DEVELOPMENT CONSULTANTS ASSOCIATION

Evaluation of Low Porosity Cement Pastes And Concretes For Desalination Plants.

Presented before Symposium
on Desalination its Scientific
Methods, Economics and
Importance to Domestic and
Agricultural Purposes in the
Arab World

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By:
Development Consultants
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Summary:

A laboratory study of low-porosity concrete is reported. Evaluation and testing were done under a variety of temperature-pressure-brine concentration conditions, simulating those prevailing in desalination plants. Corrosion of both the concrete and the reinforcing steel was assessed. Pore structure studies have shown that good protection could be offered by controlling the pore structure, and by reducing the pore size to a limit where molecular sieve action could inhibit penetration of the corrosive ions. A recomendation is offored where surface coatings and sealants should be used to protect external surface corrosion.

Introduction:

The economic feasibility of large-scale desalting plants is in part dependent upon the development of improved designs in the use of construction materials which can lead to substantial cost reduction. The extensive use of concrete and related materials in this type of construction has been proposed as a cost saving item. Very little background experience is available concerning the use of this material and the accessory materials which may be required for use with concrete under the environmental conditions that will be encountered in desalination plants.

The use of low porosity concrete seems to be a final goal for this particular application, and during the last decade efforts were directed towards the production of hardened cement pastes of low porosity (1,2). The details of preparation and the technical data were published elsewhere (1). In the meantime theoretical development of the means of pore structure analysis of these materials received considerable interest (3,4). The present investigation represents the second phase of these studies, namely those concerned with means of evaluation of the efficiency of low porosity concrete under the working conditions of temperature, pressure and salinity that will exist in an evaporator-type desalting plant. The test program consists of three related studies identified as follows:

I -- Evaluation of concrete containing natural coarse aggregate under a variety of temperature-pressure-brine concentration conditions.

II - Concrete reinforcement materials and their corrosion under the working conditions.

III - Microstructural investigations mainly concerned with pore size and pore size distribution analysis.

Brief presentation of the main results obtained would lead eventually to the conclusion ~~that the~~ efficiency of concrete for this particular use is associated with the development of microporosity, and that micropores with hydraulic radii < 10 Å might act as molecular sieves for corrosive ions for both the concrete and the reinforcement.

<u>Experimental:</u>

Evaluation of the concrete is carried out in five independent closed saline water test systems, each operating under one of the following conditions:

1 - 40 °C, 0.07 Atm., 175,000 ppm (specimen I)
2 - 95 °C, 0.80 Atm., 73,000 ppm (speciment II)
3 - 105 °C, 1.35 Atm., 73,000 ppm (speciment III)
4 - 120 °C, 2.11 Atm., 73,000 ppm (specimen IV)
5 - 140 °C, 4.08 Atm., 38,400 ppm (specimen V)

Synthetic sea water brines utilized in the 95°C 105 °C, 120 °C and 140 °C test systems were prepared using a propristary mixture of salts and tap water. This salt preparation was a formulation of 10 granular inorganic compounds most commonly found dissolved in the major oceans of the world. The type and amount of each salt compound found within this formulation is such as to meet ASTM Specification D-1141-52, Formula A, for substitute sea water. Brines used in these systems are subjected to an acid treatment prior to use to reduce the quantity of carbonates.

It was found to be impossible to dissolve enough sea salts to obtain a concentration of 175,000 ppm specified for the 40 °C brine test, because of the low solubility of calcium salts. Since this problem would be encountered in practice and would be solved by the use of ion exchange resins or other means of water softening, the final test solution was modified to duplicate a softened water by the substitution of sodium for a large percentage of the calcium and magnesium.

The concrete tested in the main program contains natural aggregate (gravel) with a maximul size of ¼ inch. The concrete consisted of 1 part by weight of cement, 2.2 parts sand and 2.8 parts gravel. The clinker is type I, and it contains as well calcium lignosulphonate (1% by weight of clinker), calcium carbonate (0.5% by weight of clinker and dissolved in the mixing water) and tap water (1,2). The water/cement ratio was 0.40. The Blaine surface area of the clinker was about 6000 cm^2/gm.

Concrete in the form of 6- by 12-inch cylinders and 4- by 4- by 30 inch bars was placed in the 12- inch-diameter test chambers of the test systems, brine was circulated at approximately 4 feet per second for the predesignated number of days, then the concrete was removed and subjected to standard concrete tests. These tests included determinations of length and weight change, modulus of elasticity, unit weight, and compressive strength. Specimens were also petrographically examined to determine microstructural cracking and chemical alternations.

Pore size analysis was done on microscopically selected specimens from which the aggregate was removed, and by using water vapour adsorption-desorption techniques (5,6). Analysis of wide pores (hydraulic redius $r_h > 20$ Å) was done by using the modelless method (3), while micropore analysis ($r_h < 20$ Å) was done by the MP-method (4).

Corrosion and corrosion inhibition of steel in concrete was evaluated by anodic polarisation measurements, in which a rapid laboratory method could be applied (7,8).

Results:

A) Compressive strength and modulus of elasticity:

High and low temperature distilled water tests proved quite conclusively that a normal high-quality concrete cannot suitably withstand the leaching effects of mineral-free waters even at only moderate temperatures. The severity of leaching of the matrix from the concrete by the low-temperature distillate was somewhat less than that which occurred from exposure to the high-temperature distillate. However, in both cases deterioration of the surfaces was sufficient to preculude the use of normal concrete in areas of flowing distilled water.

The general conditions of the low porosity concrete subjected for 2 years to the 40°C synthetic sea water brine is excellent. Concrete specimens have shown no signs of deterioration of any type; further, all dynamic, static, and petrographic tests indicate that the concrete remains sound. Compressive strengths of the concrete increased with continued brine exposure to a maximum of 8,980 psi at 1 year and then dropped slightly to 8,240 psi at 2 years' age, Figure 1. Since no deterioration could be detected by any of the microscopical tests, the cause of this reduction in compressive strength is not known. Continuously dried control concrete after a comparable age had a compressive strength of 7,750 psi. Modulus of elasticity of 5.68 million psi was above the range normally expected for good quality concrete, Figure 2.

The general condition of the concrete subjected for 1 year to the 95° synthetic sea water brine can be considered excellent. No evidence of deterioration exists, although some minor alteration is occurring on the periphery of the specimens, Figure 3. Compressive strengths of the natural aggregate concretes averaged 8,660 psi after 1 year of exposure.

The general condition of the concrete subjected 1 year to the 105 °C synthetic sea water brine can be considered good. No evidence of deterioration exists, although some minor surface alteration has occurred. Compressive strength of the natural aggregate concrete subjected this environment for 1 year averaged 8,350 psi, Figure 1. The strength progression of this concrete is comparable to that developed by similar concrete undergoing other hot brine exposure and in no way indicates deteriorated concrete.

The general condition of the concrete subjected for 1 year to the 120 °C synthetic sea water brine can be considered good. Although some surface alteration has been determined petrographically, no deterioration has taken place. Compressive strength of the natural aggregate concrete averaged 8,520 psi, Figure 1. Moduli of elasticity of the natural aggregate concretes averaged 5.86 million psi. This value is well above the 4.5 million psi considered average for good quality concrete and no evidence of deterioration exists.

The general condition of the concrete subjected for 2 years to the 140 °C synthetic sea water brine can be considered both good and marginal. The interior concrete is still sound as evidenced by high compressive strengths although somewhat less than at previous readings, and lack of microstructural cracks, expansion, or chemical reactions. The surface concrete, however, is altered chemically and deteriorated to an average depth of 11 millimeters. This deteriorated peripheral concrete, which has thickened somewhat during the past 6 months' exposure, has undergone softening, but except for removal by jarring, this surface material is still intact. Based on the original cross-sectional area of the specimens, maximum compressive strength of the concrete subjected to the 140°C brine was developed after about 90 days' exposure. Subsequently, it retrogressed from the maximum of 7,910 psi to 6,150 psi after 18 months' exposure, Figure 1. This retrogression has been somewhat proportional to the rate and depth of deterioration which indicates that the drop in compressive strength is due, for the most part, to the reduction in cross-sectional area of the sound concrete in the specimen. No deterioration of the interior concrete has been noted. Modulus of elasticity of the concrete was 4.50 million psi. This figure is average for good quality concrete and reflect no deterioration. It should be pointed out here that in l light of the surface deterioration being undergone by the concrete, its use at 140 °C would probably not be recommended.

B) Reinforcement Corrosion Studies:

To provide a nondestructive test for predicting the corrosion behaviour of concrete embedded steel, the electrochemical approach has been used by measuring the anodic polarization behaviour of the steel (7). Two types of anodic polarization experiments were carried out. In the one type the potential was measured as a function of the polarization current density per unit area of anode; and in the other type the steel potential was measured as a function of time at a constant current density of 10 microamperes per sq. cm.

Results of these tests indicate that no significant corrosion of the steel reinforcing bars has occurred as a result of their exposure to any of the five brine environments for any length of time. Table (1) summarizes the results obtained from these experiment combined with weight loss tests.

C) Pore structure studies:

Complete pore structure analysis has been carried out both for the unexposed concrete and for the concrete exposed to the five brine environments. The pore structure was measured for the mortar after the gravel was removed from the specimens. Analysis was based on measurements of the adsorption-desorption of water vapour at 35 °C. Wide pores, with hydraulic radii > 20 Å, were analyzed using the "corrected modelless method" (3), while narrow pore, with hydraulic radii < 20 Å, were analyzed using the "MP-method" (4).

Results of the analyses are shown in Figure 4. Two main significant conclusions could be drawn from these results, namely:

1 - For both the original unexposed concrete and the exposed concrete, dual distribution of pore sizes

exist, with the presence of a significant group of pores of hydraulic radii of about 5 Å. The significance of such result lies in the fact that with such narrow pores of dimensions comparable to molecular parameters, the molecular sieve action against corrosive ions could be easily understood.

2 - Since the protection of both concrete corrosion and embedded steel corrosion was offered in this investigation through molecular sieve action, the present results do not offer any protection against concrete surface corrosion. It is recommended in this respect that surface coatings and sealants be applied as well beside the control of the pore structure. Current research is now being directed to this point and promising results are now being accumulated which lead to the goal that complete protection could be assumed when control of pore structure is coupled with surface coating protection.

Conclusions:

Conclusions based on available results of tests performed on the low porosity concretes used in this investigation are as follows:

1 - Conventional portland cement concrete of normal

porosity will not withstand the leaching effects of hot flowing water.

2 - Low-porosity concrete has not been deterimentally affected by 2 year's exposure to the 38°C flowing synthetic sea water brine. It appears, therefore, that it would be suitable for use under these conditions for an extended period of time.

3 - The interior of concrete exposed to the 140°C synthetic sea water brine for 24 months is sound; however, the exterior concrete is moderately deteriorated to an average depth of 11 millimeters and shows chemical alteration, extensive microfractures, and some separation by large cracks. The life expectancy of this concrete under the subject environment cannot be predicted at this time, although its use would probably not be recommended. Its use would require some sacrificial concrete in addition to that covering the reinforcing steel on the surfaces exposed to the brine.

4 - No significant corrosion of the steel reinforcing bars has occurred as a result of exposure to flowing synthetic sea water brine regardless of temperature or length of exposure.

- Pore size analysis of the hardened cement component indicated the presence of a special group of micropores, with hydraulic radii $\ll 10$ Å; and these could possibly act as molecular sieves against corrosive ions, both for concrete and for steel reinforcement.

Table (1)

Corrosion Rates of Embedded Steel Reinforcing Bars

Specimen	Accumulative test period (days)	Corrosion rate of steel at end of test period (gm / year for the bar)
I	28	0.2
	90	0.2
	180	0.3
	270	0.4
	1 year	0.2
	18 months	** NSC
II	28	0.1
	90	0.2
	180	0.2
	270	0.3
	1 year	0.3
	18 months	NSC
III	28	3.2
	90	2.8
	180	2.2
	270	0.6
	1 year	1.0
	18 months	NSC
IV	28	1.1
	90	1.5
	180	2.4
	270	0.5
	1 year	2.2
	18 months	NSC
V	28	* L0.1
	90	L0.1
	180	L0.1
	270	L0.1
	1 year	–
	18 months	NSC
	2 years	NSC

* L = less than

** NSC = no significant corrosion

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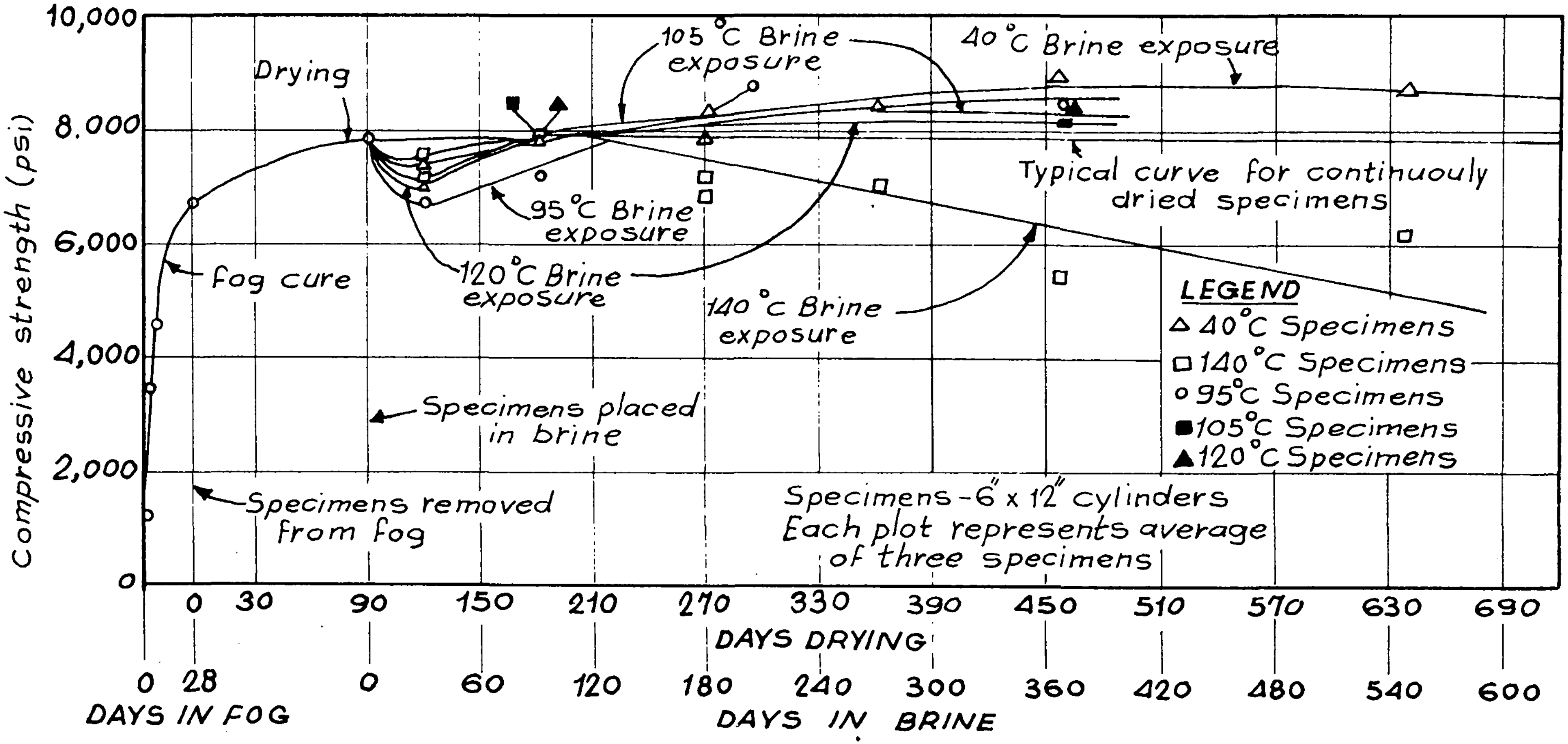

Fig. (1) Compressive strengths of natural aggregate concretes subjected to fog, drying, and various brine environments.

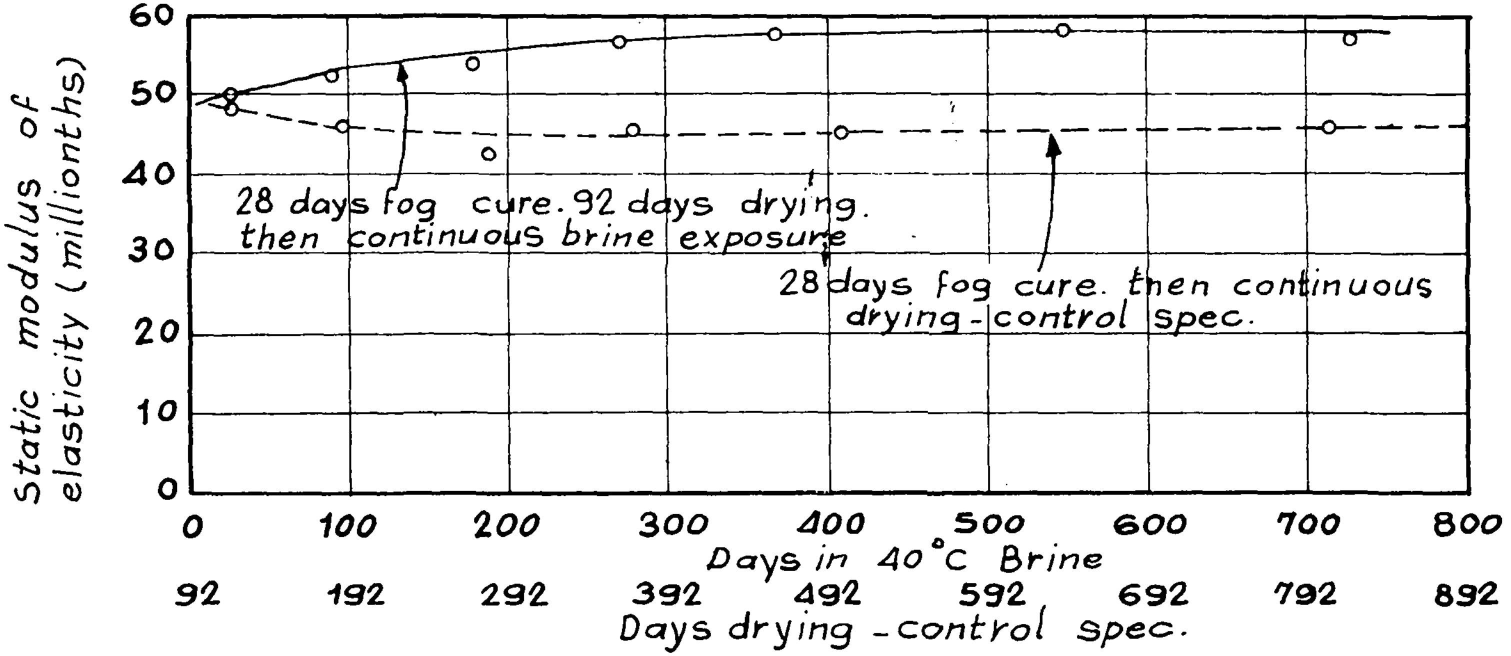

Fig.(2) Modulus of elasticity of natural aggregate concrete subjected to 40°C synthetic sea water brine, and continuously dried control concrete. points plotted at each age represents the average of three different specimens

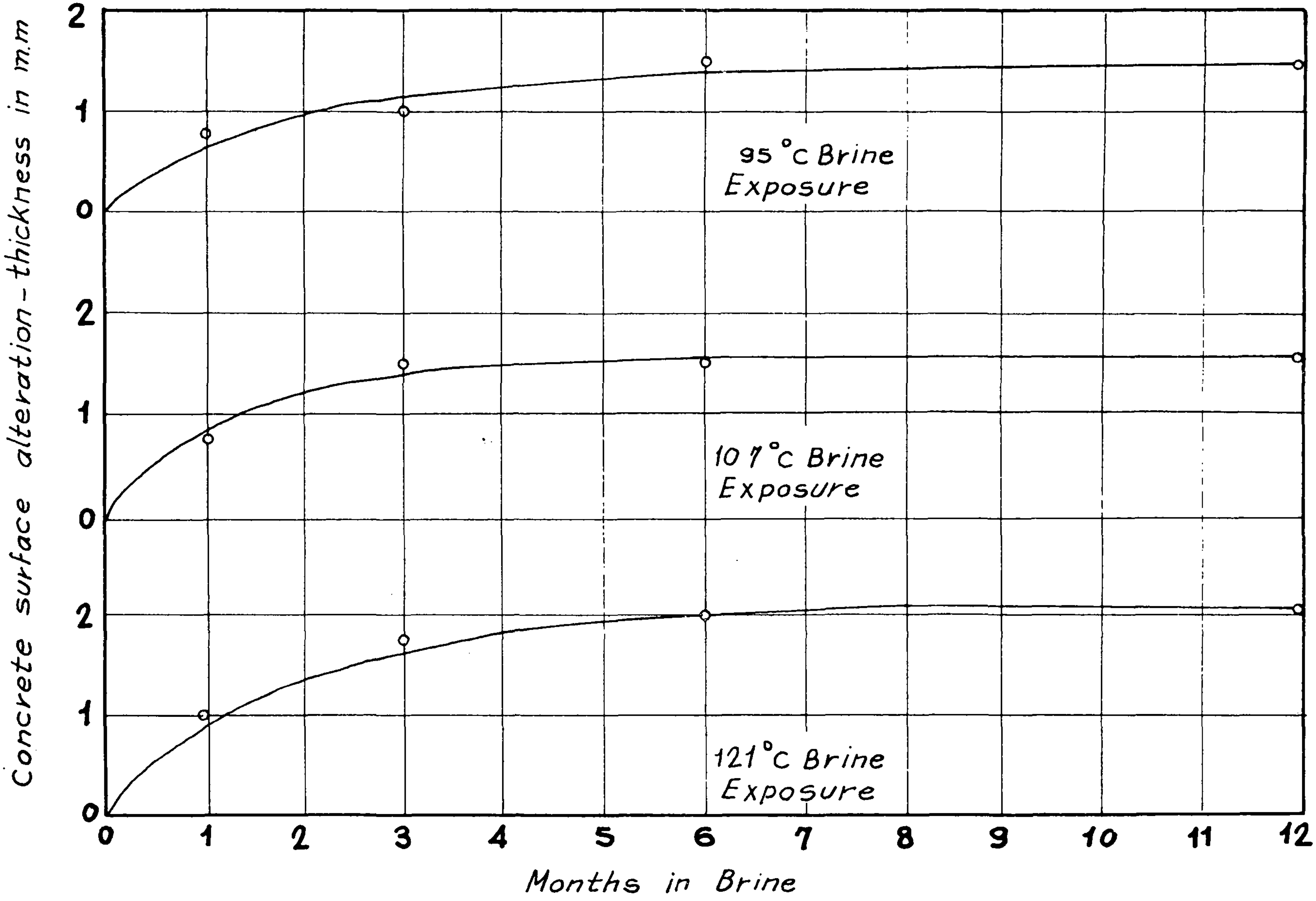

Fig. (3) Comparison of concrete surface layer alteration.

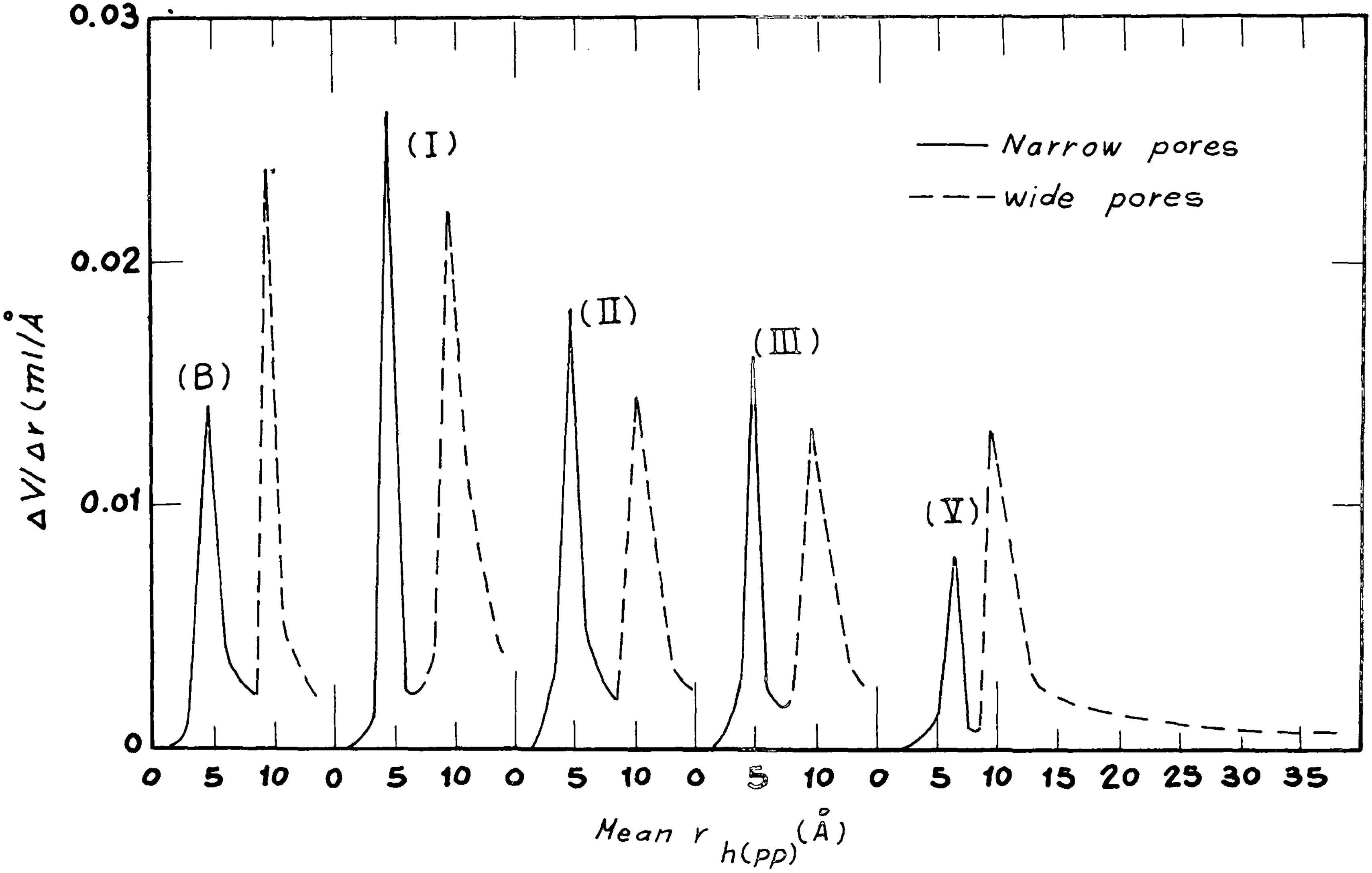

Fig. (4) Complete pore structure analysis of the unexposed morter (B), and of exposed mortars I, II, III and V.