VACUUM MICROBALANCE STUDIES OF LEAD DEPOSITS FROM NATURAL WATERS

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SUMMARY

   Studies have been made of the solubility of lead in water and its deposition
in the form of the hydroxide, carbonate and basic carbonate at different pH
levels. Removal of soluble lead by precipitation as phosphate was also
examined. The microstructure and surface activity of the precipitated and
deposited lead compounds was determined by gravimetric B.E.T. nitrogen gas
sorption and thermoanalytical techniques, supported by X-ray diffractometry.
   Generally concentrations of lead in tap water are determined from the
solubility products of the pipe-scale deposits, so that the solubility of lead
decreases as the pH increases from 6 to 9. Thermal analysis and X-ray
diffractometry results show that the scale consists of basic lead carbonate,
$Pb_3(CO_3)_2(OH)_2$, at higher pH and normal lead carbonate, $PbCO_3$, at lower pH.
   Lead hydroxide, carbonate and basic carbonate form less porous and more
compact deposits, which afford protection of the lead pipe interiors against
further lead dissolution. Where pH adjustment alone proves insufficient at
reducing plumbosolvency, phosphate dosing is used. This depends on the low
solubility of the lead phosphates, particularly $PbHPO_4$. However, the
precipitated lead phosphates are too finely-divided to form stable coatings
on the pipe linings, even after a longer time.

INTRODUCTION

   Trace elements such as lead, copper, zinc and cadmium have deleterious

environmental effects. The solubility of heavy metals in natural waters

depends largely on pH conditions and to some extent on the presence of salts.

Thus in sea water the solubility of lead is restricted by the presence of

sulphate which precipitates preferentially to the hydroxide at certain pH

levels.

   In the present research, lead has been studied in more detail due to its

well-known toxic characteristics, particularly in relation to commercial water

supplies. In July 1985 the European Community came into line with Canada and

the United States in restricting the lead concentration of "running" tap water

to 50 μgdm^{-3}, with an absolute upper limit of 100 μgdm^{-3} (ref. 1). Ideally,

lead concentrations in tap water are determined by the solubilities of pipe

scale deposits; the scale should consist of basic lead carbonate at higher pH

and normal lead carbonate at lower pH. The protective character of the inner

pipe coating against further lead dissolution, i.e., its porosity, is of great

importance in this respect. Naturally it would be advantageous to have compact deposits with low porosities. Clearly pH conditions are important in relation to deposition. If the pH level is too low, lead hydroxide, carbonate and basic carbonate dissolve, the coating therefore becomes more porous and less compact and more lead is released into the water.

There have been several strategies to reduce lead contamination in drinking water, the most effective being replacement of lead pipes with copper and plastic pipes. However this is obviously an expensive strategy. The most practical and cost-effective method has involved treatment at the water-works to reduce the plumbosolvency of the water before its distribution. The treatment may involve adjusting pH and phosphate dosing. A further consideration must be the hardness of the water. It is known that the solubility of lead in soft waters decreases as the pH increases from 6 to 9 (ref. 1). Acidic drinking waters can have their plumbosolvency reduced by adjusting the pH level to 8.0-8.5, while for high calcium waters most of the calcium is precipitated as calcium carbonate above these pH levels, e.g., Clark's Process for softening water by requisite amounts of added lime. Where pH adjustment alone proves insufficient at reducing plumbosolvency, phosphate dosing may be used. This method of control relies on precipitation of lead phosphates of very low solubility.

Experimental studies will examine the precipitation and deposition of lead from solution in the form of hydroxide, carbonate and basic carbonate and compare with that of the phosphates. Examination of the microstructure, i.e., surface area and porosity, of the precipitates and deposits will provide a comparison of their compactness and whether ageing has any appreciable effect on these qualities with regard to their protective character as inner pipe coatings.

EXPERIMENTAL

Precipitation of lead compounds from solution

The pH levels at which lead is precipitated from solution as hydroxide, basic or normal carbonate or as phosphates were determined by monitoring with a glass electrode the pH changes during the progressive addition of lead nitrate and sodium hydroxide, sodium carbonate, sodium bicarbonate and sodium phosphate solutions. The shapes of the pH curves and points of inflection also indicated the composition of the precipitates. Some of the precipitates were filtered off and their composition further established by thermal analysis and X-ray diffraction.

Physical nature of the precipitates and deposits

Surface areas and porosities were determined by a gravimetric B.E.T. method

(ref. 2) using nitrogen gas sorption at $-196^{\circ}C$ recorded on a C.I. Microforce
Mark 2B vacuum microbalance (μg to mg sensitivity using 0.25 g samples or less).
The adsorption isotherms also indicated any porosity present (from hysterersis)
and pore size ranges. Average crystallite sizes were deduced from the specific
surfaces of the less porous materials. Some of the precipitates were deposited
and aged under conditions similar to comparable deposits in lead pipes for
commercial water supply; subsequently changes in surface area, porosity and
crystallite size were determined.

RESULTS AND DISCUSSION
Conditions for precipitation and deposition of lead compounds
Lead hydroxide

Fig. 1 shows the pH changes when lead hydroxide is precipitated by the
progressive addition of 0.05M. $Pb(NO_3)_2$ to 0.1M. NaOH (25 cm^3 diluted to 100
cm^3 initially). The point of inflexion, 24.5 cm^3 almost exactly corresponds to
the theoretical 25 cm^3 for the precipitation of lead hydroxide, viz., $Pb(NO_3)_2$ +
$2NaOH \rightarrow Pb(OH)_2$ + $2NaNO_3$. However, in the reverse addition (b), the inflexion
is at 17.1 cm^3 and not 25 cm^3, indicating that the precipitate is mainly basic
lead nitrate. Empirically the composition of the product is $xPb(OH)_2$, $Pb(NO_3)_2$,
where $x/(x+1) = 17.1/25 = 0.684$, making $x = 2.16$, i.e., the product is pre-
dominantly $2Pb(OH)_2$, $Pb(NO_3)_2$ with a small amount of $Pb(OH)_2$. An approximate
estimate of the solubility product of lead hydroxide, $L = [Pb^{2+}][OH^-]^2$ may be
made from this experimental data, viz., concentration of lead remaining in
solution during precipitation and $pOH = 14 - pH$, giving a solubility product
value of 1.6×10^{-17}. Thus at pH 8, the lead solubility is 1.6×10^{-5}M or
3.3 parts per million, increasing to 330 ppm at pH 7 and 33,000 ppm at pH 6.
Lead carbonates

Fig. 2 shows the pH changes when (a) basic lead carbonate is precipitated by
progressive addition of 0.05M. $Pb(NO_3)_2$ to 0.05M. Na_2CO_3 (20 cm^3 diluted to
100 cm^3 initially). The first point of inflexion at about 13 cm^3 corresponds to
the precipitation of $2PbCO_3$, $Pb(OH)_2$ (theoretical 13.3 cm^3). However, the
initial precipitation of the basic carbonate is followed by formation of the
bicarbonate at pH levels below 8 and its decomposition to the normal carbonate,
$PbCO_3$. Theoretically the carbon dioxide formed when the lead bicarbonate
decomposes should convert all of the basic carbonate initially precipitated
into normal carbonate, but this process of converting one solid to another is
slow since both solids have low solubilities and some carbon dioxide is lost to
the atmosphere so that the second inflexion of the pH curve falls somewhat
short of the theoretical 20 cm^3. Thus the most satisfactory method of
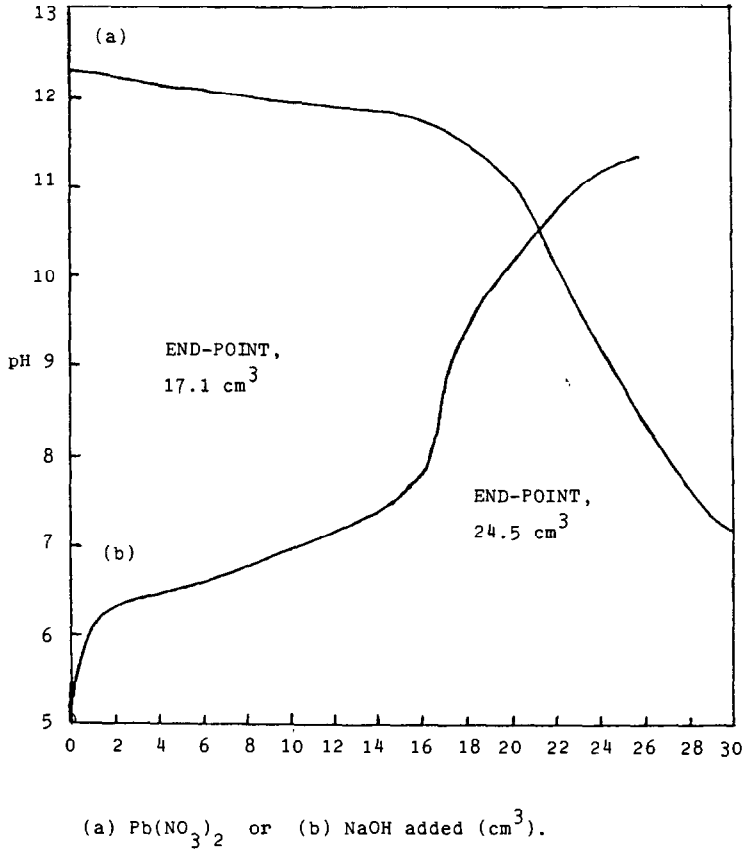precipitating the basic carbonate was to stop the addition of the lead nitrate

(a) Pb(NO$_3$)$_2$ or   (b) NaOH added (cm^3).

Fig. 1. Progressive addition of:- (a) 0.05M. Pb(NO$_3$)$_2$ to 0.1M. NaOH.
(b) 0.1M. NaOH to 0.05M. Pb(NO$_3$)$_2$.

when the pH had fallen to about 8. The normal carbonate was best prepared
below pH 8 by progressive addition of Pb(NO$_3$)$_2$ to NaHCO$_3$ as illustrated by
curve(b).

The overall reaction for the formation of the basic carbonate can be
represented as $3Pb(NO_3)_2 + 4Na_2CO_3 + 2H_2O \rightarrow 2PbCO_3,Pb(OH)_2 + 6NaNO_3 + 2NaHCO_3$,
the important partial equation being $2Na_2CO_3 + 2H_2O \rightleftharpoons 2NaHCO_3 + 2NaOH$. Below
pH 8, the following reactions lead to the precipitation of normal lead
carbonate:- $Pb(NO_3)_2 + 2NaHCO_3 \rightarrow Pb(HCO_3)_2 + 2NaNO_3$ and $Pb(HCO_3)_2 \rightleftharpoons PbCO_3 +$
$H_2O + CO_2$. If basic carbonate has been formed earlier, then $2PbCO_3,Pb(OH)_2 +$
$CO_2 \rightarrow 3PbCO_3 + H_2O$ slowly. Thus the normal carbonate, PbCO$_3$, is formed in the
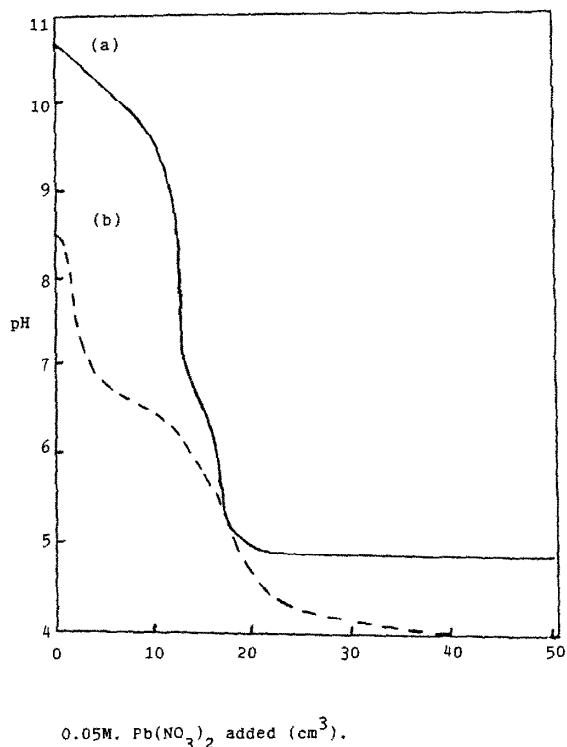pH range 6 to 8 most commonly encountered in drinking water.

0.05M. $Pb(NO_3)_2$ added (cm^3).

Fig. 2. Progressive addition of:- (a) 0.05M. $Pb(NO_3)_2$ to 0.05M. Na_2CO_3, (b) 0.05M. $Pb(NO_3)_2$ to 0.1M. $NaHCO_3$.

Thermal analysis of lead hydroxide and carbonates

Lead hydroxide

The TG curve, Fig. 3(a) obtained for lead hydroxide heated in vacuo at 10 $^\circ$C per minute on a Stanton-Redcroft Mass-flow balance MF-H5, shows a weight loss of 7.1 % compared with a theoretical weight loss of 7.46 % for $Pb(OH)_2 \rightarrow$ $PbO + H_2O$. The shape of the curve indicates a possible two-stage dehydration with formation of an intermediate (ref. 3) with the formula $PbO,Pb(OH)_2$ or $Pb_2O(OH)_2$. X-ray powder diffraction data for both the hydroxide and the oxide (massicot) confirm the thermal analysis and electrochemical data. The oxide was known to have an orthorhombic crystal lattice and this type of lattice was found also on indexing the X-ray diffraction data for the hydroxide where a = 8.79 A, b = 13.96 A, c = 8.37 A, and D_x = 7.81.
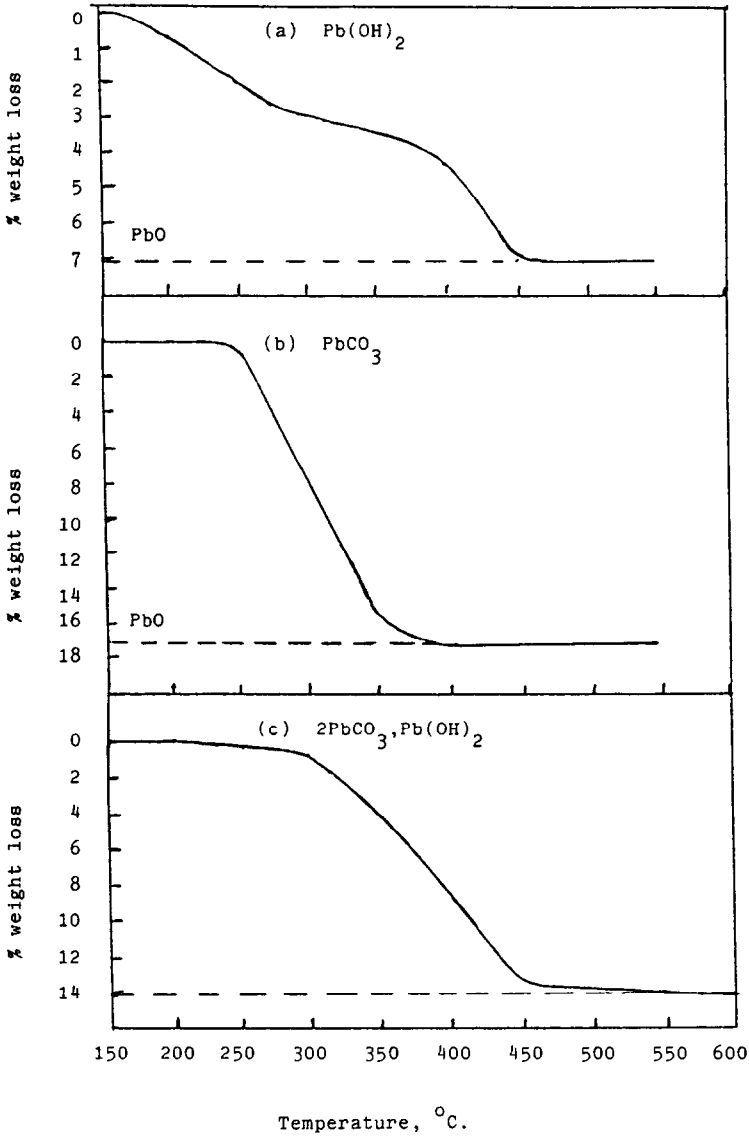
Fig. 3. TG Curves for Lead Hydroxide and Carbonates.

Lead carbonate

The TG curve, Fig. 3(b), indicates a weight loss of 17.2 % compared with the theoretical value of 16.5 % for $PbCO_3 \rightarrow PbO + CO_2$. The remaining 0.7 % is moisture which is strongly adsorbed by carbonates, cf. $CaCO_3$ which retains traces of adsorbed water up to 300 $^{\circ}C$ (ref. 4). X-ray diffraction data confirms that the sample is relatively pure, orthorhombic a = 5.18 A, b= 8.47 A,

$c = 6.13$ A and $D_x = 6.59$ which is used in subsequent surface area studies for sample buoyancy.

Basic lead carbonate

The TG curve, Fig. 3(c), shows a weight loss of 14.2 % compared with a theoretical loss of 13.7 % (2.3 % water and 11.4 % carbon dioxide) for $2PbCO_3 \cdot Pb(OH)_2 \rightarrow 3PbO + H_2O + 2CO_2$, with 0.5 % moisture. The curve indicates that adsorbed water is retained up to 300 $^{\circ}$C, but water of constitution begins to be removed above this temperature. This is in contrast to the decomposition of lead hydroxide, which does not retain adsorbed water above 150 $^{\circ}$C and loses water of constitution above this temperature.

Formation of the basic carbonate lattice $Pb_3(CO_3)_2(OH)_2$ evidently thermally stabilises the hydroxyl groups. Comparison of the basic carbonate decomposition with that of the normal carbonate indicates that loss of water and carbon dioxide occur simultaneously above 300 $^{\circ}$C. The X-ray diffraction data also indicated that the sample of basic carbonate was relatively pure, hexagonal $a = 4.51$ A, $c = 23.04$ A and $D_x = 6.36$.

Physical nature of the precipitates and deposits

Surface areas and approximate average crystallite sizes (equivalent spherical diameters) of the precipitated lead hydroxide and carbonates are tabulated as follows.

Table 1

	$S, m^2 g^{-1}$	Average crystallite size, μm
Lead hydroxide, $Pb(OH)_2$	4.4	0.17
Basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$	4.7	0.18
Lead carbonate, $PbCO_3$	3.2	0.28

The small surface areas indicate low porosities and high compactness, giving high protective character when the deposits age on the inside surfaces of lead piping. In practice, the hydroxide only occurs in extremely alkaline waters. The basic carbonate and more commonly the normal carbonate occur in the presence of drinking water. The full nitrogen sorption isotherm for lead carbonate (Fig. 4) shows a limited amount of hysteresis in the relative pressure range 0.38 to 0.96, corresponding (according to the Kelvin equation) to the mesopore range of pore diameters between 2 and 50 nm, with complete absence of micropores (below 2 nm diameter). Thus lead carbonate, $PbCO_3$, is found to form a good protective coating on the inside of lead pipes, provided that the pH of the water remains above 6.

Phosphate dosing of drinking waters

It was investigated whether phosphate dosing of drinking waters reduces the amount of lead released into the water, by causing the deposition of less
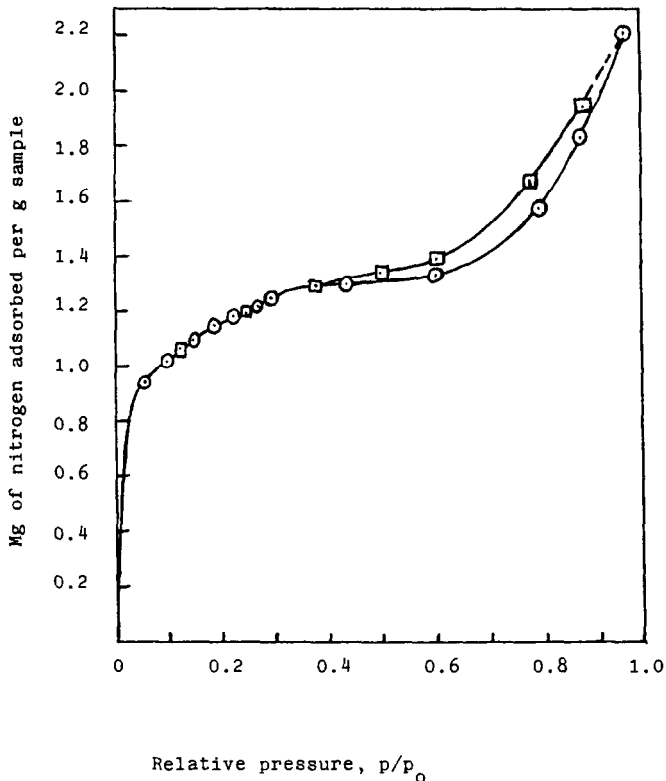
Fig. 4. nitrogen adsorption isotherm on lead carbonate.

soluble lead phosphate. Also the surface area of the lead phosphate would indicate whether it could form a compact and protective layer on the pipe interiors. Electrochemical data (Fig. 5) showed that at the higher pH levels, 9 to 11.5, basic lead phosphate, $3Pb_3(PO_4)_2 \cdot Pb(OH)_2$ or $Pb_5(PO_4)_3OH$ (lead analogue of hydroxy apatite) is precipitated, while at lower pH levels, 6 to 9, lead hydrogen phosphate, $PbHPO_4$, is formed. This was confirmed by X-ray diffraction data, which for $PbHPO_4$ indexed for an orthorhombic lattice, $a = 4.30$ A, $b = 16.30$ A, $c = 13.23$ A and $D_x = 7.30$.

Thus basic lead phosphate was precipitated by addition of the stoichiometric amount of 0.05M. $Pb(NO_3)_2$ (31.25 cm^3) to 0.05M. Na_3PO_4 (25 cm^3 diluted to 100 cm^3). Lead hydrogen phosphate was prepared best by adding 0.05M. $Pb(NO_3)_2$ to 0.05M. Na_2HPO_4 (25 cm^3 diluted to 100 cm^3).

The surface area of the lead hydrogen phosphate was 31.1 $m^2 g^{-1}$ compared with 35.5 $m^2 g^{-1}$ for the compound obtained in more alkaline conditions. These are much higher surface areas than those for the lead hydroxide and lead carbonates in Table 1, indicating that lead phosphate deposits would not be very protective
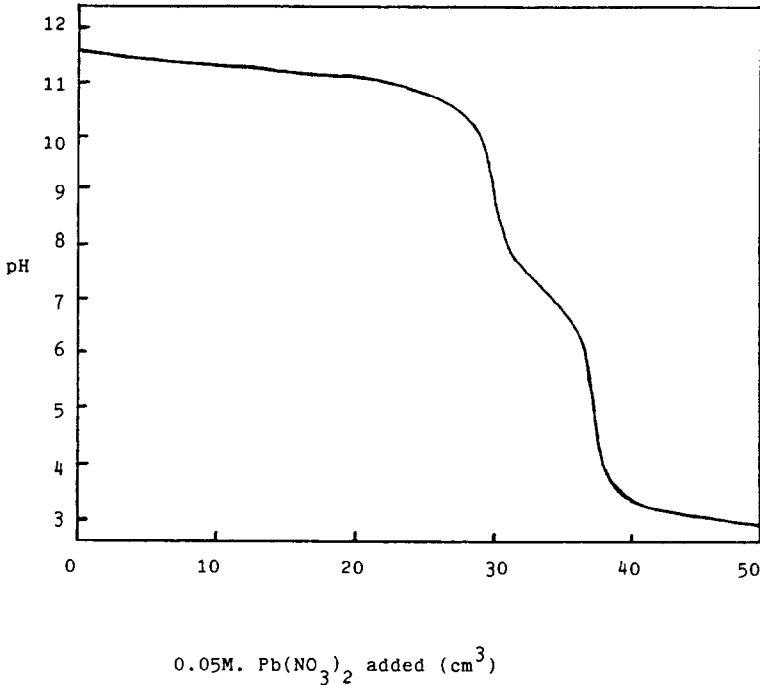
0.05M. $Pb(NO_3)_2$ added (cm^3)

Fig. 5. progressive addition of 0.05M. $Pb(NO_3)_2$ to 0.05M. Na_3PO_4.

as pipe linings due to higher porosity and less compactness. On phosphate dosing at the more usual pH levels of drinking water, lead hydrogen phosphate would be formed and the above sample did not age greatly in water at room temperature. Its surface area only decreased from 31 to 26 m^2g^{-1} after 1 month and then remained almost constant for a further 2 months, decreasing slightly to about 24 m^2g^{-1} with some loss of mesoporosity, indicated by the decrease in size of the adsorption hysteresis loop in the isotherms shown in Fig. 6.

The average crystallite size of the aged material is approximately 0.03 μm, so that although crystallites of this submicron size can form aggregates readily, the very low solubility of the phosphate restricts dissolution of the smaller crystallites and redeposition on the larger ones with possible coalescence of adjacent crystallites. The latter process would reduce macroporosity and promote the formation of stable coatings in pipes. Thus although phosphate dosing is an effective method of reducing plumbosolvency in drinking water by the low solubility of lead phosphates, it does not produce stable coatings to diminish further dissolution of lead, even after a longer time.
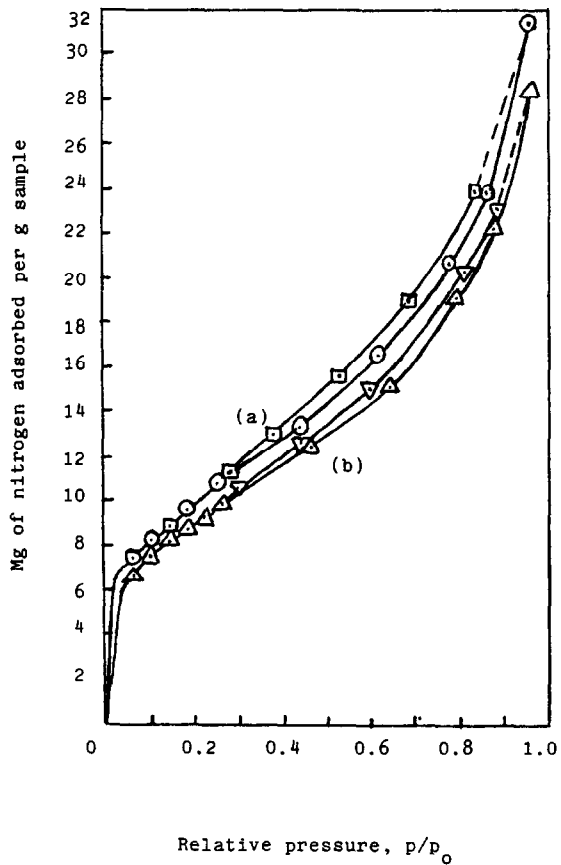
Fig. 6. nitrogen adsorption isotherms on lead hydrogen phosphate aged
(a) 1 month, (b) 3 months.

REFERENCES

1.   S.J. de Mora and R.M. Harrison, Chemistry in Britain, Oct. 1984,
      pp. 900-6.
2.   D.R. Glasson, J. Chem. Soc., 1956, pp. 1506-10.
3.   J.R. Partington, "Inorganic Chemistry" 5th Edn. Macmillan, London, (1943),
      p. 905.
4.   D.R. Glasson, "Analysis of Calcareous Materials", (1964), S.C.I.
      Monograph No. 18, pp. 401-6.