized to water which is then removed from the permanent gases (mainly air) by adsorption in a molecular sieve bed. Because of the hazardous nature of tritium highly efficient recovery at very low concentration levels is necessary. The air fed to the adsorbent bed is expected to have a humidity level (all H₂O isotopes) within the range of a few hundred to about 1000 ppm (volume) and it is desirable to adsorb as much of this moisture as possible in the adsorbent bed to give an effluent containing less than 10 ppm moisture.

Adsorption of moisture on molecular sieve adsorbents has been widely studied but in most practical applications one is concerned with higher humidity levels. (A report summarizing the results of an extensive study of the performance of 4A and 13X molecular sieves at humidity levels of 1,200-8,000 ppm was prepared for Ontario Hydro in May 1981)/1/. However, at humidities below 1000 ppm the available information is fragmentary and often contradictory. Indeed, even at 1200 ppm the results of our previous study/1/ showed the capacity of the adsorbents, under more or less practical drier operating conditions, to be significantly lower than predicted on the basis of equilibrium isotherm data provided by the adsorbent manufacturers whereas at the higher humidity levels there was good agreement. The present limited study was therefore undertaken to achieve four main objectives:

- (i) To measure accurately the equilibrium isotherms for water on 4A sieve at very low humidities,
- (ii) To verify experimentally the assumption, which has been generally made in the past, that there is no significant difference in adsorptive behaviour between the different isotopic forms of water.
- (iii) To account for the anomalies observed at low concentration between statically and dynamically measured equilibrium isotherms.
- (iv) To obtain the necessary kinetic data to allow a detailed mathematical simulation of the performance of a full scale adiabatic adsorbed bed.

A.2 APPARATUS AND EXPERIMENTAL METHODS

Three types of experiment were performed. The measurements of the static isotherms were carried out in a gravimetric vacuum system while the kinetic measurements and the measurements of dynamic capacity were carried out in a small packed column - similar but not identical to that described previously/1/.

A.2.1 Determination of 'Static' Isotherms

The experimental measurements were carried out in a standard Cahn vacuum microbalance system fitted with a two stage (diffusion plus rotary) vacuum pump. Pressure was monitored continuously on a Barocell electronic (capacitance) manometer. A vacuum of 10^{-5} Torr was readily attainable. A single molecular sieve pellet (1/8") was used as the adsorbent. Prior to each isotherm determination the sample was outgassed to constant weight at 400°C , 10^{-5} Torr. The temperature was raised to this level gradually over a 24 h period to avoid any possibility of damage to the adsorbent. The bulk of the moisture was removed during this 24 h heating period but a smaller quantity of moisture was desorbed rather slowly over the next 36 h so that overall about three days were required for a

full regeneration. Representative curves showing the approach to constant weight are shown in Figure 1. (The initial heating period is not shown).

A limited number of uptake rate curves were also measured in the vacuum system in order to investigate the diffusional properties of the adsorbent. After dehydration and cooling to room temperature (as noted above) the sample was subjected to a step change in moisture pressure and the uptake curve was followed gravimetrically. Since no air is present in the system, the conditions of these experiments are far removed from those of a practical system. The presence of air may significantly alter the uptake rate, which is controlled by intraparticle diffusion, but it will have a negligible effect on the equilibrium uptake. Provided that the regeneration conditions are comparable the equilibrium data obtained in these measurements are directly relevant to a practical system, but the uptake rates will almost certainly be different.

A.2.2 Measurement of Effective Diffusivities

In our previous study the effective diffusivities of a number of molecular sieve adsorbents were determined from an analysis of the experimental breakthrough curves. The same method is in principle applicable within the low humidity range. However, the complete breakthrough curve (to saturation) is required and the time required for such a measurement becomes inconveniently long (several days) at very low humidities. An alternative technique was therefore adopted using a small differential adsorbent bed (~2.5 cm long). The column containing the differential bed was dehydrated overnight in a pre-dried air (dew point < -70°C) or helium stream at 330°C and then cooled to 30°C. An air stream of controlled flowrate and humidity was then switched to the bed and the effluent concentration monitored continuously with a Beckman trace moisture analyzer, as in the measurement of a breakthrough curve. The difference is that with the differential bed, breakthrough occurs almost immediately and a different method of data analysis is therefore required. Relatively high air velocities (30-60 cm/s, superficial basis), typical of actual drier operating conditions, were used.

A.2.3 Measurement of Breakthrough Curves

The measurements were performed in a system essentially similar to that described previously/1/. Only two full breakthrough measurements were performed since at these very low humidity levels such experiments are tedious and time consuming.

A bed of 4A molecular sieve (about 7.5 cm length) was contained in a 12.5 cm long column of diameter 2.5 cm. The adsorbent bed was contained between two wire gauges and the fore and aft sections of the column were packed with glass beads of similar diameter to the adsorbent. The column was insulated with fibreglass although at these low humidity levels the temperature rise amounts only to 1-2°C and heat effects are therefore of minor importance.

Prior to an experiment the adsorbent was dehydrated overnight at 330°C in a stream of He or air which had been pre-dried in a large 4A sieve column to better than -70°C dew point. Controlled humidities in the inlet stream were achieved using a standard bubbler and by-pass arrangement. Outlet moisture concentrations were monitored using a Beckman trace moisture analyzer. Further details of the experimental conditions are given in Table 3.

A.3 RESULTS AND DISCUSSION

A.3.1(a) Equilibrium Isotherms (4A)

Equilibrium isotherms were measured for H₂O on Linde 4A sieve (1/8" pellet) at 30, 200 and 250°C and for D₂O at 30°C and 250°C. For comparison, isotherms were also measured at 30°C and 250°C with unaggregated Linde 4A crystals. The results are summarized in Figure 2. At pressures above about 0.01 Torr (~10 ppm), the isotherms were found to be reversible and reasonably reproducible, provided that the adsorbent was properly degassed initially. There is clearly no significant difference between the isotherms for D₂O and H₂O so it is reasonable to conclude that the isotherms for the other isotopic species, in particular HTO and T₂O, will be similar.

At 30°C, the isotherm is highly favourable¹ and for the pellet is reasonably well approximated by the simple Langmuir equation:

$$\frac{q}{33} = \frac{17p}{1 + 17p} \quad (1)$$

where q is the equilibrium loading (wt%) and p is the water pressure (or partial pressure) in Torr. The saturation limit (~33% wt) is approached at pressures greater than about 1 Torr. This isotherm is similar to that given by Breck/2/ but appreciably higher than most reported isotherms for H₂O-4A sieve.

At vapour pressures above about 0.1 Torr the 30°C isotherm for the crystals lies somewhat below the pellet isotherm, approaching a saturation capacity of about 25% wt (compared with 33% wt for the pellet) but at low concentrations the crystal isotherm lies slightly above the pellet isotherm. This is understandable since the pellet contains approximately 20% wt of clay binder. At very low water vapour pressures the binder does not adsorb significantly so that pellet capacity may be expected to be about 80% of the crystal capacity. At higher water pressures the clay binder shows some adsorption and there is also the possibility of capillary condensation in the smaller macropores. These effects appear to be sufficient to increase the high pressure capacity of the pellet above that of the unaggregated crystals.

The experimental data points obtained at 30°C and at pressures less than 0.01 Torr proved to be unreproducible with points obtained by desorption lying consistently above points obtained during adsorption. The probable explanation is that in this region the kinetics are too slow to allow attainment of equilibrium within a reasonable time frame and these points have therefore been discarded as unreliable.

¹ A favourable isotherm is one which is concave downwards towards the pressure axis (Type I of Brunauer's classification). As the isotherm becomes increasingly favourable it approaches rectangular or irreversible form.

In Figure 3, the present isotherms (30°C and 250°C) are compared with the equilibrium data provided by the adsorbent manufacturers as well as with the isotherms determined by Kyte/3/ for Laporte 4A sieve. The initial dehydration conditions employed by the manufacturers are not stated but Kyte states that he dried the adsorbents under 'vacuum' (single mechanical pump, probably 10^{-2} - 10^{-1} Torr) at 330°C to "constant weight". It seems likely that the difference between these isotherms can be attributed mainly to the difference in regeneration conditions. In the present study rigorous dehydration conditions were employed (400°C, 10^{-5} Torr for many hours) in order to determine the ultimate capacity of the sieve. The conditions employed by Kyte and by the adsorbent manufacturers are considerably less severe and represent more closely what is achievable under practical operating conditions. However, since there is evidently an appreciable contribution from adsorption by the binder some of the difference may be due to differences in the binders used by the different manufacturers.

One may also calculate equilibrium points from the overall mass balance in the kinetic runs:

$$\begin{array}{c}
 L \\
 \begin{array}{ccc}
 \begin{array}{c} \epsilon v \\ c_0 \end{array} \longrightarrow & \boxed{\text{Bed Voidage } (1-\epsilon)} & \begin{array}{c} \epsilon v \\ c(t) \end{array} \longrightarrow \\
 \end{array} \\
 \int_0^{\infty} (1 - c/c_0) \cdot dt = \left(\frac{1-\epsilon}{\epsilon v} \right) \cdot \left(\frac{q_0}{c_0} \right) \cdot L \quad (2)
 \end{array}$$

where q_0 is the adsorbed phase concentration, expressed as moles/cm³ adsorbent pellet, in equilibrium with the feed concentration c_0 (moles/cm³ gas). The values of q_0 derived in this way from the kinetic runs are summarized in Table 1 and Figure 3. In these experiments the sieve was regenerated in a pre-dried air or He purge overnight at 330°C. The resulting equilibrium points lie

close to Kyte's static isotherm, which was obtained following dehydration at the same temperature and well below the present static isotherm which was measured after dehydration at 400°C. The range of the equilibrium data points obtained at 1200 ppm in our earlier experiments/1/ is also shown in Figure 3. In these experiments the sieve was dehydrated at 260°C and the measured equilibrium points fall somewhat below Kyte's isotherm. There appears to be no difference between statically and dynamically measured isotherms² since Kyte's data were obtained by both methods. However, there appears to be a clear correlation between the dehydration temperature and the sieve capacity. The difference in loading between our static isotherm (400°C dehydration) and Kyte's isotherm (330°C dehydration) is shown in Figure 4. The effect of an increased dehydration temperature appears not to be simply a (constant) reduction in the residual moisture level but rather it is as though additional adsorption sites become available which can then adsorb an increasing amount as the water pressure is increased.

A.3.1(b) Equilibrium Isotherms (5A)

At very low loadings the heat of sorption of water on the 5A (CaA) is somewhat higher than on 4A (NaA). It was therefore considered worthwhile to make a few comparative equilibrium measurements with the 5A sieve in order to see whether it would offer any advantage in the present application.

Equilibrium isotherms were measured at 30°C and 250°C with a Linde 5A pellet (1/8"). The dry weight was established by dehydration under the same conditions as employed previously for 4A (400°C, 10⁻⁵ Torr for three days). The isotherms

² The term 'static isotherm' is used to denote an isotherm measured in a closed vacuum system by equilibrating the adsorbent with water vapour at a known pressure as described in Section A.2.1. The term 'dynamic isotherm' refers to equilibrium data obtained by overall mass balance from breakthrough measurements with a packed adsorption column (Equation 2). Provided dehydration conditions are comparable, the 'static' and 'dynamic' measurements should coincide.

which are shown in Figure 5 are quite reproducible. However, even after two or three days pumping at 400°C, 10^{-5} Torr, the dry weight never returned to the level achieved in the first dehydration. There was a residual moisture level of about 5% wt which could probably be removed only by raising the dehydration temperature further.

The 5A isotherm at 250°C is almost flat at about 6.5% wt for pressures above 10^{-2} Torr. This corresponds approximately with about seven molecules per cage or one H₂O molecule for each cation and is therefore consistent with the simple picture that the bulk of water within the cage is desorbed with relative ease but the last few molecules cling tenaciously to the Ca⁺⁺ cation and can be removed only at very high temperatures.

The 30°C and 250°C isotherms for the 4A and 5A sieves are compared in Figure 5a. It may be seen that at 30°C there is a crossover with the 5A sieve having the higher capacity at pressure below about 6×10^{-2} Torr and the lower capacity at higher pressures. At 250°C the 5A isotherm lies consistently above the 4A isotherm. Thus, although the 5A sieve has a potential advantage when very low ultimate humidity is required the regeneration of 5A sieve is evidently more difficult than 4A. To take full advantage of the very low humidities achievable with the 5A sieve it may therefore be necessary to regenerate at temperatures above 400°C and this may not be economically feasible.

From the practical point of view the important factor in comparing the two adsorbents is the difference in equilibrium loading, at a given vapour pressure, between the adsorption and desorption temperature. Such a comparison, based on adsorption at 30°C and desorption at 250°C, is shown in Figure 6. It may be seen that over the entire pressure range of interest the useful capacity of 4A is greater than that of 5A. Since 5A is also somewhat more expensive 4A would appear to be the better choice for the proposed application.

It is also clear that if an effluent partial pressure of less than 10 ppm H₂O is to be achieved efficient regeneration of the adsorbent will be essential.

There is a significant difference in the ultimate capacities of the 4A and 5A sieves (33% wt vs 25% wt at 30°C). Comparison with the isotherms for 4A crystals shows that some of the additional capacity of the 4A pellet must be attributed to adsorption in the clay binder and within the smaller macropores. The pore size distributions of the 4A and 5A pellets, as measured by mercury porosimetry, are shown in Figures 7 and 8. It should be noted that the porosimeter used is not reliable at pore diameters less than 0.01 μm, so the apparent cut-off below this figure is probably not genuine. The 4A sieve has a somewhat larger fraction of small macropores but it seems unlikely that this difference would be sufficient to account for the difference in saturation capacities. It is however quite possible that the clay binders may not be the same for both adsorbents and this would appear to be the most likely explanation of the difference. A more detailed investigation would, however, be required to confirm this conclusion.

A.3.2 Kinetic Data - Gravimetric Uptake Rate Measurements

Since the isotherm for water is highly favourable, approaching irreversible or rectangular form, for a sufficiently large pressure step the uptake curve may be represented by the irreversible model³ (see previous report, page 32-35)/1/.

$$\frac{t}{\tau} = \frac{1}{2} - \frac{1}{3} \left(\frac{m_t}{m_\infty} \right) - \frac{1}{2} \left(1 - \frac{m_t}{m_\infty} \right)^{2/3} \quad (3)$$

where m_t = mass adsorbed at time t
 m_∞ = mass adsorbed as $t \rightarrow \infty$

³ For the derivation of this equation see, for example Ruthven, "Principles of Adsorption and Adsorption Processes", Chapter 6, Wiley, New York, 1984.

$$\tau = \frac{R_p^2}{\epsilon_p D_p} \cdot \left(\frac{q_s}{c_o}\right) = \frac{R_p^2}{\epsilon_p D_p} \cdot \frac{\Delta q}{\Delta c}$$

c_o = gas phase concentration (Δc = change in gas phase concentration)

q_s = equilibrium adsorbed phase concentration at saturation (Δq = change in adsorbed phase concentration)

R_p = pellet radius

ϵ_p = porosity (approx 0.34)

By matching experimental transient uptake rate curves to this expression one may therefore easily determine the diffusional time constant (τ) and hence the effective pore diffusivity. This method has the advantage that in an irreversible system the uptake curve, at least in the initial region, is very little affected by the temperature rise accompanying sorption, thus greatly simplifying the analysis of the experimental data. However, the method is applicable only in a pure system (no inert present) and at low water vapour pressures (~1 Torr). These conditions are very different from the conditions prevailing in an actual drier and the diffusivities measured in this way are therefore of limited direct practical value. Nevertheless the experiment is easily performed during the isotherm measurements. The results of four such experiments are summarized in Table 2 and Figures 9 and 10. It is clear that the simple irreversible model (Equation 3) provides an excellent representation of the form of the uptake curves. Furthermore, the pore diffusivity values derived from the analysis of the uptake curves are clearly almost independent of temperature, suggesting Knudsen diffusion. The values (see Table 2) are of the expected order of magnitude and are consistent with a tortuosity factor of about 3.0.

A.3.3 Kinetic Data - Column Experiments

A rigorous analysis of the column data is more complicated. However, since the bed is short, one may as an approximation consider the system as an

infinitesimal bed and analyze the uptake data in essentially the same way as for a batch system. The fractional loading is calculated as a function of time from the mass balance over the column (as in Equation 2 above):

$$\int_0^t (1 - c/c_0) \cdot dt = \left(\frac{1-\epsilon}{\epsilon V}\right) \frac{q}{c_0} \cdot L \quad (4)$$

$$\therefore \frac{q(t)}{q_s} = \frac{\int_0^t (1-c/c_0) \cdot dt}{\int_0^\infty (1-c/c_0) \cdot dt} \quad (5)$$

The uptake data $q(t)/q_s$ are then plotted in the form suggested by Equation 3 and the diffusional time constants are found from the slope of such plots just as in the case of the gravimetric experiments. Experimental conditions, calculated diffusivities and representative uptake curves are given in Table 1 and Figures 11 and 12. According to Equation 3, the lines of Figure 12 should pass through the origin. However, it must be remembered that Equation 3 is strictly applicable only to a batch system. In applying this equation to a finite adsorbent bed one may expect a time delay, as observed. The kinetic data obtained with the two different adsorbent particle sizes (1/16" and 1/8") are clearly consistent since essentially the same values are obtained for the effective diffusivity. These values are similar to the values obtained previously at higher moisture levels (Table 3.5 of Reference (1)). (The sample of sieve used in these experiments was, unfortunately, not from the same batch as that used previously).

A.3.4 Breakthrough Curves

Experimental breakthrough curves were measured in a 7.5 cm bed packed with 4A sieve (1/16" and 1/8" pellets). The apparatus used was similar to that described in the earlier report/1/. The experimental conditions are summarized in Table 3 and the curves are given in Figure 13.

The breakthrough curve for the 1/16" pellets is much sharper indicating that macropore diffusional resistance to mass transfer is probably dominant. At these low humidities the temperature rise is less than 1.5°C and the system may be regarded as essentially isothermal. The saturation capacity is similar to that found from the dynamic experiments under the same dehydration conditions and comparable with Kyte's isotherm.

Even at this low humidity level, the length of unused bed (LUB) is quite modest. It is thus possible to obtain an adequate dynamic capacity coupled with a low outlet humidity, provided that the adsorbent bed is properly dehydrated initially. (The regeneration conditions used in these experiments are probably more severe than would be feasible in an industrial situation).

A series of numerical simulations were also carried out using the parameters determined from the equilibrium and kinetic measurements. The conditions and the parameters used in the simulation are summarized in Table 4 and the calculated temperature response and breakthrough curves are shown in Figure 14. The temperature rise was always less than 1.5 degree. If the bed is fully dehydrated initially a very low outlet humidity is obtained in the early stages and the LUB amounts only to 7-10 cm (increasing as C_0 decreases). However, if the bed is imperfectly regenerated it becomes impossible to achieve a really dry effluent even in the early stages (see curve 3 which is calculated for a uniform initial moisture level of 5% wt).

CONCLUSIONS

1. There is no significant difference between the isotherms for D_2O and H_2O on 4A sieve and one may therefore safely use the H_2O isotherms as representative of the behaviour of all isotopic species.

2. The 5A sieve has a greater affinity for water than 4A and therefore the capacity at very low humidities is somewhat higher. Unfortunately, to take advantage of this capacity requires regeneration at temperatures greater than 400°C and this may not be economically feasible. For regeneration under milder conditions the useful capacity of 4A appears to be somewhat greater than that of 5A. Since 4A is also somewhat cheaper it may be the preferred adsorbent. However, the hydrothermal stability of 5A sieve is somewhat greater than that of 4A, so adsorbent life may be improved. The main disadvantage of 5A is the high regeneration temperature which may not be easily achieved in a practical system.
3. The dynamic experiments and the numerical simulations suggest that the kinetic behaviour of the adsorbent at these low concentrations does not differ greatly from the behaviour observed previously at higher concentration levels. The lost bed height due to mass transfer resistance amounts to no more than about 7 cm under practical operating conditions. Given a reasonably well designed bed and a sufficient depth of adsorbent the effect of mass transfer resistance should therefore not be of any great significance.
4. The major problem in meeting the requirements of the proposed process is to achieve adequate regeneration conditions. To achieve an effluent humidity of less than 10 ppm, (-60°C dew point), even during the initial stages of the cycle, will require that the adsorbent be well dehydrated to a residual moisture level of less than about 2% wt. This will require regeneration with either very dry purge gas or at temperatures greater than about 300°C. Regeneration with pre-dried air at a temperature between 300 and 400°C would appear to be the most reasonable solution. For regeneration at 300°C the humidity of the purge stream should be less than 100 ppm (-42°C dew point). Regeneration at a higher temperature will increase somewhat the allowable level of humidity in the purge. There is therefore, some freedom for economic optimization in the choice of regeneration conditions since a

higher humidity purge may be compensated for by raising the regeneration temperature.

Counter-current regeneration (ie, reverse flow regeneration) will be essential for the proposed application.

5. The present experimental data should be sufficient to allow a reasonable estimate of the purge requirements under various regeneration conditions. However, if further experimental work is contemplated this may be the most useful area for further study.

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1. D.M. Ruthven, Report on Molecular Sieve Adsorbents (for Ontario Hydro), May 11, 1981.
2. D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, (1974).
3. W.S. Kyte, Ph.D. Thesis, University of Cambridge, England (1970).

ACKNOWLEDGEMENT

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APPENDIX B
UNB ADDENDA TO FINAL REPORT

B.1 ESTIMATION OF PURGE REQUIREMENT
FOR REGENERATION OF SATURATED BED

A simple approximate estimate of the purge gas required to regenerate the adsorbent bed may be obtained from equilibrium theory in the following way. The velocity of the desorption front (w) is given by:

$$w = \frac{\epsilon v}{\epsilon + (1-\epsilon)(dq^*/dc)}$$

where ϵv is the superficial velocity of the purge gas, ϵ is the bed voidage and dq^*/dc is the limiting slope of the equilibrium isotherm at regeneration conditions. Equilibrium isotherms for Linde 4A sieve have been measured at 200°C and 250°C. Calculated desorption times for regeneration at these temperatures are summarized in Table 5.

The following trends are clearly evident:

- (i) The purge requirement increases dramatically as the residual moisture level is decreased.
- (ii) For a given residual moisture level an increase in temperature of 50°C (from 200 to 250°C) reduces the purge requirement by a factor of more than 10.
- (iii) The humidity requirement for the purge gas becomes less severe as the regeneration temperature is increased.

It seems clear that it would be difficult to obtain a satisfactory dehydration to meet the demands of the proposed application except at temperatures in excess of 300°C. We did not measure the equilibrium isotherm at temperatures higher than 250°C but, based on a simple extrapolation of the present data, one may estimate that at 300°C one would require a purge time of about 40 mins and a regen. gas volume/bed volume ratio of about 800 to achieve a 3% residual humidity level. This would be the maximum tolerable level for a satisfactory outlet humidity in the drying cycle. A regeneration temperature of 350°C would be better and should allow a further reduction in the purge requirement without significant reduction in adsorbent life.

B.2 CHOICE OF REGENERATION CONDITIONS FOR
ADSORPTION OF WATER AT LOW PARTIAL PRESSURES

To establish the minimum regeneration conditions required to ensure adequate dehydration of the adsorbent, a series of high temperature isotherms was measured at 250°C, 300°C and 350°C. The results are shown in Figure 15. Most of the measurements were carried out with unaggregated 4A zeolite crystals, rather than with pelleted material in order to avoid uncertainties introduced by adsorption in the secondary pore structure.

To achieve satisfactory drier performance at low humidity we must dehydrate the adsorbent to a residual moisture level of less than about 2% wt. The minimum purge gas humidity and corresponding purge gas volume required for regeneration to this residual moisture level may be estimated from the isotherms:

DEHYDRATION TEMP (°C)	MAX ALLOWABLE DEW POINT OF PURGE GAS (°C)	PURGE VOLUME (STP) ADSORBENT BED VOLUME
250	-52	100,000
300	-20	7,000
350	-2	1,400

It is evident that to achieve the required degree of dehydration at 250°C will require a very large volume of dry purge gas whereas at 350°C the required residual moisture level should be obtained relatively easily.

One may conclude that for a practical process a minimum dehydration temperature of 350°C and a purge gas with a dew point lower than -2°C will be required. A somewhat higher dehydration temperature may in fact be preferable since this will reduce the purge volume requirement and increase the allowable level of purge humidity. However, temperatures above 400°C are probably not desirable since at these temperatures the sieve tends to lose capacity due to hydrothermal aging.

TABLE 1: SUMMARY OF COLUMN KINETIC AND EQUILIBRIUM STUDIES

EXPERIMENT NO	SIEVE	c_o (ppm)	L (cm)	WT OF SIEVE (g)	$u = \epsilon v$ ($\text{cm} \cdot \text{s}^{-1}$)	$\int_0^{\infty} (1-c/c_o) dt$ (min)	q_o (g/g)	q_o/c_o	$\frac{\epsilon_p D_p}{R_p^2}$ (s^{-1})	$\epsilon_p D_p$ ($\text{cm}^2 \cdot \text{s}^{-1}$)
1	4A-1/16"	770	3.2	11.2	45	152	0.14	2.13×10^5	-	-
2	4A-1/16"	800	3.2	11.2	33.5	197	0.14	2.05×10^5	-	-
3	4A-1/16"	445	3.2	11.2	63.4	157	0.12	3.1×10^5	2.1	0.021
4	4A-1/16"	530	3.2	11.2	19.0	437	0.12	2.6×10^5	2.4	0.024
6	4A-1/8"	660	2.9	10.1	32.7	137	0.09	1.53×10^5	0.71	0.025
7	4A-1/8"	300	2.9	10.1	36.5	117	0.09	1.46×10^5	0.81	0.028

Carrier: Air at 30°C, one atmosphere

Sieve dehydrated overnight in pre-dried air or He (dew point < -70°C) at 330°C.

R_p for 1/8" pellets ≈ 0.18 cm; for 1/16" pellets, 0.1 cm.

$\int_0^{\infty} (1-c/c_o) dt$ is the stoichiometric time (see Equation 2)

q_o/c_o is the ratio of adsorbed phase to fluid phase concentrations $\left(\frac{\text{Moles/unit pellet volume}}{\text{Moles/unit gas volume}} \right)$

TABLE 2: SUMMARY OF BATCH KINETIC UPTAKE RATE MEASUREMENTS

(H₂O - Linde 4A Pellet R_p = 0.156 cm)

EXPT	T(DegC)	p ₁ (Torr)	p ₂ (Torr)	q ₁ (g/100g)	q ₂ (g/100g)	Slope (s ⁻¹)	Δq/Δc	ε _p D _p /R _p ² (s ⁻¹)	ε _p D _p cm ² .s ⁻¹
1	200	0.0031	4.85	2.839	5.787	5.6x10 ⁻⁴	1.1x10 ⁴	6.1	0.143
3	250	0.00061	4.4	0.816	4.98	3.32x10 ⁻⁴	1.89x10 ⁴	6.1	0.143
5	30	0.0043	3.6	8.05	34.46	6.09x10 ⁻⁵	8.647x10 ⁴	5.3	0.124
8	30	0.003	3.7	2.57	34.17	5.143x10 ⁻⁵	0.99x10 ⁵	5.1	0.12

- (i) Assuming Knudsen diffusion: $D_K = 9700 r \frac{T}{M}$; $D_p = D_K/\tau$. With $\epsilon_p = 0.33$, $r = 500 \times 10^{-8}$ cm we obtain $\tau \approx 3.0$.
- (ii) $p_2 - p_1$ is the pressure step over which the uptake curve is measured.
- (iii) $\Delta q/\Delta c$ is the ratio of the change in adsorbed phase and fluid phase concentrations (moles/unit pellet volume)/(moles/unit gas volume) over which the uptake curve is measured (see Equation 3).
- (iv) Slope refers to plots such as Figure 10.

TABLE 3: DETAILS OF BREAKTHROUGH EXPERIMENTS AT 30°C

ADSORBENT (4A)	BED LENGTH (cm)	STOICHIOMETRIC TIME (Min)	BREAK TIME* (Min)	TOTAL CAPACITY (g/g)	LUB (cm)	ΔT MAX
1/8"	7.5	860	300	0.16	5	
1/16"		880	500	0.165	3	-1.5°C

Sieve regenerated overnight in He purge at 330°C.

Superficial velocity 34 cm/s.

Inlet moisture ~660 ppm in both experiments.

Breakthrough point ~10 ppm.

TABLE 4 - THEORETICAL SIMULATION OF BREAKTHROUGH CURVES

(4A Sieve 1/8" PELLETS AT 30°C)

Column Length: 50 cm
Sup. Velocity: 40 cm/s

CURVE NO	HUMIDITY (ppm)	INITIAL H ₂ O LOADING (g/g)	$\frac{-\Delta H C_o}{\rho C_p T_o}$	$\frac{q_o}{c_o}$	$\frac{b_o c_o}{1+b_o c_o} = \frac{q_o}{q_s}$	BREAK TIME (HR)	STOICH TIME (HR)	LUB (CM)
1	300	0	0.00235	1.3×10^6	0.8	210	265	10.4
2	600	0	0.0047	7.3×10^5	0.88	130	152	7.2
3	600	0.05	0.0047	7.3×10^5	0.88	0	Premature Breakthrough	

2

Common Parameters: $-\Delta H/RT=28.2$, $k_g R_p/D_p = 20$, $R_p v/LD_p = 0.3$, $vL/D_L = 100$

[D_p = pore diffusivity, D_L = axial dispersion coefficient, k_g = external mass transfer coefficient,

R_p = particle radius, c_o = gas phase concentration at inlet, q_o = corresponding equilibrium concentration in adsorbed phase, q_s = saturation concentration in adsorbed phase at high water vapor concentrations in gas phase].

TABLE 5 - SUMMARY OF THE EFFECT OF REGENERATION CONDITIONS

RESIDUAL MOISTURE (wt%)	REGEN. TEMPERATURE (°C)	MAX. ALLOWABLE HUMIDITY OF REGEN. GAS (Torr), (°C dew point)	dq*/dc	REGEN. TIME (Min)	REGEN. GAS VOL (STP)
					BED VOL
4	250	4 (-2)	2,200	39	700
3	250	0.25 (-31)	25,000	435	7,800
2	250	0.02 (-52)	370,000	6,440	116,000
4	200	0.25 (-31)	20,400	430	7,700

Based on 50 cm bed, superficial velocity of regen. gas 15 cm/s measured at 1 atm, 25°C.

$\frac{dq^*}{dc}$ is the slope of the equilibrium isotherm at regeneration conditions.

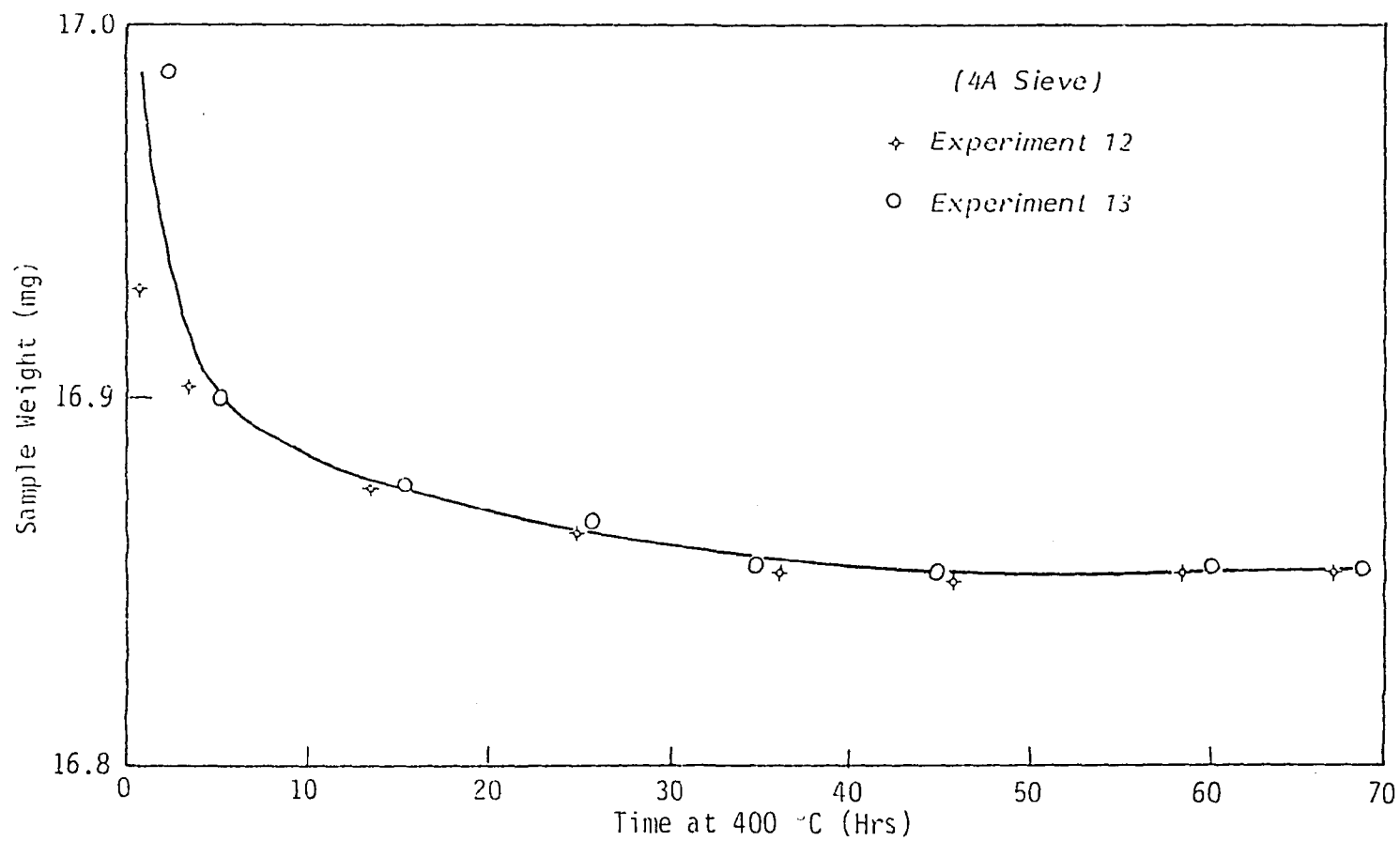


FIGURE 1
THE APPROACH TO CONSTANT WEIGHT

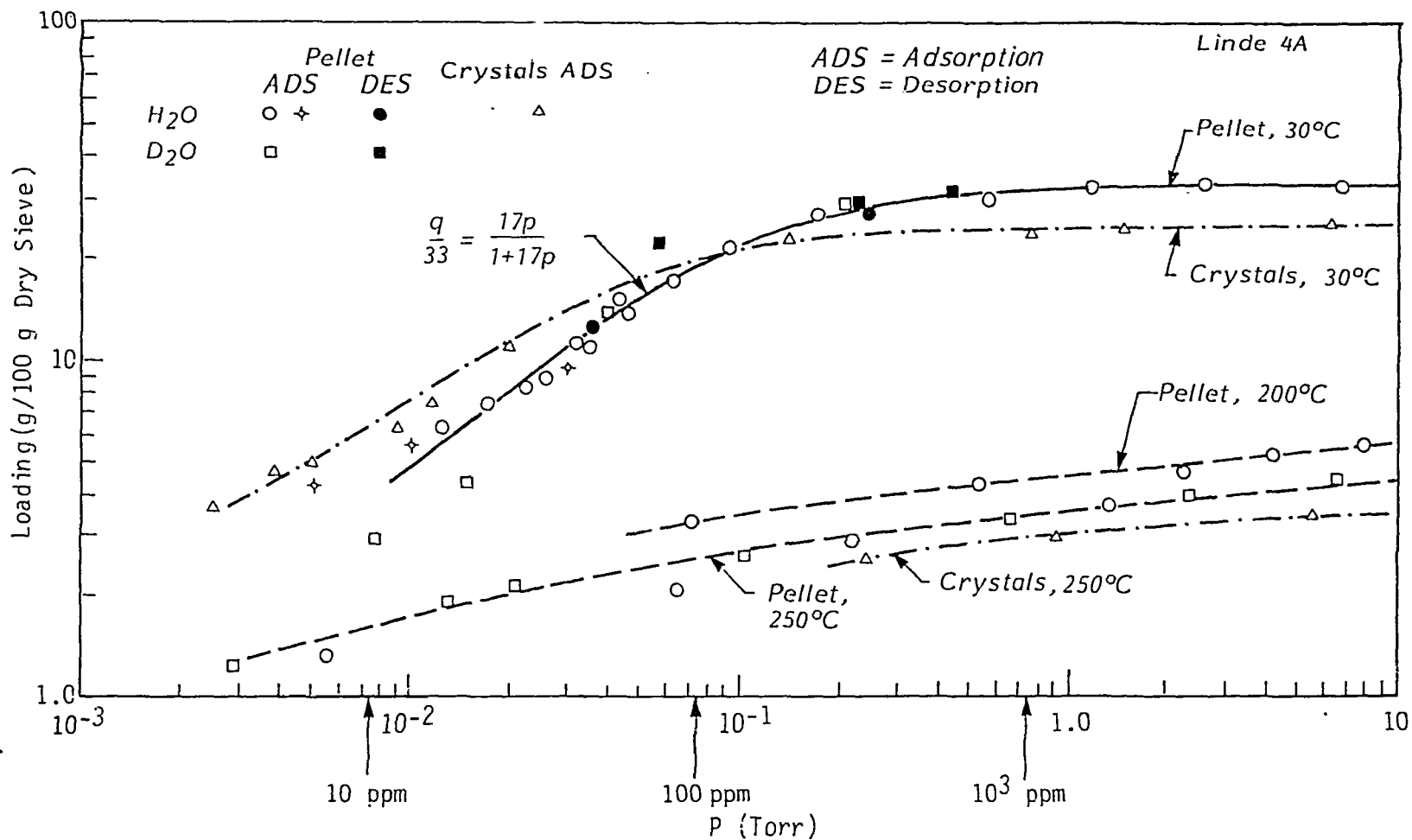


FIGURE 2
 EXPERIMENTAL EQUILIBRIUM ISOTHERMS FOR
 H₂O AND D₂O ON LINDE 4A SIEVE

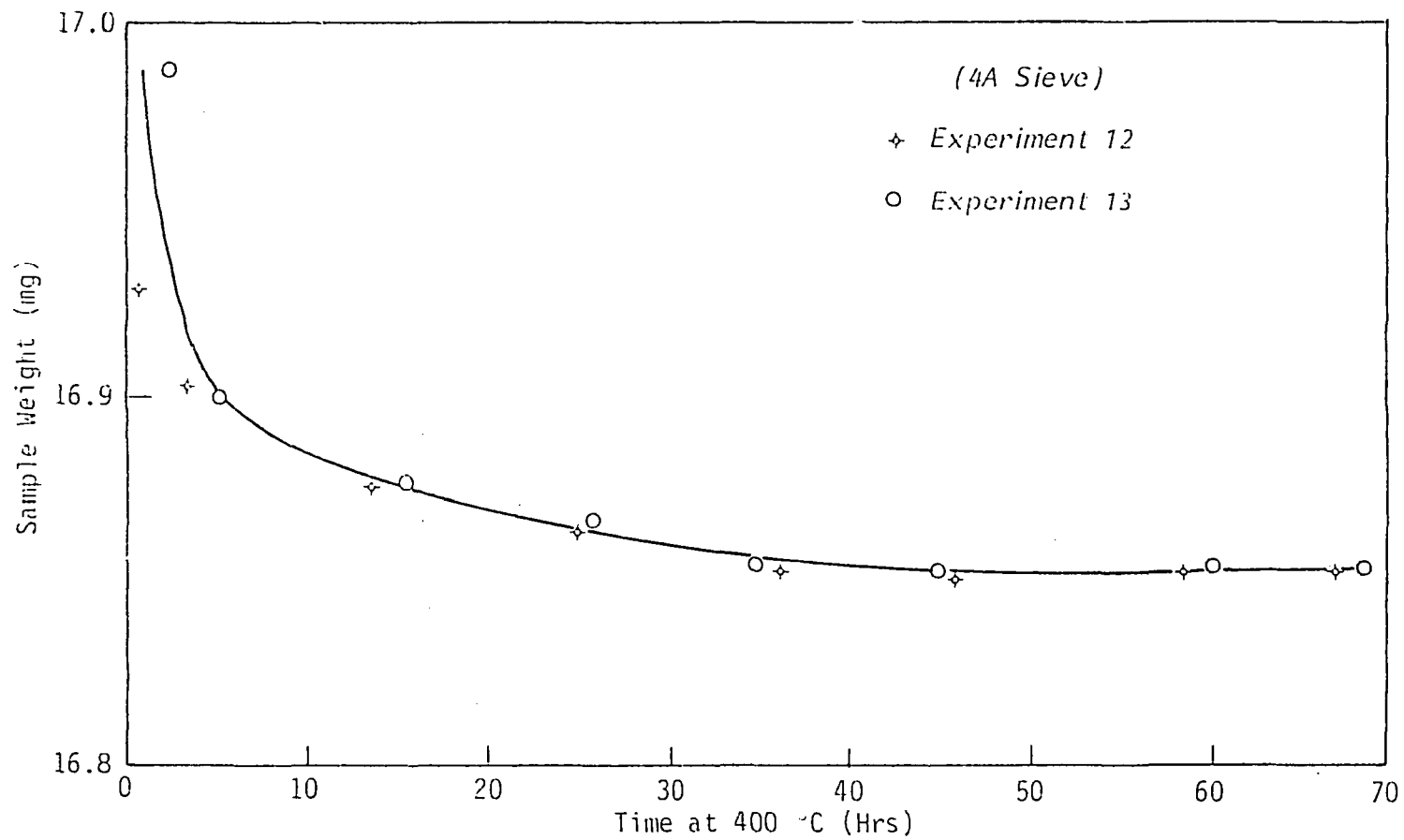


FIGURE 1
THE APPROACH TO CONSTANT WEIGHT

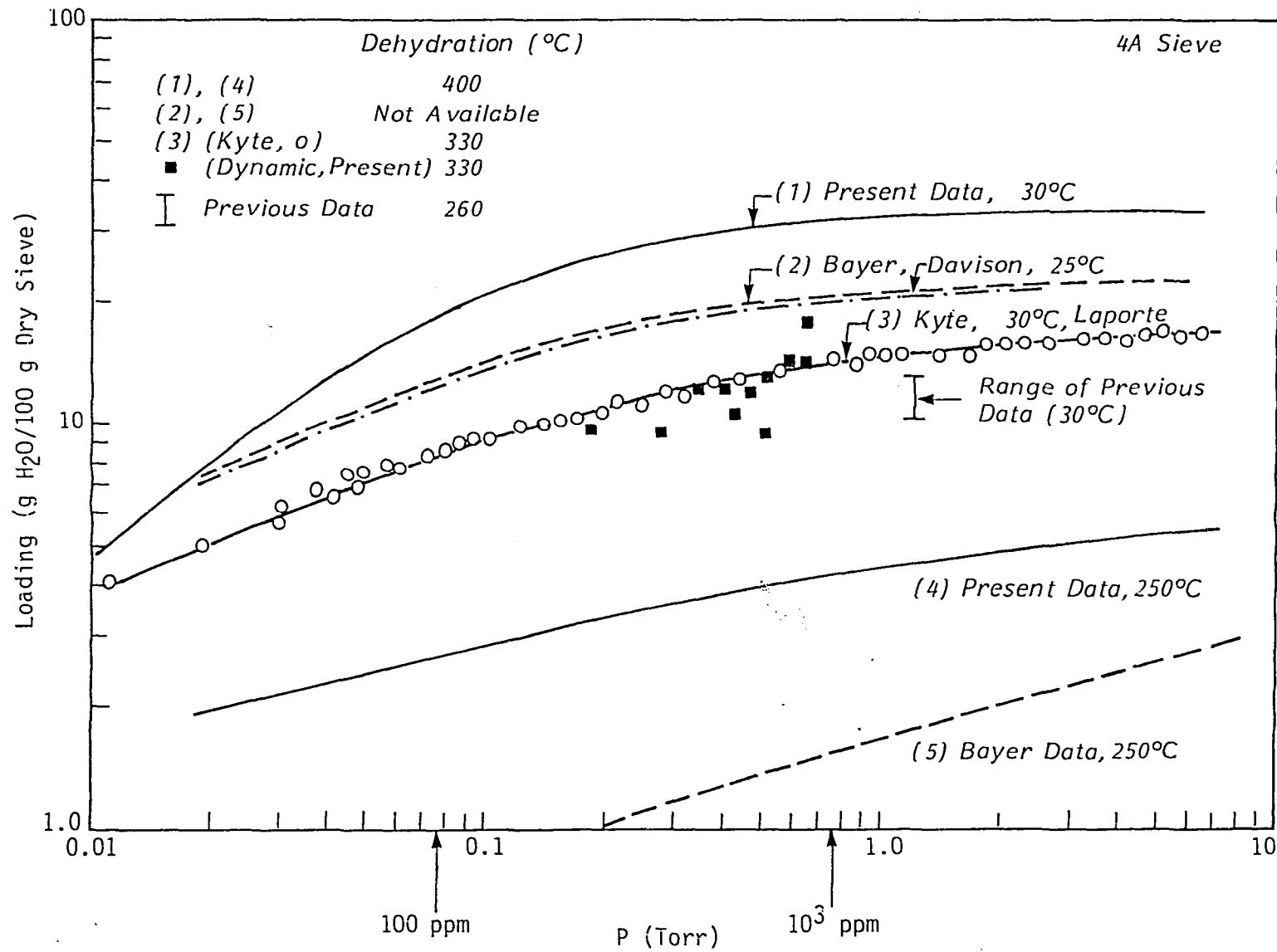


FIGURE 3

COMPARISON OF PRESENT STATIC ISOTHERMS, MANUFACTURER'S ISOTHERMS
 KYTE'S EXPERIMENTAL DATA AND PRESENT DYNAMIC ISOTHERMS (■) FOR 4A SIEVE

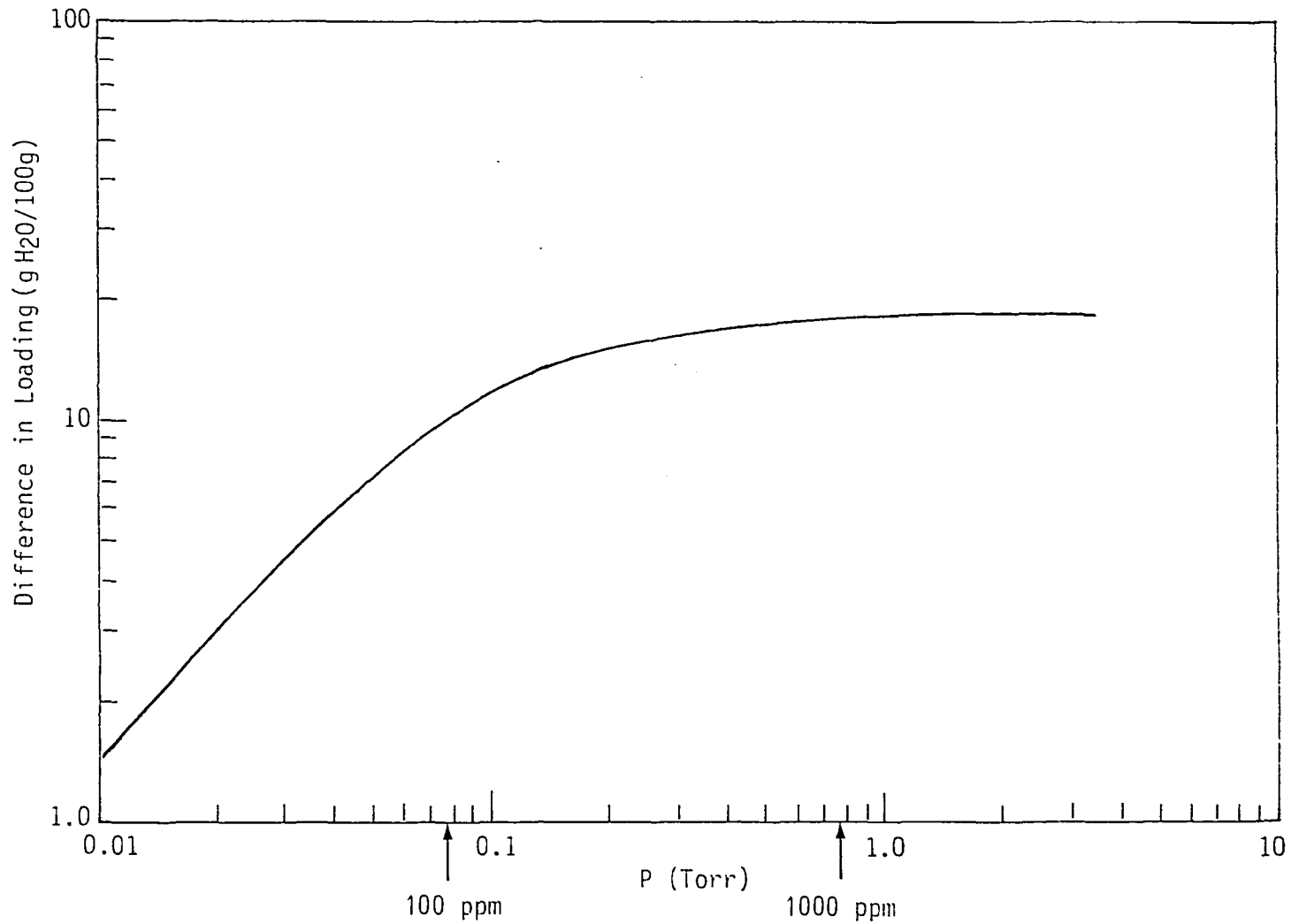


FIGURE 4

DIFFERENCE BETWEEN PRESENT STATIC ISOTHERM
 (DEHYDRATION AT 400°C) AND ISOTHERM
 OF KYTE (DEHYDRATION AT 330°C)

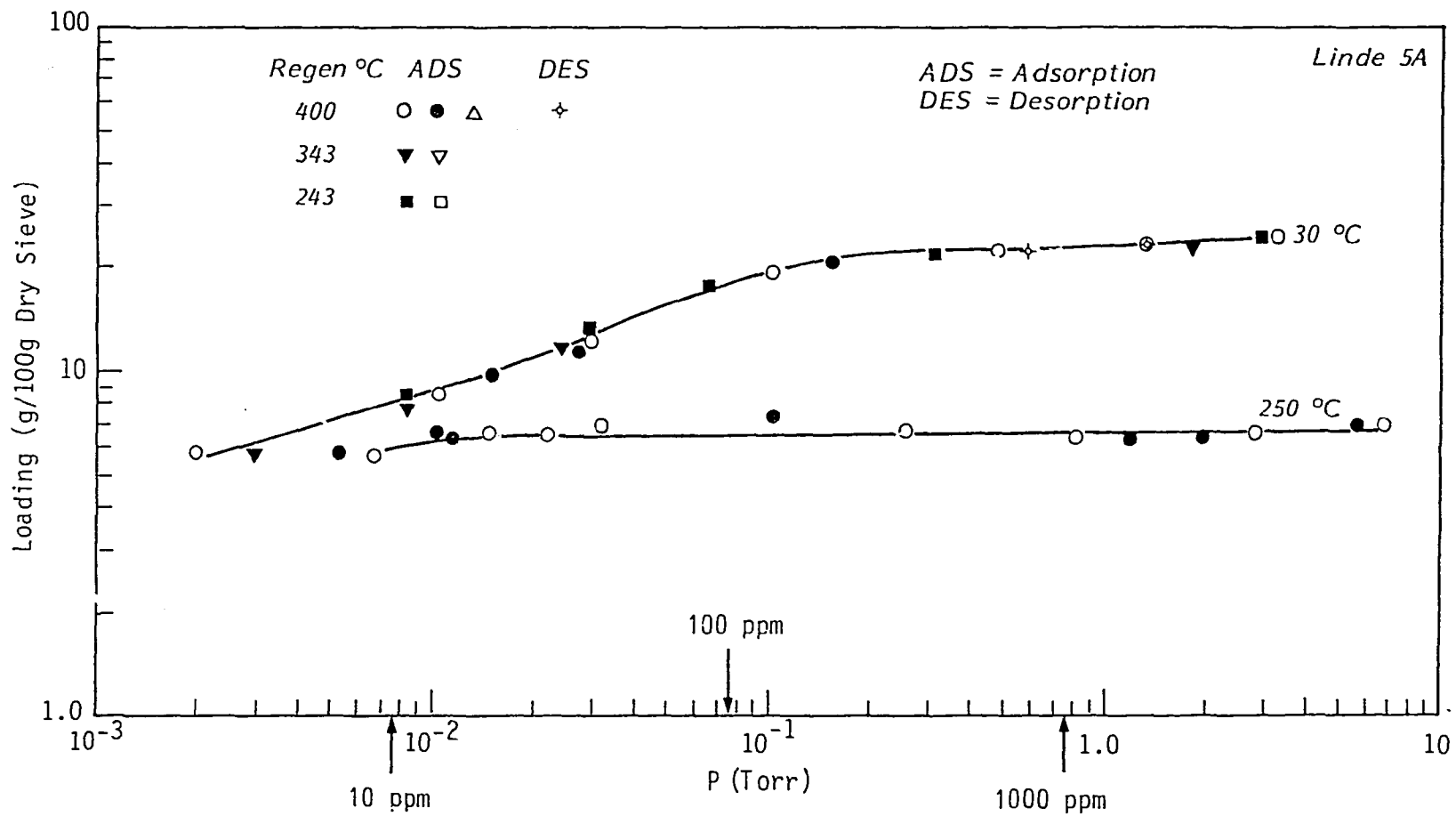


FIGURE 5
 STATIC ISOTHERM FOR ADSORPTION OF WATER ON
 LINDE 5A SIEVE AT 30°C AND 250°C

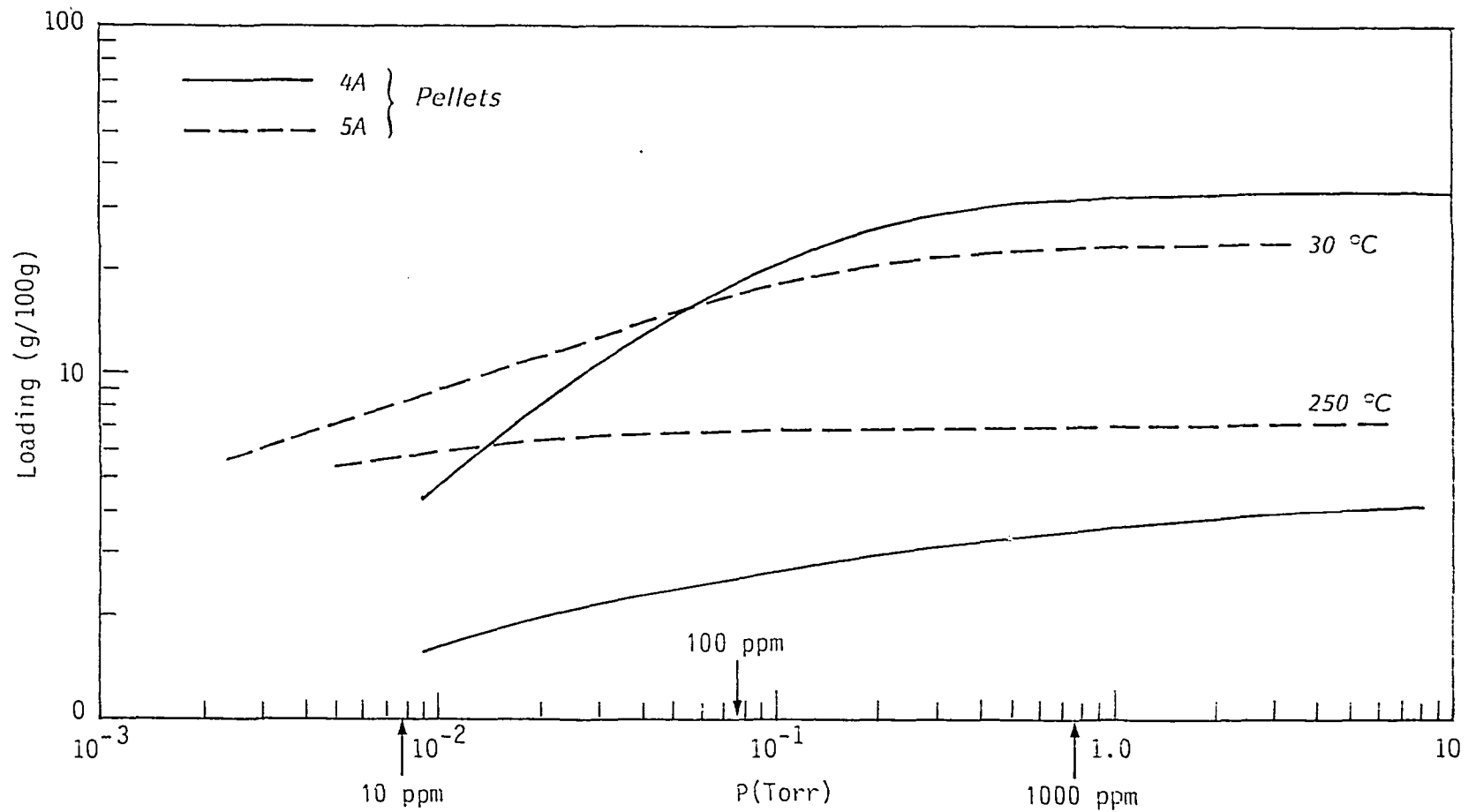


FIGURE 5a
 COMPARISON OF EXPERIMENTAL ISOTHERMS FOR H₂O
 ON LINDE 4A AND 5A PELLETS

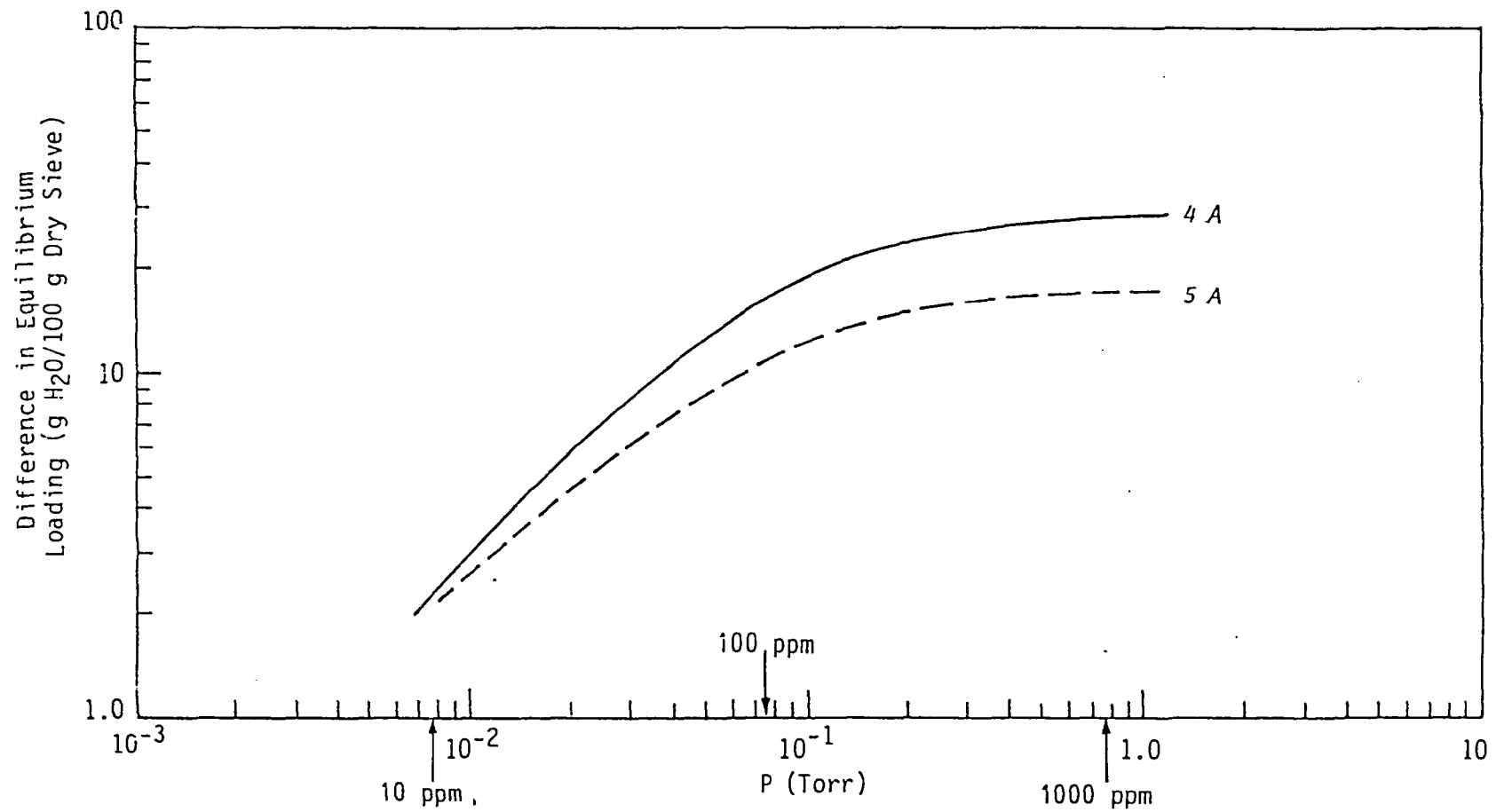


FIGURE 6
 DIFFERENCE IN H₂O EQUILIBRIUM LOADING AS A FUNCTION OF WATER
 VAPOUR PRESSURE FOR ADSORPTION AT 30°C AND DESORPTION AT 250°C
 (CALCULATED FROM EXPERIMENTAL DATA OF FIGURES 2 AND 5)

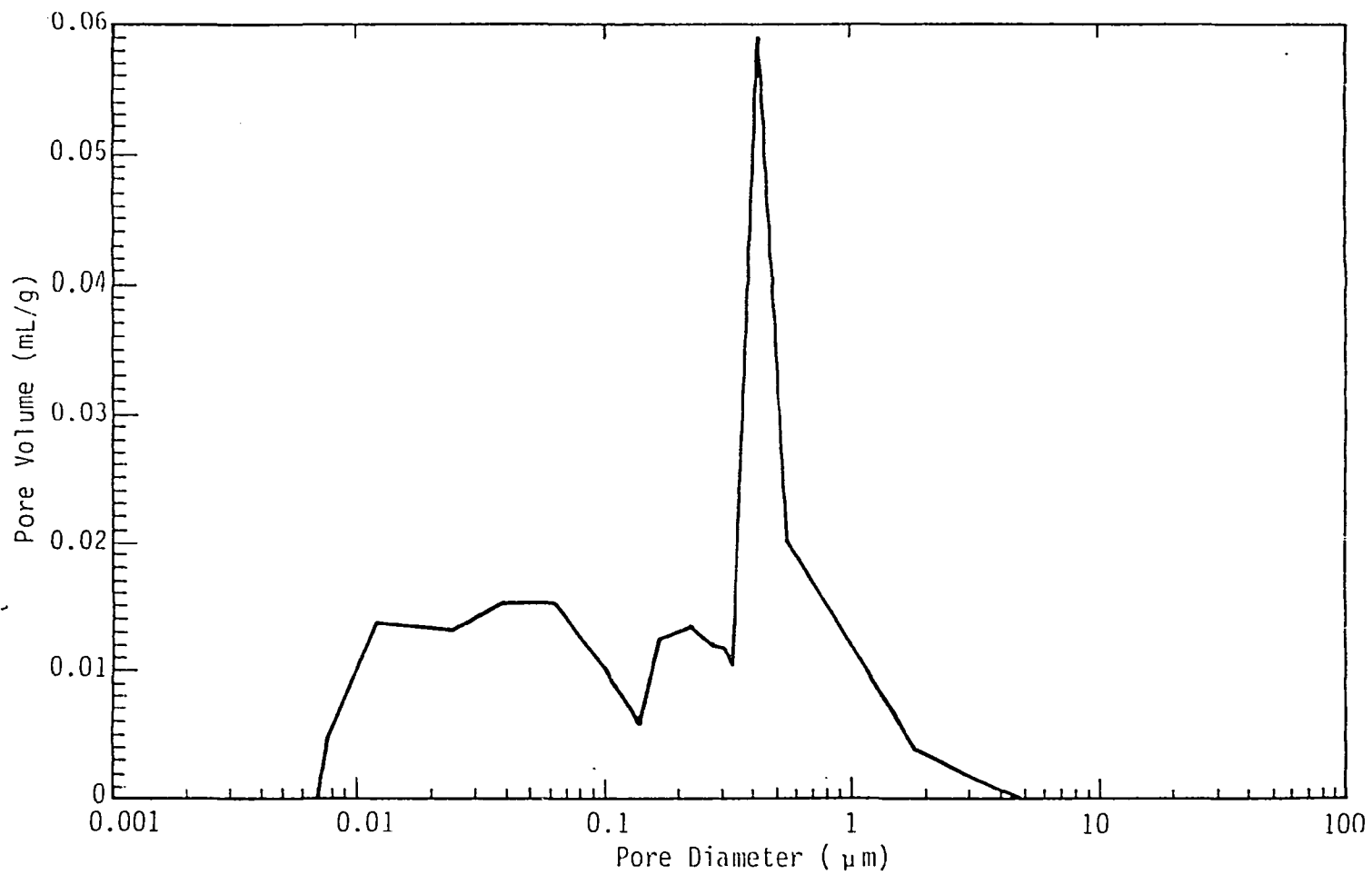


FIGURE 7
DIFFERENTIAL PORE SIZE DISTRIBUTION FOR LINDE 4A SIEVE

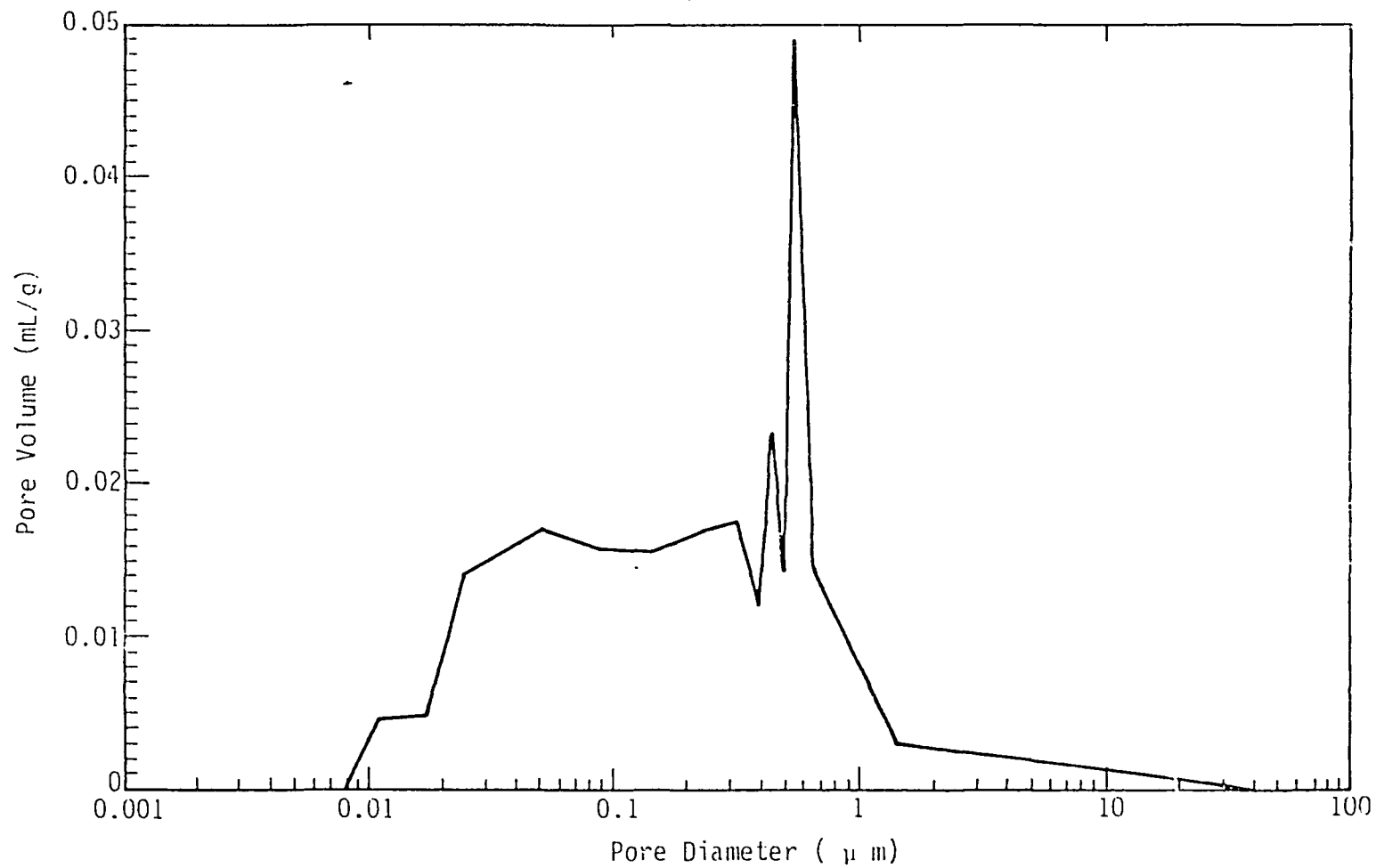


FIGURE 8
DIFFERENTIAL PORE SIZE DISTRIBUTION FOR LINDE 5A SIEVE

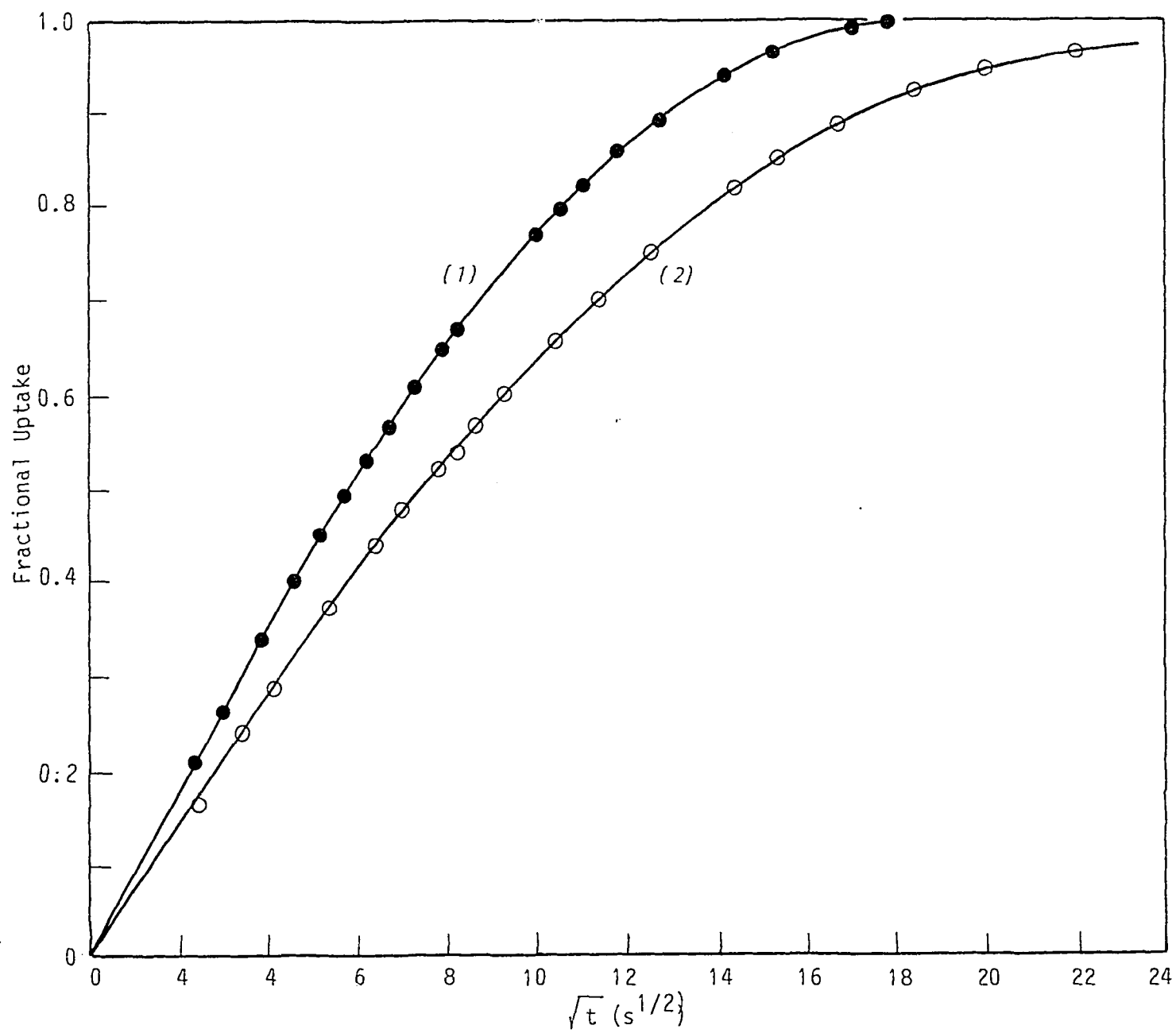


FIGURE 9

EXPERIMENTAL UPTAKE CURVES FOR H₂O IN A LINDE 4A PELLET
 (R = 0.156 cm) [(1) - EXPERIMENT 1; (2) - EXPERIMENT 3 - SEE TABLE 2 FOR DETAILS]

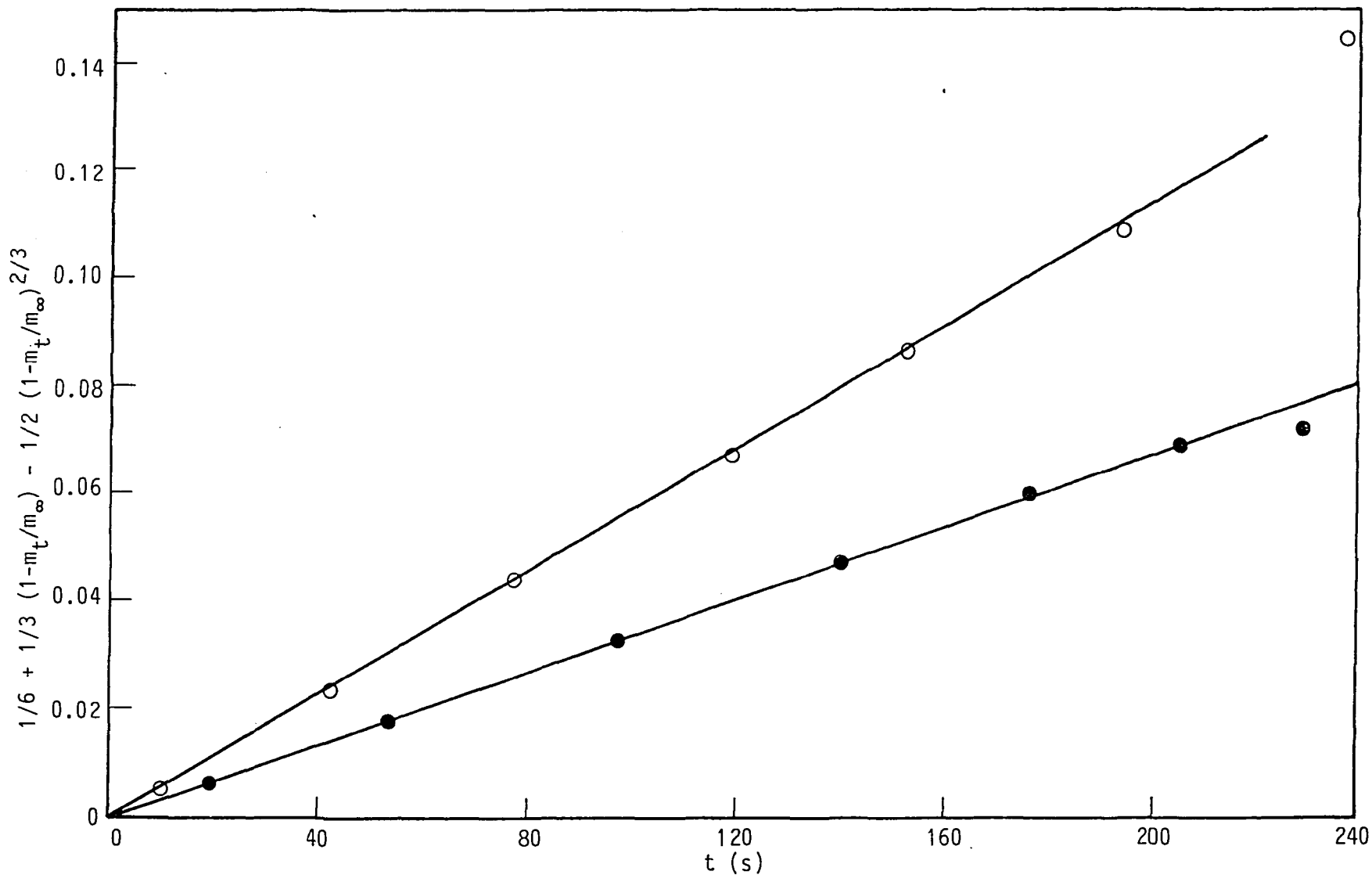


FIGURE 10

ANALYSIS OF UPTAKE CURVES FOR H₂O IN LINDE 4A PELLET
 ACCORDING TO RECTANGULAR ISOTHERM MODEL (EQN. 3)
 [EXPERIMENT 1, 200°C, ●; EXPERIMENT 3, 250°C, ○ - SEE TABLE 2 FOR DETAILS]

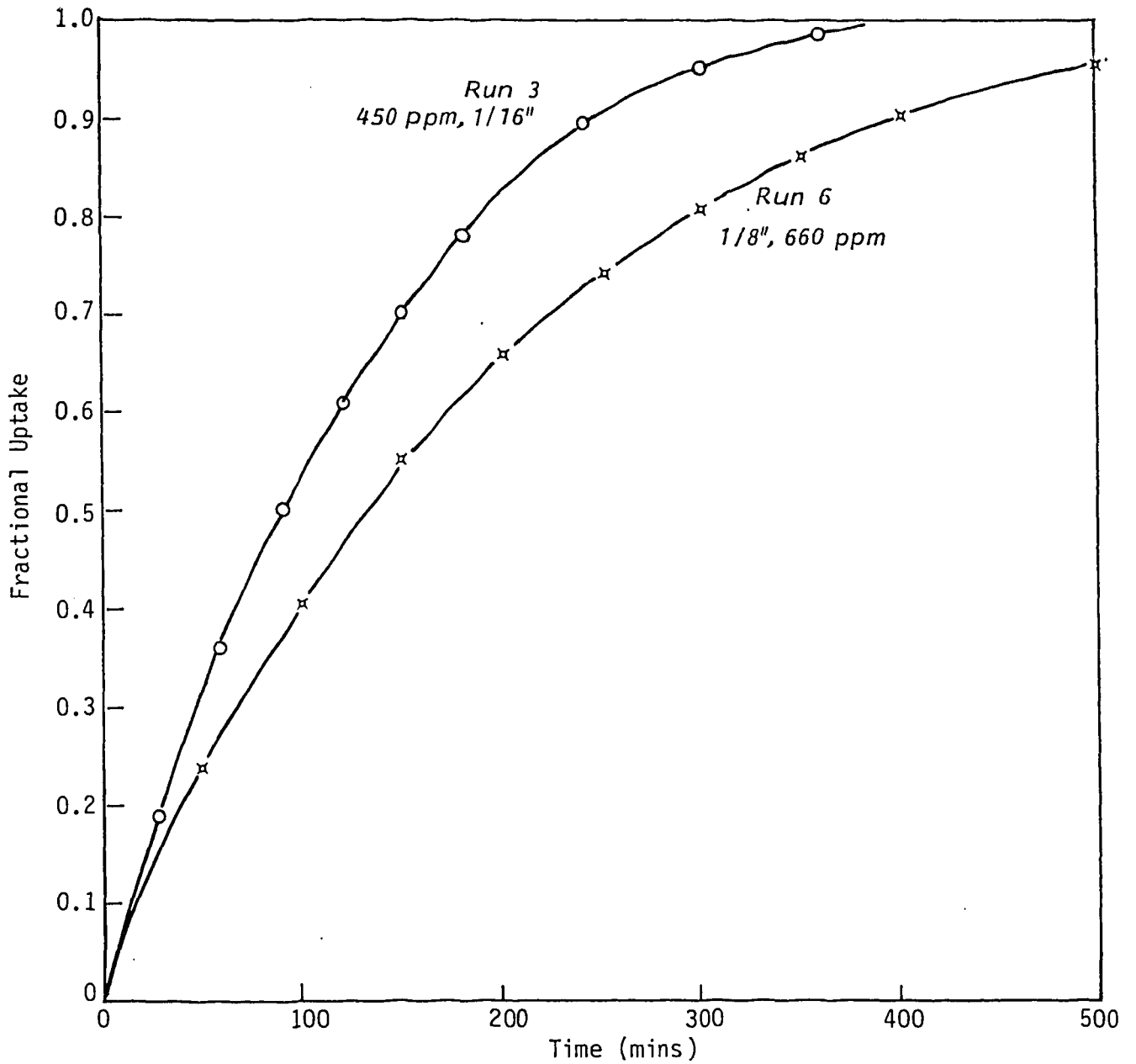


FIGURE 11

EXPERIMENTAL UPTAKE CURVES DERIVED FROM MEASUREMENTS WITH A DIFFERENTIAL ADSORBENT BED

$$\text{FRACTIONAL UPTAKE} = \frac{\text{MASS OF H}_2\text{O ADSORBED AT TIME } t}{\text{MASS OF H}_2\text{O ADSORBED AS } t \rightarrow \infty}$$

(See Table 1 for details)

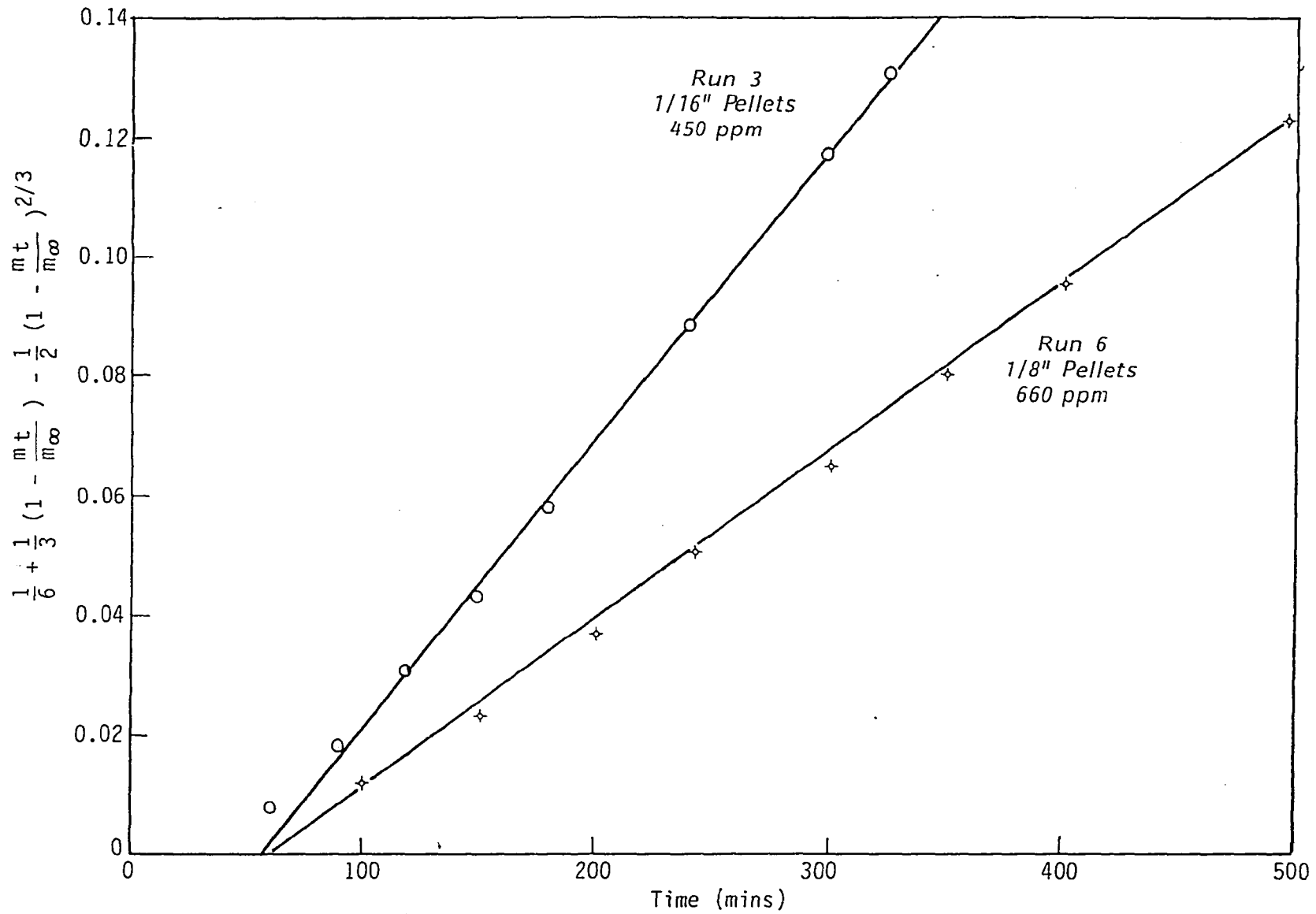


FIGURE 12
 UPTAKE CURVES FROM DYNAMIC MEASUREMENTS
 PLOTTED ACCORDING TO EQUATION 3

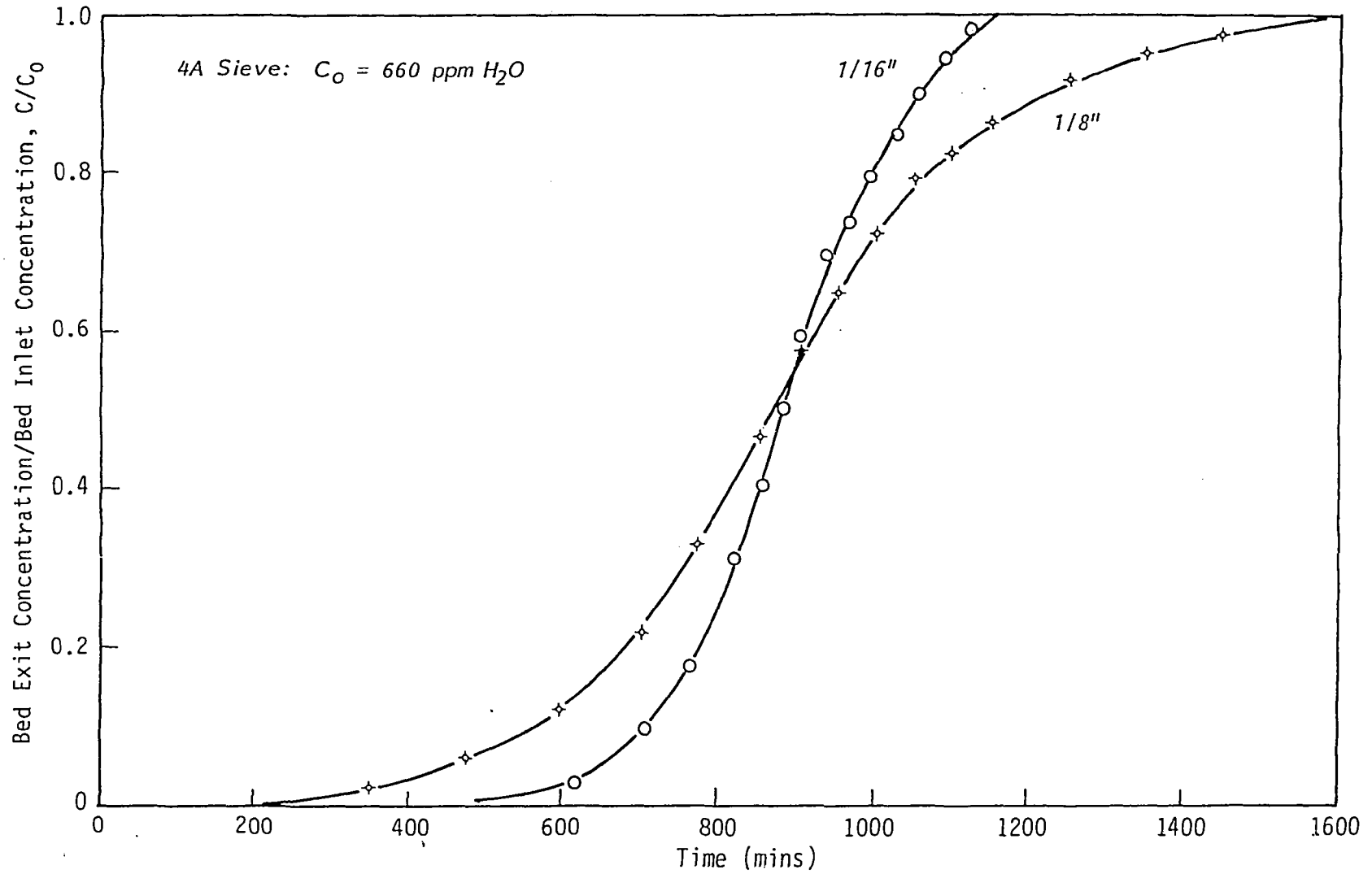
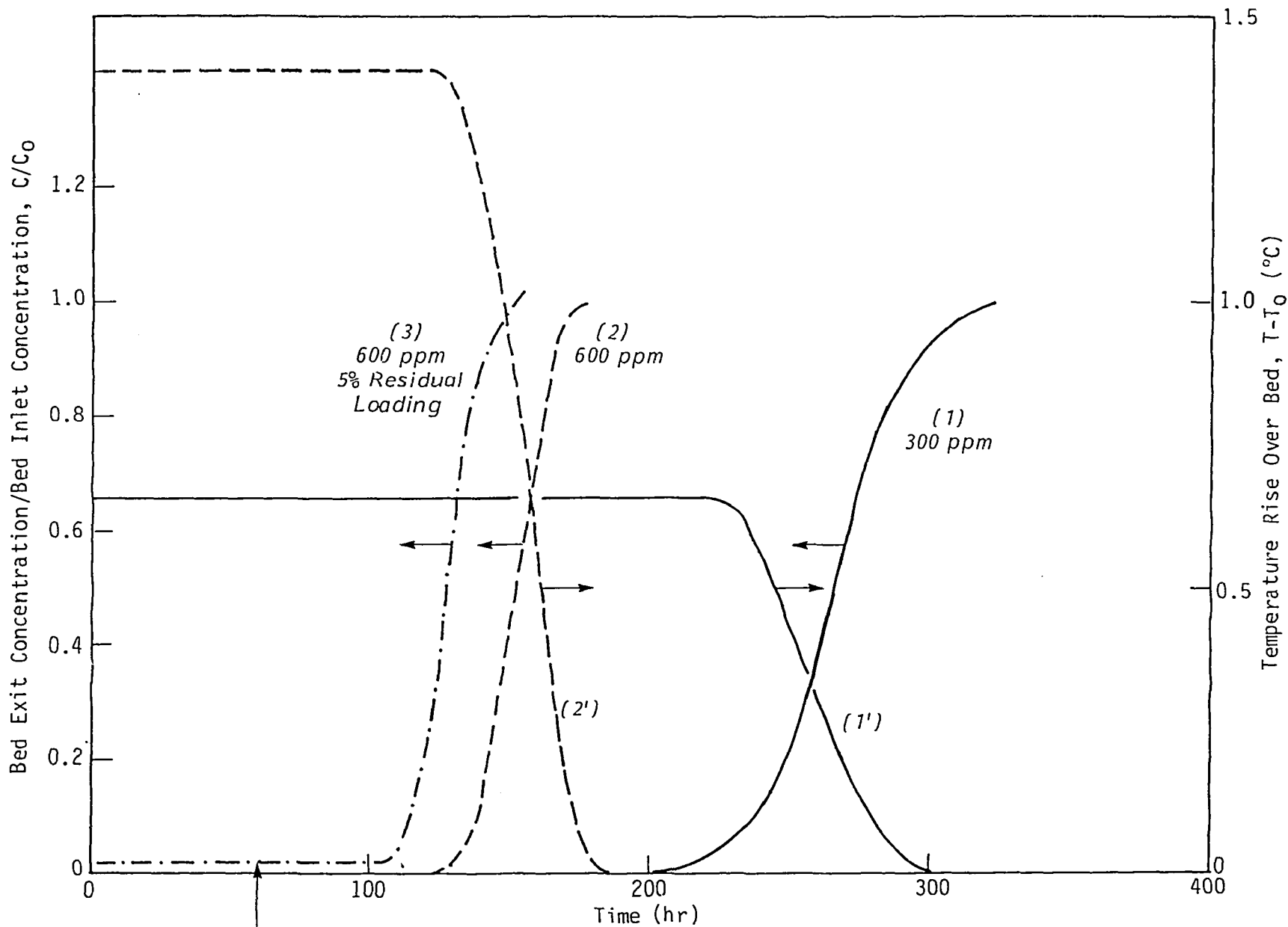


FIGURE 13
 EXPERIMENTAL BREAKTHROUGH CURVES FOR 1/16" AND 1/8" LINDE 4A SIEVE
 DETAILS ARE GIVEN IN TABLE 3



Premature Breakthrough
10 ppm for all t

FIGURE 14

SIMULATED BREAKTHROUGH CURVES FOR
H₂O - LINDE 4A SIEVE (1/8") - SEE TABLE 4
(PPM LEVELS REFER TO INLET HUMIDITIES (C₀). TEMPERATURES REFER TO BED EXIT)

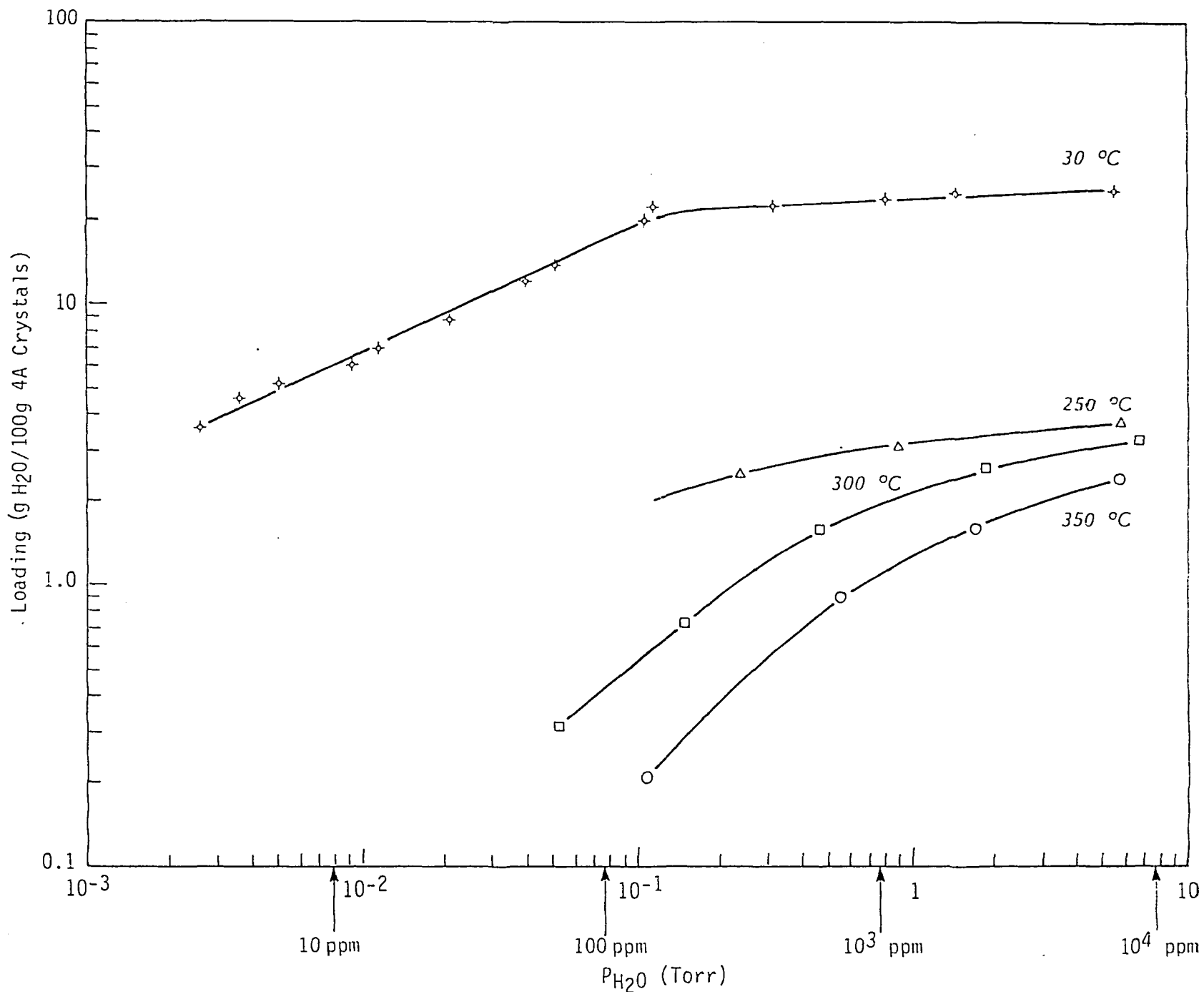


FIGURE 15

WATER ADSORPTION ISOTHERMS FOR LINDE 4A CRYSTALS