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Studies of Surface Area and Pore Structure on Portland Cement Produced in Bajil and Amran, Yemen

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دراسة المساحة السطحية و التركيب المسامي لإسمنت بورتلاندي أنتج في باجل وعمران باليمن

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خلاصة: تم تحضير مجموعة من عجائن الإسمنت ذو المواصفات البورتلاندية مختلفة المسامية وبنسبة ماء/إسمنت 0.30، 0.35، 0.40، 0.45، 0.50 و 0.55 مستخدمين أزمنة تميؤ مختلفة بدءًا من 0.021 يوماً إلى 28 يوم. التركيب المسامي وكذا منحنيات الحجم – سمك الطبقة الممتزة (V_L–t) لعجائن الإسمنت المجففة تم قياسها باستخدام غاز النتروجين الممتز. وقد وجد أنه يمكن ربط النتائج التي تم الحصول عليها مع ميكانيكية التميؤ وذلك من خلال ملاحظة النظام المسامي للعينات المجففة، كما لوحظ أن كافة أنواع منحنيات الامتزاز الأيزوثرمية للعينات الجافة تتبع الصنف الثاني. أما منحنيات الامتزاز وتحرير الامتزاز الأيزوثرمية فقد دلّت على عدم إمكانية عودة المادة الممتزة بشكل انعكاسي إلا في بعض الحالات النادرة.

ABSTRACT: Portland cement pastes of various porosities were prepared using water/cement ratios of 0.30, 0.35, 0.40, 0.45, 0.50 and 0.55; and were hydrated for various time intervals ranging from 0.021 to 28 days. Pore structure and V_L–t plots (plots of volume vs. thickness) of the hardened cement pastes were measured using nitrogen gas as the adsorbate. The results were found to be related to the mechanism of hydration as controlled by the pore system of the hardened pastes. Type II adsorption isotherms of nitrogen were obtained for all hardened cement pastes. The adsorption-desorption isotherms indicated the existence of closed hysteresis loops for most of the investigated samples and in some other cases, these isotherms were fully reversible.

KEYWORDS: Surface area; Pore size; Portland cement; Cement paste; Adsorption.

1. Introduction

Studies of surface area and pore structure of Portland cement pastes have significant values in understanding the nature of this compound material. In the present investigation, we study the surface area and pore structure of two types of Portland cement produced in Yemen by two main factories, Bajil and Amran. This work constitutes a second part of a previous investigation, in which the kinetics of hydration was studied (Babaqi *et al.,* 2001).

The hardened cement pastes were prepared at various initial water/cement (W/C) ratios and hydrated for various time intervals ranging from 0.021 to 28 days. As reported by Abo-El-Enein *et al.* (1982), nitrogen was used as adsorbate to measure the surface area and porosity of the cement pastes. The results of adsorption of nitrogen gas for the hydrated cement pastes are represented graphically. Each graph represents a number of adsorption isotherms obtained after various hydration time intervals of a certain paste made with a definite W/C ratio (initial porosity). All adsorption isotherms graphs were found to be similar in shape to type II of Brunauer classification (Brunauer and Emmett, 1935, Brunauer *et al.,* 1940), which is characterized by a low pressure region concave to the pressure axis, a high pressure region convex to the pressure axis, and an intermediate almost linear portion.

2. Materials and experimental

In the present investigation, we used two types of ordinary Portland cement produced by Amran and Bajil cement factories in Yemen. Their surface area was 3100 cm^2/g. Table 1 lists the chemical oxide compositions of these two types. Henceforth, we will refer to Amran and Bajil cement as "Sample A" and "Sample B", respectively.

Table 1. Chemical oxides compositions and ignition loss (%) of the two samples of ordinary Portland cement

Oxides	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	SO_3	Ignition Loss
Sample A	21.35	5.20	3.05	2.11	61.98	1.96	1.48
Sample B	21.31	5.58	4.16	1.93	64.25	2.11	1.85

2.1 Hydration treatment

Various cement pastes were prepared for the two types of the ordinary Portland cement by mixing dry weighed cement with distilled water continuously for 3 minutes. The W/C ratios were by weight; and each fresh paste was moulded into polyethylene plastic bottles and cured at 100% relative humidity for 24 hours. The specimens were remoulded and cured under water for the desired times of hydration.

All pastes were hydrated for various time intervals of 0.021, 0.083, 0.25, 1, 3, 7 and 28 days. At each time interval, the hydration reaction was stopped by immersing about 10 g of the ground specimen in about 100 ml of methanol/acetone mixture (1:1 by volume) and magnetically stirring for about one hour. The solid sample was then filtered with G4-sintered glass washed with about 30 ml of methanol and then dried at 80 to 90 ºC for 3 hours. The dried samples were kept in a desiccator until the time of testing.

2.2 Adsorption measurements

The surface characteristics of the hardened cements pastes were studied from the adsorption of nitrogen gas at liquid nitrogen temperature (–195.8 ºC). The apparatus used was a volumetric apparatus of conventional type. It was made from a Pyrex glass that could be divided into two parts, a vacuum line and an adsorption system.

Before carrying out a run, it was necessary to calibrate the dead space of the bulb and its connecting tubes. Calibration was made by use of pure helium (99.9% pure, supplied from British Oxygen Company, London). The dead space was divided into two parts: A small dead space enclosed by stopcocks, which constitutes the volume of the tube connecting the manometer to the burette; and a big dead space, which includes the total volume.

For calibration, the adsorbent was thoroughly vacuumed in situ to a pressure of approximately 10^{-5} mmHg at the required temperature. After purging, the adsorption bulb was immersed and a suitable amount of pure helium was introduced to the dead space. After attaining thermal equilibrium, the pressure of the helium in the burette was measured. Successive higher pressures were obtained by further raising the mercury in the gas burette to known volumes. For each pressure and known volume of the gas burette, the corresponding volume of the big dead space was calculated. The same procedure was repeated for determining the volume of the small dead space. In the latter case, the sample bulb was isolated by closing the connecting stopcock. The adsorption isotherm was determined by introducing measured volumes of the adsorbent (nitrogen gas) to the sample bulb and measuring the equilibrium pressure. The adsorbed amount could then be calculated. Successive higher pressures were obtained by raising the level of mercury in the gas burette. The saturated vapor pressure of the adsorbate was determined periodically during the adsorption run by measuring the pressure directly, which was in equilibrium with liquid adsorbate in the liquid nitrogen thermometer. The adsorption data were plotted for volume of nitrogen adsorbed, V (cm^3/g), as a function of equilibrium relative vapor pressure, P/P_0, where P is the equilibrium pressure and P_0 is the saturated vapor pressure of adsorbate. The pressure was read with the aid of a cathetometer to 0.01 mm. All readings were corrected for mercury depression and temperature.

3. Results and discussion

3.1 Surface area and pore structure

A great deal of information concerning the properties of an adsorbent is known when its surface area is determined. A well developed method is to estimate the specific area of a solid from measurements of the adsorption of gases or vapors. The method depends on the fact that it is possible, from the adsorption isotherms, to find and evaluate the volume of gas or vapor adsorbed when the entire surface of the absorbent is covered with a complete unimolecular layer known as the monolayer capacity.

Many theories have been put forward to estimate the monolayer capacity of an active solid. Great variations, however, were encountered as adsorbents are not alike in their external or internal surface and differ in their molecular structure, capillary, and pores size. Langmuir equation was the first successful theoretical trial to estimate the monolayer capacity, V_m, from adsorption isotherms. However, the equation failed to yield reliable V_m values for isotherms other than type I isotherm of Brunauer's classification (Brunauer *et al.,* 1938). The most familiar method of determining the monolayer capacity and hence the specific surface area is the one that is based on the Brunauer, Emmett, and Teller (BET) equation (Brunauer *et al.,* 1938), which can be written in a linear form as:

$$\frac{P}{V(P_0-P)}=\frac{1}{V_m C}+\frac{C-1}{V_m C}\cdot\frac{P}{P_0}, \tag{1}$$

where V is the volume of the gas adsorbed at a relative vapor pressure (P/P_0) and C is a constant characteristic of the heat of adsorption in the first adsorbed layer, which is a measure of the energy of interaction between the gas and the solid surface.

The plot of $\frac{P}{V(P_0-P)}$ vs. $\frac{P}{P_0}$ is linear within a limited range of relative vapor pressure, generally between 0.05 and 0.3. Values of V_m can be calculated from the slope $\frac{C-1}{V_m C}$ and the intercept $\frac{1}{V_m C}$ at a zero relative pressure. Using Equation (1), it was possible to describe type II and type III isotherms depending on the values of the constant C. Reliable values of V_m were obtained with type II isotherms having well-defined knee bends (i.e., those of high values of C). The surface area, $\sum$, was evaluated from:

$$\sum = \frac{V_m}{22400} N\sigma, \tag{2}$$

where V_m is the monolayer capacity in ml (N.T.P.) per g , N is Avogadro's number, and σ is the area occupied by a single molecule adsorbed on the surface. If the monolayer capacity (S_m) is expressed in g/g., then Equation (2) will take the form:

$$\sum = \frac{S_m}{M} N\sigma, \tag{3}$$

where M is the molecular weight of the used vapor.

3.2 Adsorption-desorption isotherms

Adsorption-desorption isotherms of nitrogen gas were measured volumetrically at liquid nitrogen temperature on the hardened pastes made from Sample A and Sample B cements with low (W/C = 0.30) and high (W/C = 0.50) initial porosities. Pastes made from Sample A cement were designated as IA and VA and those made from Sample B cement were designated as IB and VB.

The results of adsorption of nitrogen gas for the hydrated pastes made from Sample A and Sample B cements are given in terms of the adsorbed amount S (expressed in cm^3/g), the adsorbent, and the equilibrium relative vapor pressure of the adsorbate. These results are represented graphically in Figures 1–4. Each of these figures represents a number of adsorption isotherms obtained after various hydration time intervals of a certain paste made with a definite W/C ratio (initial porosity). All isotherms show common characteristics, and the adsorption isotherms of nitrogen gas on the various hardened cement pastes seem to belong to type II of Brunauer's classification (Brunauer and Emmett, 1935, Brunauer *et al.*, 1940), which consists of a low pressure region that is concave to the pressure axis, a high pressure region convex to the pressure axis, and an intermediate almost linear portion. This linear portion converses a long range of intermediate relative vapor pressures.

The behavior of adsorption-desorption isotherms indicates the existence of closed hysteresis loops for a number of the investigated hydrated samples while for other samples, the adsorption-desorption isotherms are fully reversible (i.e., the desorption branches are consided on the adsorption branches of the isotherms). This behavior has been noticed in other investigations made by using nitrogen gas as an adsorbate or by using other vapors (Mikhail and.Abo-El-Enein, 1972, Abo-El-Enein *et al.*, 1974, Mikhail *et al.*, 1975, Mikhail *et al.,* 1978, Abo-El-Enein *et al.*, 1978, Abo-El-Enein *et al.*, 1985, Hekal *et al.*, 1987, Abo-El-Enein *et al.*, 1990). The results of Figures 1–4 also indicate that the sigmoid shape of the isotherms depends primarily on the initial porosity of the hardened cement pastes, as controlled by the initial W/C ratio of the paste, as well as the age of hydration of the paste.

3.3 Surface areas and pore volumes

From the adsorption isotherms, the specific surface areas were evaluated by applying BET equation (Brunauer *et al.*, 1938). The total pore volumes, V_p, were taken as the saturation values of the isotherms. The mean hydraulic radii, Γ_n (Å), were also calculated from:

$$\Gamma_n\,(\text{Å}) = \frac{V_p}{S_{BET}} \cdot 10^4 \tag{4}$$

where S_{BET} is the BET specific surface area.

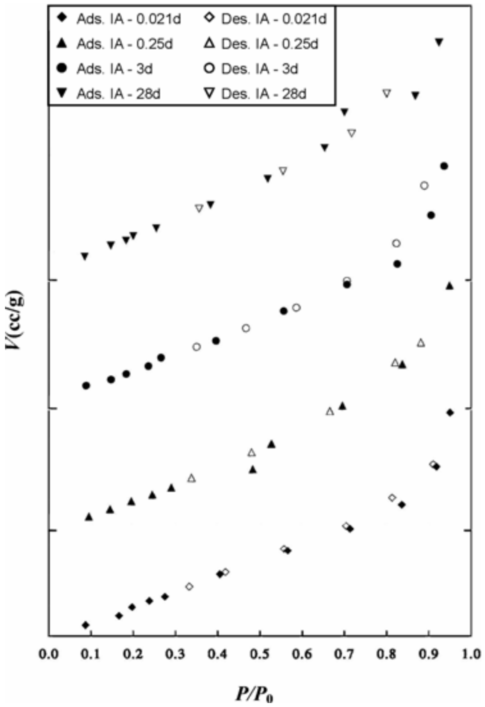

Figure1. Adsorption-desorption isotherms of nitrogen on the hardened cement pastes IA made with W/C ration at various ages of hydration (0.021, 0.25, 3, and 28 days).

Table 2. Some surface characteristics of the hardened cement pastes IB and VB made with low and high initial porosities from nitrogen adsorption.

Sample	S_{BET} (m^2/g)	BET *C*-constant	V_p (ml/g)	Mean Γ_n (Å)
Pastes IB (W/C = 0.30)				
IB - 0.021 days	118.58	5	0.1248	10.52
IB - 0.083 days	84.91	4	0.1685	19.84
IB - 0.25 days	108.74	4	0.1014	9.32
IB - 1 day	104.22	4	0.1326	12.72
Pastes VB (W/C = 0.50)				
VB - 0.021 days	50.00	5	0.1248	24.96
VB - 0.083 days	45.61	4	0.0655	14.36
VB - 0.25 days	46.17	4	0.0624	13.52
VB - 1 day	51.60	5	0.0936	18.14

The calculated values of S_{BET} (m^2/g), the BET *C*-constants, V_p (ml/g), and Γ_n (Å) of the total pore system, are all summarized in Tables 2 and 3 for pastes made from Sample B (pastes IB and VB) and Sample A (pastes IA and VA) cement, respectively. The values of S_{BET} and V_p listed in Table 2 for pastes made from Sample B cement indicate that pastes with low porosity (pastes IB) possess higher surface areas and pore volumes than those of high porosity (pastes VB). These behaviors are mainly related to the crystalline characteristic and physical state of hydration products formed within the pore system of the hardened pastes. Evidently, hydrates formed with low porosity pastes (IB) are almost more amorphous with ill-crystallized character as compared with those of crystalline hydrates formed with high porosity pastes (VB).

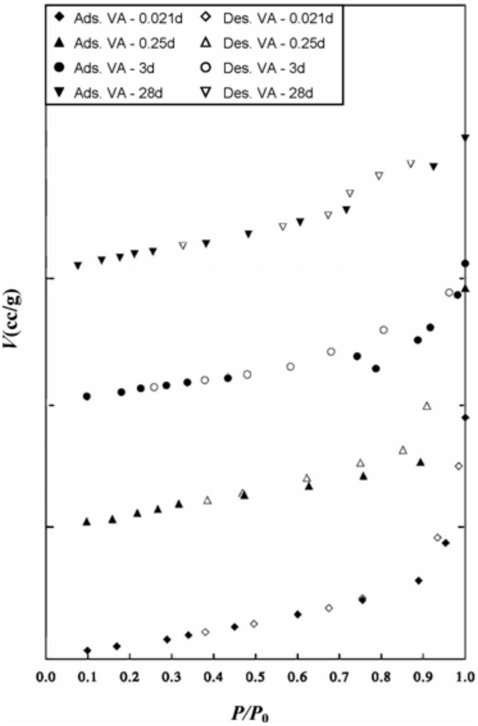

Figure 2. Adsorption-desorption isotherms of nitrogen on the hardened cement pastes VA made with W/C ration at various ages of hydration (0.021, 0.25, 3, and 28 days).

Since Γ_n represents the average width of the total pore system accessible to nitrogen molecules, the relatively low values of Γ_n obtained for the lower porosity pastes (IB) are mainly a consequence of the increased accessibility of nitrogen molecules used to measure larger fractions of the total pore system of the hardened pastes for the higher porosity pastes (VB). However, Γ_n values are relatively high, which indicate a decreased accessibility of the nitrogen molecules towards the pore system of these hardened pastes (VB). In addition, the total pore volumes measured by nitrogen are higher for pastes made with a low initial W/C ratio (pastes IB) than those made with a high initial porosity (pastes VB).

Table 3 lists the main surface characteristics of the hardened pastes made from Sample A cement (pastes IA and VA) at different ages of hydration, namely, 0.021, 0.25, 3 and 28 days. Evidently, the BET surface areas as well as the total pore volumes are higher for pastes made from low initial W/C ratio (pates IA) as compared with those made with high initial W/C ratio (pastes VA). These results are easily explained in terms of the different degrees of crystallinity of hydrates formed in the lower porosity pastes (IA) when compared with those formed in the higher porosity pastes (VA).

The values of the *C*-constants of BET equation reported in Tables 2 and 3 are very low for all of the hardened cement pastes investigated in this study (pastes IB, VB, IA and VA). Since the BET *C*-constant can be taken as a rough indication for the degree of interaction between the solid surface and the adsorbate molecules, hence, it is an adequate measure for the heat of adsorption in the first adsorbed layer. Therefore, the heat of adsorption of nitrogen gas on the various hardened cement pastes (IB, VB, IA and VA) is very low, indicating non-specific adsorbent-adsorbate interactions.

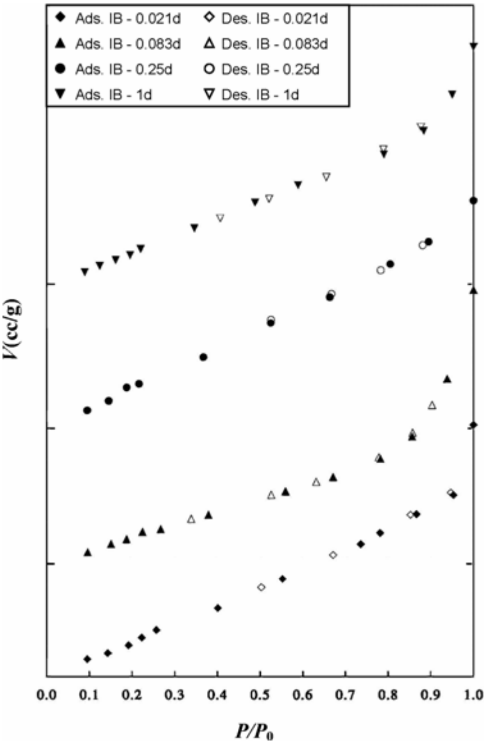

Figure 3. Adsorption-desorption isotherms of nitrogen on the hardened cement pastes IB made with W/C ration at various ages of hydration (0.021, 0.083, 0.25, and 1 day).

Table 3. Some surface characteristics of the hardened cement pastes IA and VA made with low and high initial porosities from nitrogen adsorption.

Sample	S_{BET} (m^2/g)	BET *C*-constant	V_p (ml/g)	Mean Γ_n (Å)
Pastes IA (W/C = 0.30)				
IA - 0.021 days	66.12	4	0.2469	37.75
IA - 0.25 days	82.58	5	0.1919	23.23
IA - 3 days	80.32	7	0.1704	22.34
IA - 28 days	87.00	9	0.1638	18.83
Pastes VA (W/C = 0.50)				
VA - 0.021 days	36.60	5	0.1365	37.30
VA - 0.25 days	42.20	4	0.1310	31.04
VA - 3 days	70.00	7	0.1606	22.94
VA - 28 days	94.00	26	0.1599	16.97

3.4 Pore structure and V_L–*t* plots

Several investigators have offered *t*-curves for nitrogen. Cranston and Inkley (1957) derived a composite curve from nitrogen isotherms on 15 nonporous materials. Another *t*-curve, based on a variety of other nonporous adsorbents was derived by De Boer and coworkers (Lippens *et al.,* 1964, De Boer *et al.,* 1965).

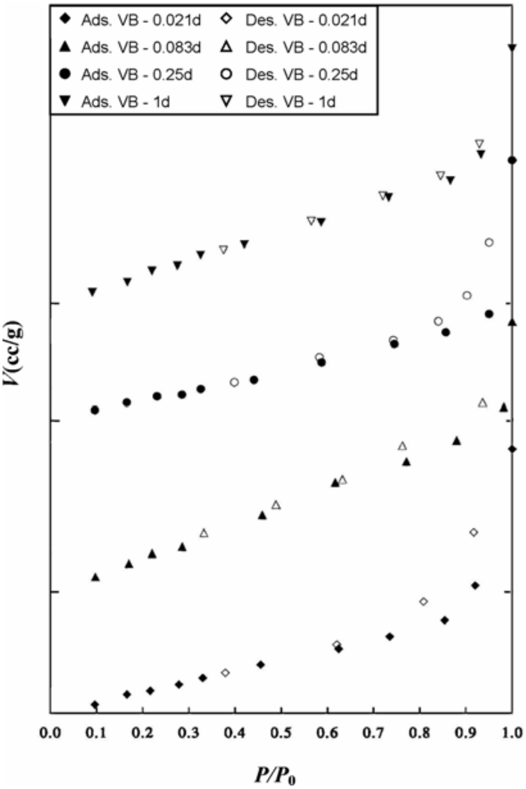

Figure 4. Adsorption-desorption isotherms of nitrogen on the hardened cement pastes VB made with W/C ration at various ages of hydration (0.021, 0.083, 0.25, and 1 day).

If we restrict ourselves to nitrogen and to only one temperature (liquid nitrogen temperature), it is a fortunate fact that for a wide variety of adsorbents, the multi-molecular adsorption curve (the *t*-curve) proved to be identical. This fact has led De Boer to the claim of a "universal" multi-molecular adsorption curve for nitrogen. Other investigators (Mikhail *et al.,* 1968), however, have shown that even for nitrogen, the existence of the so-called universal multi-molecular adsorption curve can be considered as an oversimplified statement for the actual situation. To obtain a "correct" *t*-curve suitable for a particular application, Mikhail *et al.,* (1968) considered another factor besides the absence of porosity, namely, the *C*-constant of BET equation. They emphasized the importance of using the "correct" *t*-curve in a particular pore structure analysis. By "correct" *t*-curve, they meant a *t*-curve on which the heat of adsorption of nitrogen is of the same order of magnitude as the heat of adsorption of the sample under study. The statistical thickness *t*(Å) of the adsorbate can be obtained from :

$$t = \frac{MV_{\mathrm{sp}}}{22{,}414} \cdot \frac{V_{\mathrm{a}}}{S_{\mathrm{BET}}} \cdot 10^4, \tag{5}$$

where M is the molecular weight of nitrogen, V_{sp} is the specific volume of nitrogen in ml/g, V_{a} is the amount adsorbed in cm^3/g at STP, and S_{BET} is the specific area in m^2/g.

In calculating the value of *t*, the density of the adsorbate is considered to be equal to the density of liquid nitrogen at the temperature of the isotherms (–195.8 °C). A practical way to use the *t*-curve for nitrogen is to plot experimental adsorption curves as a function of *t*-values; hence, $V = f(t)$ is taken instead of $V = f\left(\frac{P}{P_0}\right)$.

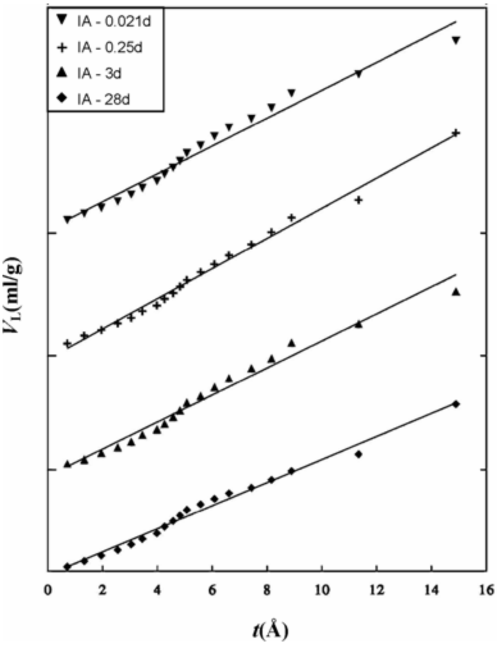

Figure 5. V_L–t plots of nitrogen adsorption on the low-porosity cement pastes IA at various ages of hydration (0.021, 0.25, 3, and 28 days).

In any normal case of multi-molecular adsorption, the experimental points should fall on a straight line passing through the origin. The slope of this line gives the specific surface area S_t in m^2/g according to the following equation:

$$S_t = \frac{V_L}{t} \cdot 10^4, \qquad (6)$$

where V_L is the volume in ml/g of nitrogen adsorbed and t is the statistical thickness in Å.

Concerning the shape of the V_L–t plots, Lippens and De Boer (1965) have pointed out three possibilities with regard to the slope of the V_L–t plot (straight line, deviates upwards, or deviates downwards from the straight line). In the present investigation, the V_L–t plots were constructed on the basis of the adsorption branches of isotherms by using the *t*-values published for solids, having low values of the *C*-constant of the BET equation (i.e., low heat of adsorption) as obtained from the adsorption of nitrogen on a number of nonporous oxides.

Figures 5–8 show the V_L–t plots for the hardened cement pastes IA, VA, IB, and VB, respectively. A definite criterion for the correctness of the V_L–t plot is the close agreement between the surface areas obtained from these plots (known as *S*) and the BET surface areas (S_{BET}). This agreement is shown in Tables 4 and 5 for the hardened pastes made from Sample A and Sample B cements, respectively, which support the use of the suggested *t*-curve for the adsorption of nitrogen on the hardened cement pastes. The V_L–t plots shown in Figures 5–8 indicate, in most of the investigated cases, downward deviations from the initial straight lines, which pass through the origin. In some other cases, a slight upward deviation is noticed, indicating the presence of mesopores with limited sizes. The downward deviations, however, demonstrate the existence of narrow pores in the pore system of the hardened cement pastes.

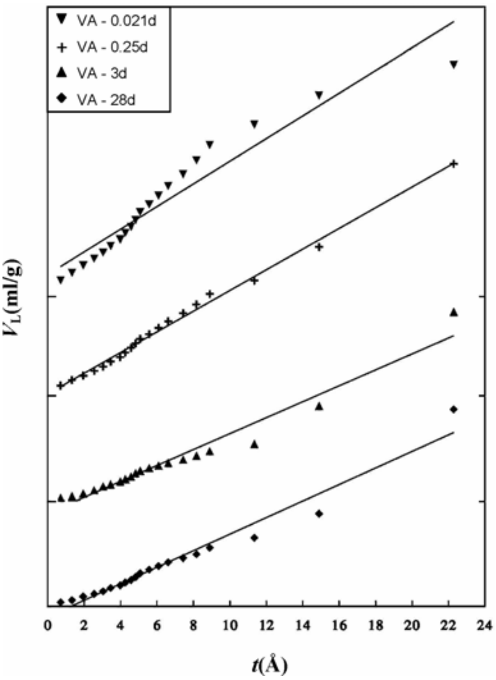

Figure 6. V_L–t plots of nitrogen adsorption on the low-porosity cement pastes VA at various ages of hydration (0.021, 0.25, 3, and 28 days).

Table 4. The BET surface area S_{BET} as compared with the surface area S_t obtained from the V_L–t plots for the hardened cement pastes IB and VB made with low and high initial porosities.

Sample	S_{BET} (m^2/g)	S_t (m^2/g)
Pastes IB (W/C = 0.30)		
IB - 0.021 days	118.59	1106.50
IB - 0.083 days	84.91	85.50
IB - 0.025 days	108.74	100.10
IB - 1 day	104.22	100.30
Pastes VB (W/C = 0.50)		
VB - 0.021 days	50.00	52.10
VB - 0.083 days	45.61	47.20
VB - 0.25 days	46.17	45.20
VB - 1 day	51.60	51.10

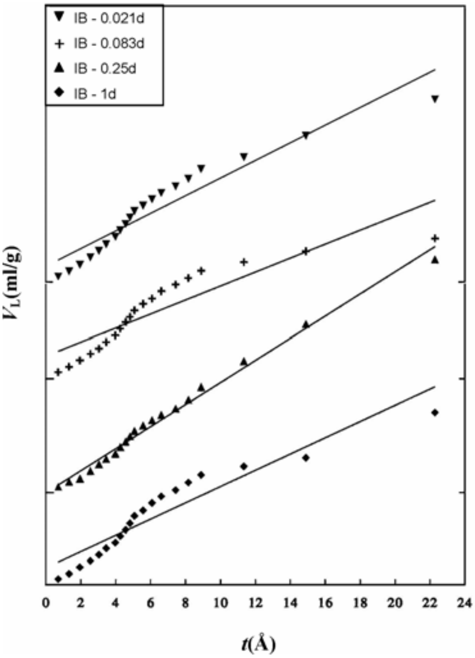

Figure 7. V_L–t plots of nitrogen adsorption on the low-porosity cement pastes IB at various ages of hydration (0.021, 0.083, 0.25, and 1 day).

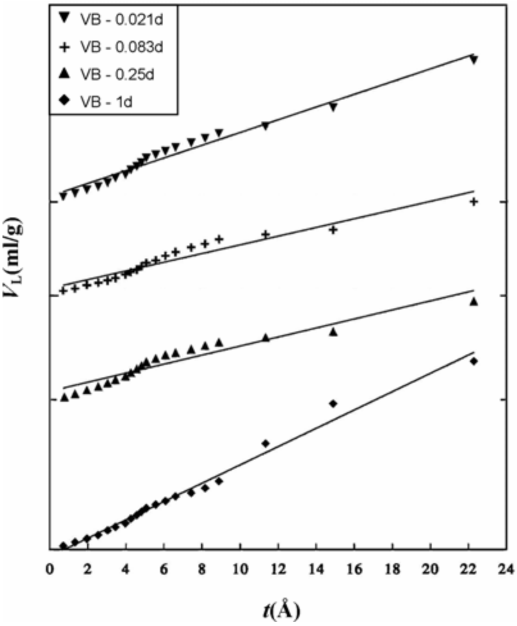

Figure 8. V_L–t plots of nitrogen adsorption on the low-porosity cement pastes VB at various ages of hydration (0.021, 0.083, 0.25, and 1 day).

Table 5. The BET surface areas S_{BET} as compared with the surface areas S_t obtained from the V_L–t plots for the hardened cement pastes IA and VA made with low and high initial porosities.

Sample	S_{BET} (m^2/g)	S_t (m^2/g)
Pastes IA (W/C = 0.30)		
IA - 0.021 days	66.12	62.10
IA - 0.025 days	82.58	80.00
IA - 3 days	80.32	80.70
IA-28 days	87.00	85.00
Pastes VA (W/C = 0.50)		
VA - 0.021 days	36.60	38.10
VA - 0.25 days	42.20	39.20
VA - 3 days	70.00	72.00
VA - 28 days	94.20	98.80

Evidently, the V_L–t plots shown in Figures 5 and 6 for Sample A low and high porosity cement pastes indicate the existence of only upward deviations from the initial straight line passing through the origin. This fact leads to a conclusion that the entire pore system of the hardened cement pastes IA and VA consist mainly of meso-pores. The results of Figure 7 obtained for Sample B low porosity cement pastes (IB), however, show only downward deviations from the initial straight line passing through the origin. Therefore, the pore system of these pastes consists mainly of micro-pores. For Sample B high porosity cement pastes (VB), the pore system is found to be consisting mainly of micro-pores at the early ages of hydration (0.021–1 days) whereas at the later ages of hydration (3–28 days), only meso-pores are detected.

4. Conclusion

Type II adsorption isotherms of nitrogen were obtained for all of the investigated hardened cement pastes. In addition, the adsorption-desorption isotherms indicated the existence of closed hysteresis loops for most of the investigated samples. In some other cases, the adsorption-desorpion isotherms were fully reversible. The BET surface areas as well as the total pore volumes were found to be higher for the lower porosity cement pastes (IA and IB) than those made with higher initial porosities (pastes VA and VB). This is mainly due to the different crystalline habit of the hydrates formed within the pore system of the various investigated cement pastes. On the other hand, the mean hydraulic radii of the total pore system accessible to nitrogen molecules were found to have lower values for the lower porosity pastes (IB) compared with the higher porosity pastes (VB). The *C*-constant values of the BET equation are very low, which indicate a very low heat of adsorption of nitrogen gas on the various hardened cement pastes. This indicates non-specific interactions between the adsorbate (nitrogen) and the adsorbent (cements pastes). The constructed V_L–t plots indicate the existence of both micro- and/or meso-pores of limited sizes.

5. References

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