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Effects of Sodium Hydroxide Solutions
On the Permeability of Magnesium Clays

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INTRODUCTION

Definition of the Problem - Disposal of hazardous wastes is limited to three basic methods. The waste can be chemically treated to make it less hazardous, it can be incinerated, or it can be permanently buried in a landfill. Treatment is better from an ecological standpoint, but the cost can be prohibitive. Burial in a landfill is usually more cost efficient, but steps must be taken to insure that the waste will remain contained within the site. Current practice is to line the site with a barrier to flow. Presently both synthetic and compacted clay barriers are used. The performance of clay barriers or "liners" is in dispute when the clay is subjected to a wide variety of permeants commonly found in hazardous waste management facilities.

Score of the Investigation - It has been found that flow of a concentrated NaOH solution through a magnesium clay will cause a precipitation of $Mg(OH)_2$ within the pores of the soil. This blocks the flow and lowers the coefficient of permeability. This research is an attempt to discover the conditions of formation and possible destruction of this precipitate.

STATE OF KNOWLEDGE

Darcy's Law - The general effect of a permeant on a clay soil is a complex combination of many different factors. Darcy's Law describes the flow of water through a porous media according to equation 1:

$$v = ki \quad \text{.......................................} \quad 1.$$

where: v = flow velocity

k = coefficient of permeability

i = gradient of pore pressure

Darcy's Law has been well verified by many other researchers. The effects of the different viscosities and unit weights of different permeants are taken into account by using the absolute permeability:

$$K = k(u/w) \quad \text{.....................................} \quad 2.$$

where: K = absolute permeability

k = coefficient of permeability

u = viscosity of fluid

w = mass density of fluid

Therefore, Darcy's Law, for a fluid other than water is:

$$v = K(w/u)i \quad \text{.................................} \quad 3.$$

Thus, the absolute permeability, K, should remain a constant property of the particular soil, independent of permeant. Factors which affect the absolute coefficient of permeability are changes in the adsorbed double layer and alterations of the soil mass properties.

Double Layer Effects - The absorbed double layer is bound to clay particles by electrical forces. Unbalanced negative charges on the surface of a clay particle attract cations in the pore fluid. In the presence of a polar pore fluid, these cations attract and are surrounded by permeant molecules. This forms a tightly attached boundary of pore fluid called the double layer. The double layer extends away from the surface of the clay particle, and reduces the effective pore space available for fluid flow. Any factor which tends to increase (or decrease) the thickness of the double layer will block off more (or less) of the effective pore space, and will decrease (or increase) the permeability of the clay. Different permeants can affect the double layer in several ways. Non-polar pore fluid molecules will not be attracted to the adsorbed cations, and no double layer will be formed. This will free up the entire pore space for fluid flow and increase the permeability. Conversely, a Highly polar pore fluid will be more attracted to the cations. The resulting thicker double layer will cause a lower permeability. A higher dielectric constant of the pore fluid will retard the transmission of electrical attraction, and will push the double layer out farther, resulting in a lower permeability (Mesri, 1971; Anderson, 1982).

Water is both highly polar and has a high dielectric constant. This results in a very thick double layer. Most any other fluid which could permeate a soil will result in a thinner double layer and a higher coefficient of permeability.

Other effects on the double layer are associated with ions present in aqueous solutions. An increase in the concentration of cations in the permeant has two effects. First, it reduces the thickness of the double layer by osmotic pressure from the pore fluid. Secondly, it will increase the likelihood of an ion exchange if the ions in the pore fluid differ from those adsorbed to the surface of the clay (i.e. the ions in the double layer). A monovalent cation (such as sodium) can be exchanged for a multivalent ion (such as calcium or magnesium). In order to neutralize the same surface charge on the surface of the clay, only half as many divalent cations would be required as monovalent ions. This would reduce the double layer and increase the permeability (D'Appolonia, 1980).

The magnitude of all of the aforementioned double layer effects should be directly related to the cation exchange capacity, CEC, or more generally to the specific surface of the clay mineral. The amount of change should be greater in a clay which has more surface area within the sample, and less in a clay which has less surface area within the sample. This trend seems to be evident in the data presented by Mesri and Olson, but this was not discussed by the authors (Olson, 1970; Mesri, 1971).

Structural Changes - A permeant can affect the permeability of a soil by changing the structural mass characteristics of the clay particles. Several researchers have reported an aggregation of clay particles into larger "clumps" during the course of a permeability test. This leaves larger channels open between the clumps, increasing the permeability (Mesri, 1971; Anderson, 1982).

Dissolution of clay particles by the permeant has long been a concern, and has been reported by many sources. Anderson (1982) noted problems with the solutioning with almost all permeants used. D'Appolonia (1981) reports problems with solutioning using a 5% NaOH solution. In this investigation, a dark color was produced in the effluent when NaOH solutions of comparable strength were used. It is believed that this color is due to the presence of humic acids (organics). The standard environmental laboratory technique for isolating humic acid is by dissolving it in a strong NaOH solution. These acids only represent a small fraction of the soil mass, and their removal should not greatly affect the permeability. The silica tetrahedra of the clay mineral should be soluble in high pH solutions. This is a very slow reaction and would only reveal itself as a problem in a very long duration test.

Another chemical reaction within the soil is a precipitation within the pores of the soil. This has been reported by Horst (1982) when he permeated a concentrated NaOH solution (pH = 13) through a magnesium clay. The permeability of the sample was reduced by 13 times. He believed that this was caused by an ion exchange phenomenon. However, subsequent research has shown that this was not the case. Another sample of the same clay was permeated with solutions of NaCl, with no change in the permeability. The effluent was then mixed with a solution of NaOH, and a precipitate was formed consisting of a mixture of magnesium hydroxide ($Mg(OH)_2$) and calcium carbonate ($CaCO_3$). The sodium ions in the permeant replace the magnesium ions adsorbed onto the surface of the clay. After exchange, the magnesium ions combine with hydroxyl ions to form $Mg(OH)_2$, which is highly insoluble at high values of pH, and precipitates out. The precipitate partially fills the void space and blocks flow thereby decreasing the permeability.

TESTING EQUIPMENT AND PROCEDURE

Objective of Research - This study investigates the effects of a sodium hydroxide, NaOH, solution on the coefficient of permeability of a magnesium clay. Data was collected from triaxial flexible wall (TXFW) permeability tests and samples of the effluent were collected. The changes in coefficient of permeability with time, the changes in pH of the effluent with time, and the changes in the ion content of the effluent with time was studied using NaOH solutions of different ionic strengths.

Sample Preparation - As a basis for comparison, the soil used in this investigation was the same soil used by Horst, 1982. It is a magnesium clay, with the following properties:

Liquid Limit	98
Plastic Limit	61
Plasticity Index	37
% Finer than 2 micron	46%
Activity	0.80
Specific Gravity	2.65

To insure uniformity of results, the samples were prepared by mixing a slurry of dry soil and a solution of 50 mg/l of $MgSO_4*7H_2O$. This permeant insures that the ions adsorbed to the surface of the clay particles are magnesium ions. After hydrating for 24 hours or more, the slurry was poured into a consolidation tube and any air pockets were removed with a mechanical vibrator. Consolidation was completed under a 25 psi load. The samples were then removed, measured for moisture content, wrapped and stored until use.

Testing Apparatus - The samples were tested using a triaxial falling head flexible wall (TXFW) permeability testing apparatus

(Figure 1). This apparatus allows back-pressure saturation of the soil specimen as well as allowing volume change within the sample during the test without forming preferential flow paths around the outside of the sample.

The apparatus has a cell capable of maintaining a confining pressure on the sample. Flow is induced through porous cap stones. These cap stones are connected to plexiglass standpipes which monitor the flow of permeant through the sample. Air pressure is surcharged on the top of the standpipes to increase the applied gradient. Pressure gages provide rough regulation, while a pressure transducer was used for precise monitoring of the inflow, outflow and cell pressures.

Procedure - The cap stones and filter paper were boiled for at least 10 minutes to remove any entrapped air, then allowed to cool. Soil specimens were cut 0.5 inches long. The specimen, filter paper, and cap stones were mounted and covered by a latex membrane, taking care to avoid trapping any air inside the membrane. A consolidation pressure of 20 psi was applied to the cell to consolidate the sample. The cell pressure was then increased to 27 psi while increasing the pressure on the standpipes to 10 psi backpressure. After one full day of backpressure saturation, flow was initiated by increasing the surcharge on the inflow pipe to 25 psi while maintaining the surcharge on the outflow pipe at 10 psi. The total head across the sample consisted of the difference in elevation of the

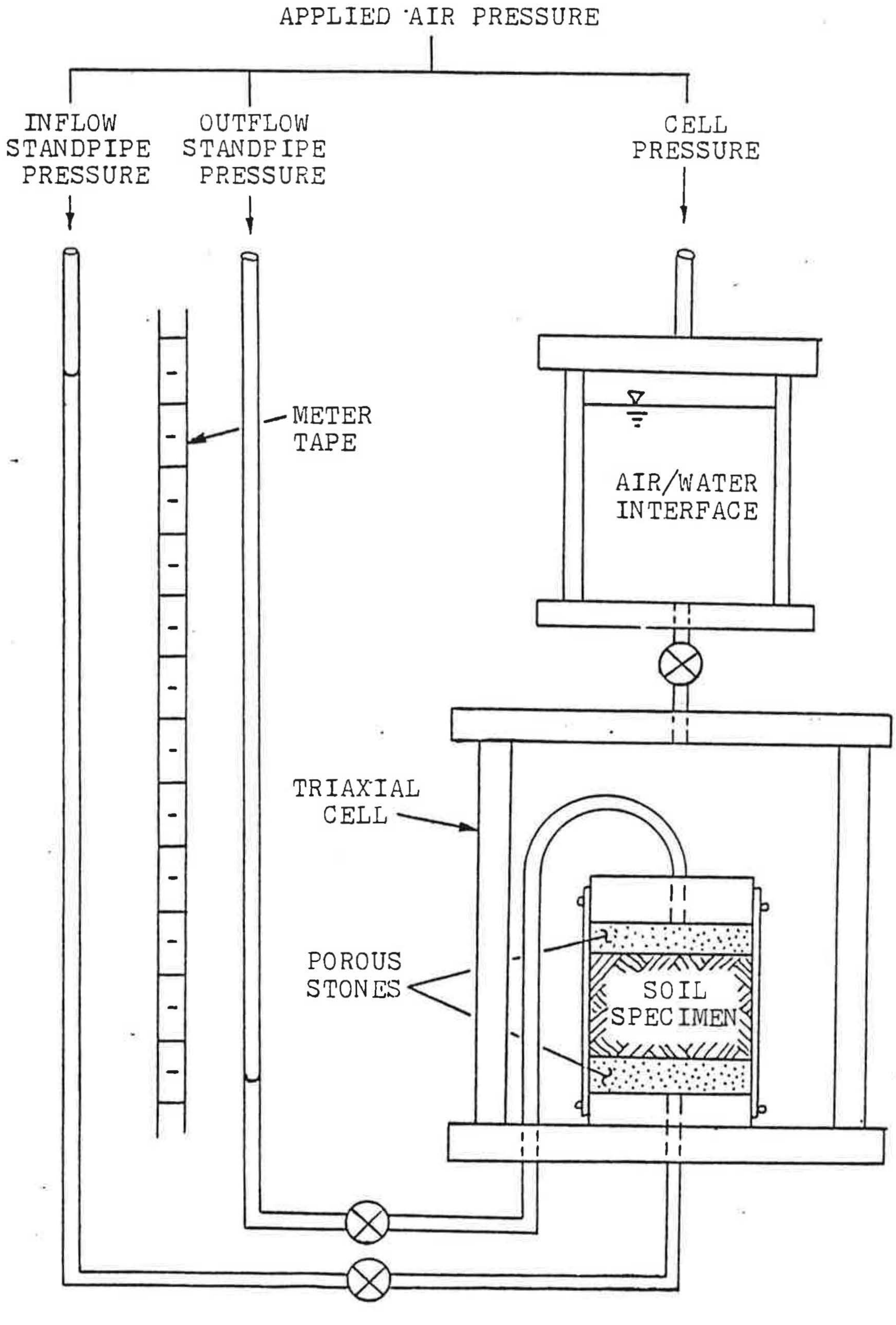

Figure 1. Triaxial Falling Head Permeability Testing Apparatus.

permeant in the columns, plus the difference in the surcharge. The permeability was computed by the following equation:

$$k = \frac{al}{At} \ln \frac{H_o}{H_f} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad 4.$$

where: k = coefficient of permeability

a = cross sectional area of standpipes

l = length of the sample

t = time elapsed between readings

Ho =initial head across sample

Hf = final head across sample

Readings were taken as needed to maintain continuity of the data. This varied from every 3 hours to every 24 hours.

RESULTS AND DISCUSSION

General - A total of seven permeability tests were run. The proposed sequence for these tests was to permeate each sample with a 50 mg/l solution of $MgSO_4*7H_2O$, to establish a base permeability value, and then to change the permeant to NaOH solutions of varying concentrations. This procedure met with widely varying degrees of success. The permeability of three of the samples was successfully reduced as had been expected. Three other samples produced a gas upon exposure to the NaOH solution. The seventh sample was contaminated by aluminum chlorohydrate residue in the standpipes of the permeameter.

Tests 1-3 - In all of the samples in which the permeability was successfully reduced, the samples were permeated with a NaOH solution from 0.345N to 1.000N. It is important that the strength of these solutions be expressed in terms of normality. The probe of an ordinary pH meter is very sensitive to high concentrations of sodium ions giving false readings. Thus, it is almost impossible to draw any comparisons with the results of Horst's work, since he expressed the strength of his solutions in terms of pH. Other considerations which should be taken into account are the changes in chemical composition and pH due to reaction of the NaOH solution with atmospheric carbon dioxide. This can take place while in solution or while the NaOH is in pellet form. Thus, the NaOH solutions used in this investigation are only roughly standardized.

In Test 1 (Figures 2 and 3), the specimen was permeated with a NaOH solution of pH 13, later found to be approximately 0.345N. The permeability was reduced by a factor of 45, but it immediately increased again to give a final reduction factor of 6.5 from the original permeability. This temporary drop in permeability may have been due to testing error, and the actual permeability of the clay may have remained at its lowest value. The permeant was then changed to de-aired, distilled water, with an increase in permeability by a factor of 1.25. Subsequent permeation with a solution of 50 mg/l $MgSO_4*7H_2O$ caused no change in the permeability. Finally, the NaOH (pH = 13) solution was reintroduced. The permeability was temporarily reduced by a factor of 1.45, but returned to its original value.

In Test 2 (Figure 4), the specimen was permeated with a 0.345N solution of NaOH. The resulting permeability was reduced from the original value by 5.4 times.

In Test 3 (Figures 5-9), the permeability was reduced by a factor of 5.2. Subsequent permeation with a solution of 50 mg/l $MgSO_4*7H_2O$ resulted in no change in permeability. The permeant was then changed to 0.1N HCl. The permeability was temporarily reduced by a factor of 1.2, but the ultimate value apparently remained unchanged. A pressure disturbance during this part of the test left pronounced wrinkles in the confining membrane. This resulted in a corresponding increase in the permeability (Figure 6).

Samples of the effluent taken after the 0.1N HCl were tested for pH and Mg ion content. The results are shown in Figure 9. The results show that the pH remained a a high value (approximately 11.5) for a very long period (18 pore volumes) and then decreased suddenly to a value between 6.0 and 6.5. The increase in Mg ion content as the pH dropped correlates well with the increase in solubility of the Mg ion as the pH drops.

Tests 4-6 - Three of the samples produced a gas upon contact with the NaOH solution. Subsequent study indicates that this was caused by reaction with the aluminum base in the permeameter cell.

Test 7 - The seventh sample (Figure 9), was contaminated when the $MgSO_4*7H_2O$ permeant picked up trace residue of aluminum chlorohydrate in the standpipes of the permeameter. The aluminum chlorohydrate had reduced the permeability of the previous specimen to essentially zero. Thus it is understandable that a trace amount could reduce the permeability as it did. The reaction which took place is believed to have been with the carbonate elements in the soil.

CONCLUSIONS

It is evident from the observed reductions in permeability that the expected reaction and precipitation of $Mg(OH)_2$ can occur within the pores of the clay. This precipitation caused the permeability to be reduced by a factor of approximately 6 times in each case. Subsequent permeation with distilled water and solutions saturated with magnesium ions show that the precipitate is rather permanent. Subsequent permeation with a 0.1N HCl solution removed some of the Mg ions, but resulted in no apparent increase in the permeability of the sample.

The results of this investigation indicate the possible use of sodium hydroxide solutions in the control of cracked or otherwise leaking hazardous waste sites.

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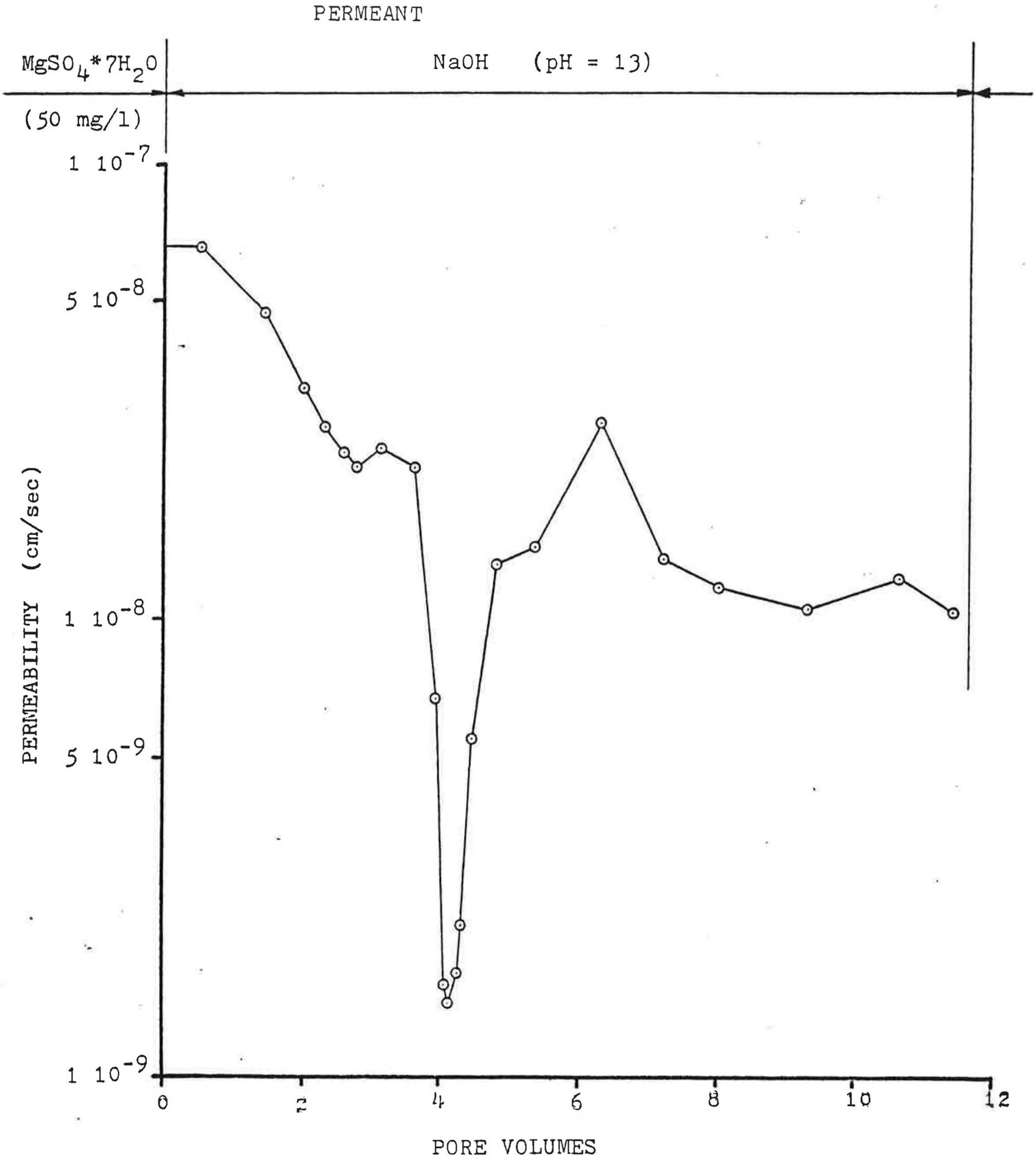


Figure 2. Permeability Vs. Pore Volumes (Test 1)

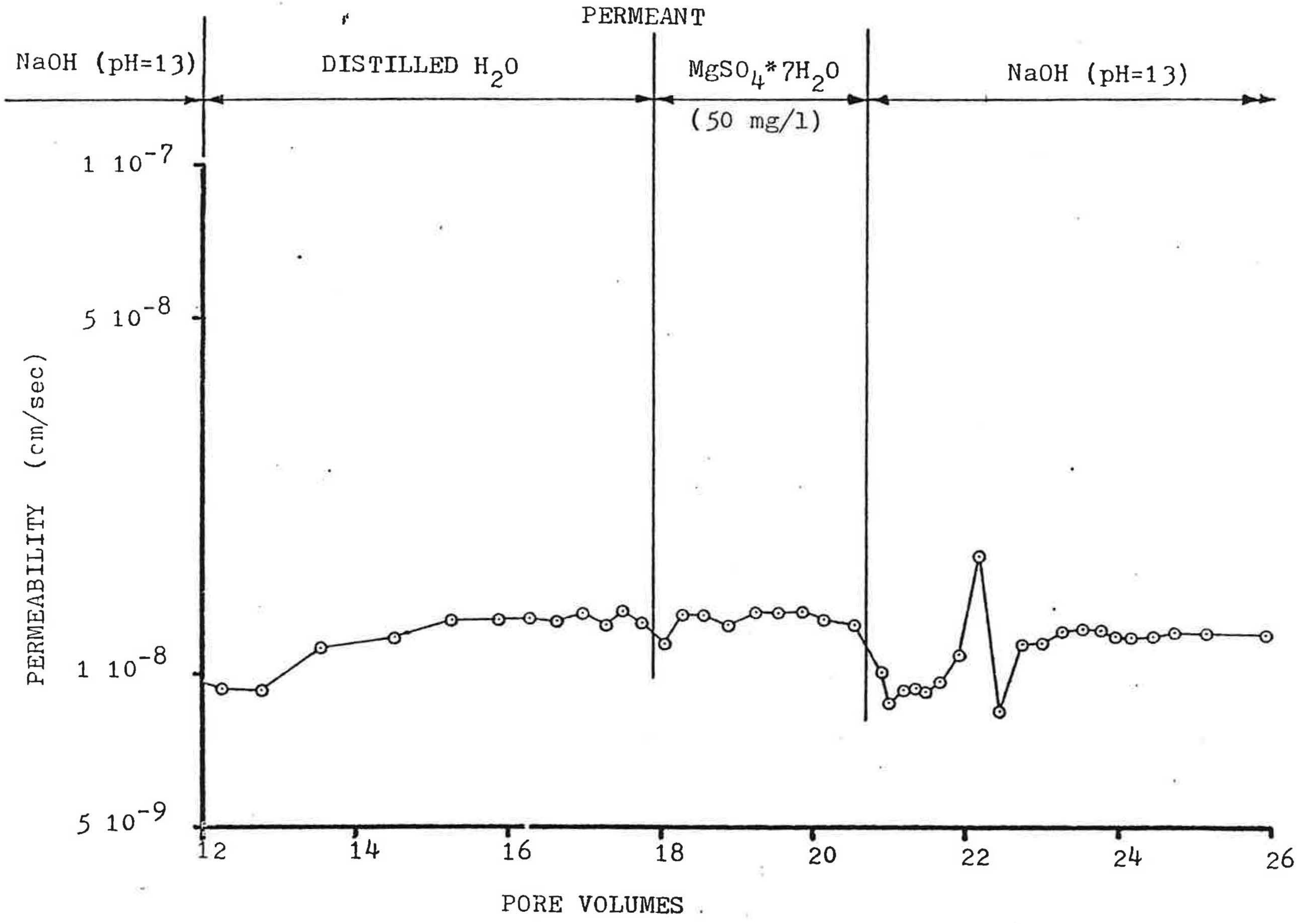


Figure 3. Permeability Vs. Pore Volumes (Test 1)

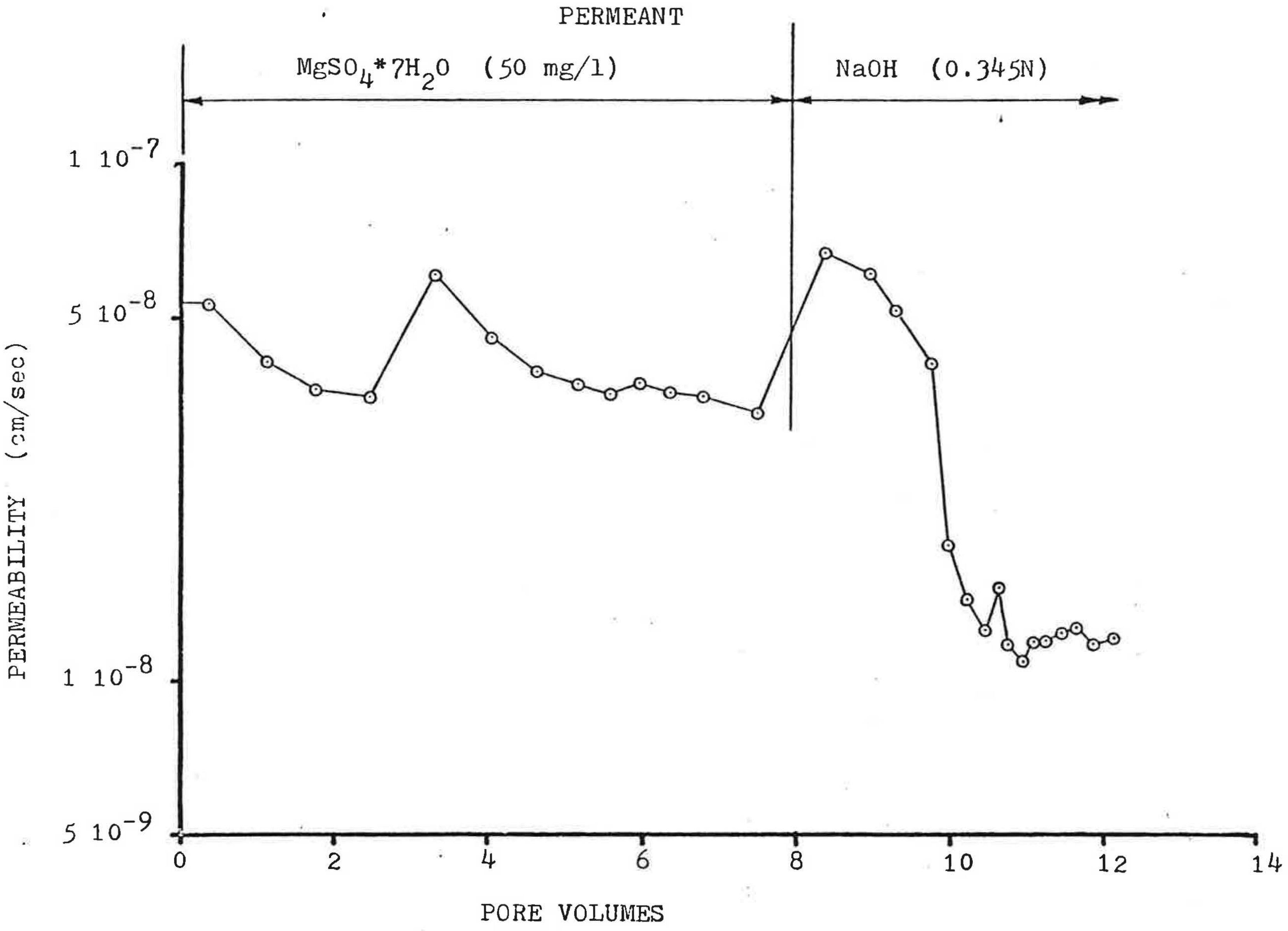


Figure 4. Permeability Vs. Pore Volumes (Test 2)

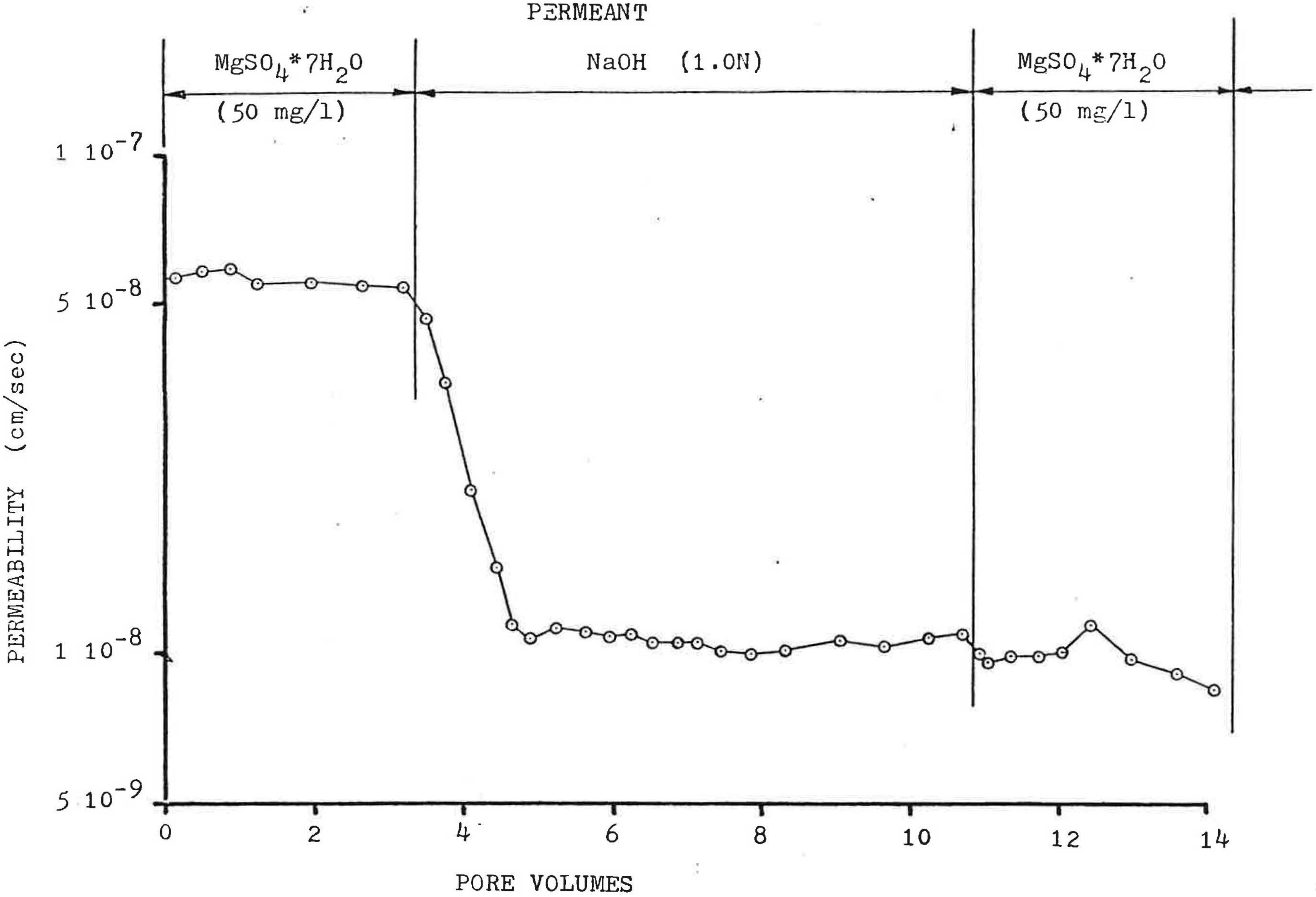
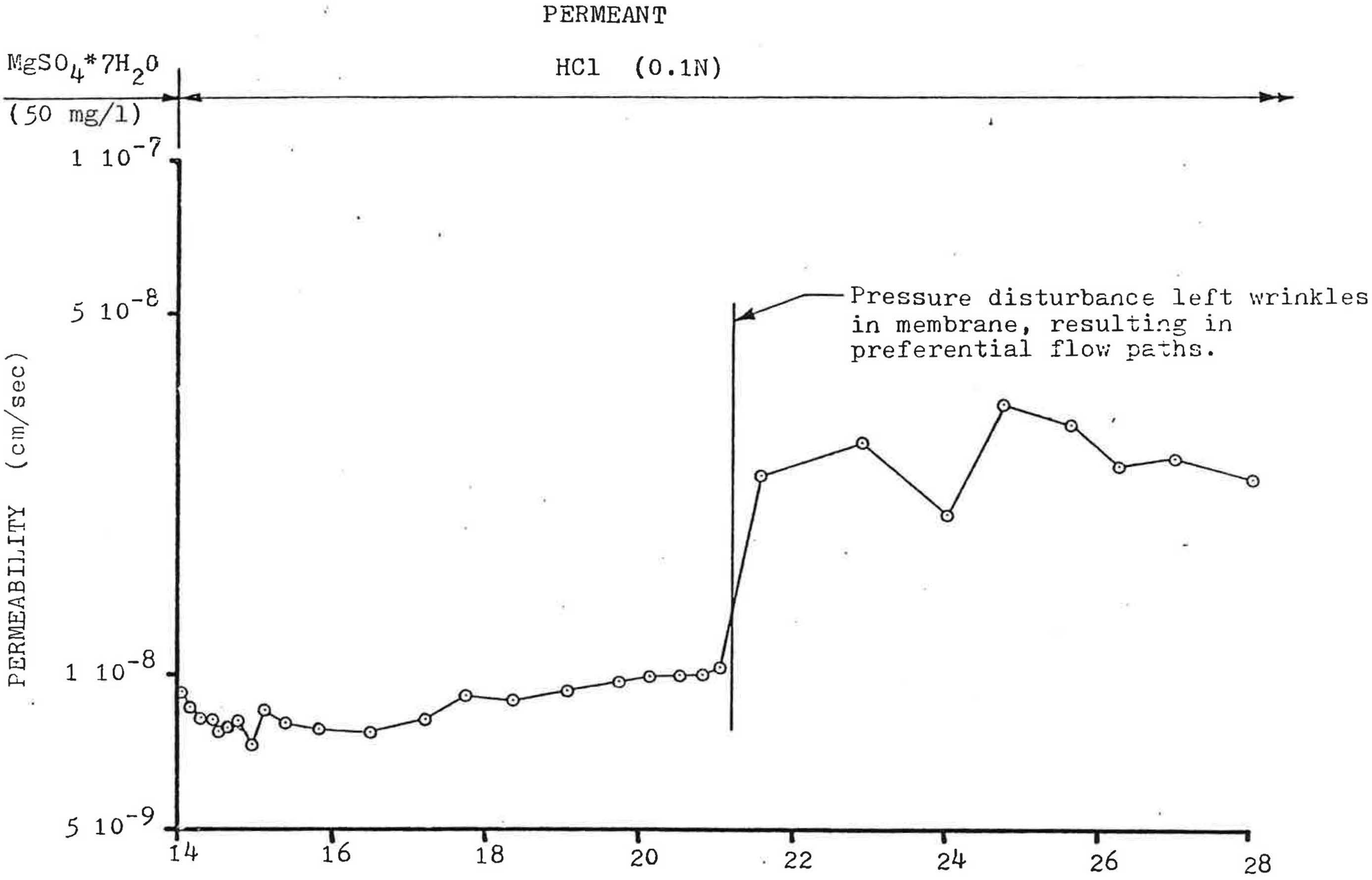


Figure 5. Permeability Vs. Pore Volumes (Test 3)



Pressure disturbance left wrinkles in membrane, resulting in preferential flow paths.

Figure 6. Permeability Vs. Pore Volumes (Test 3)

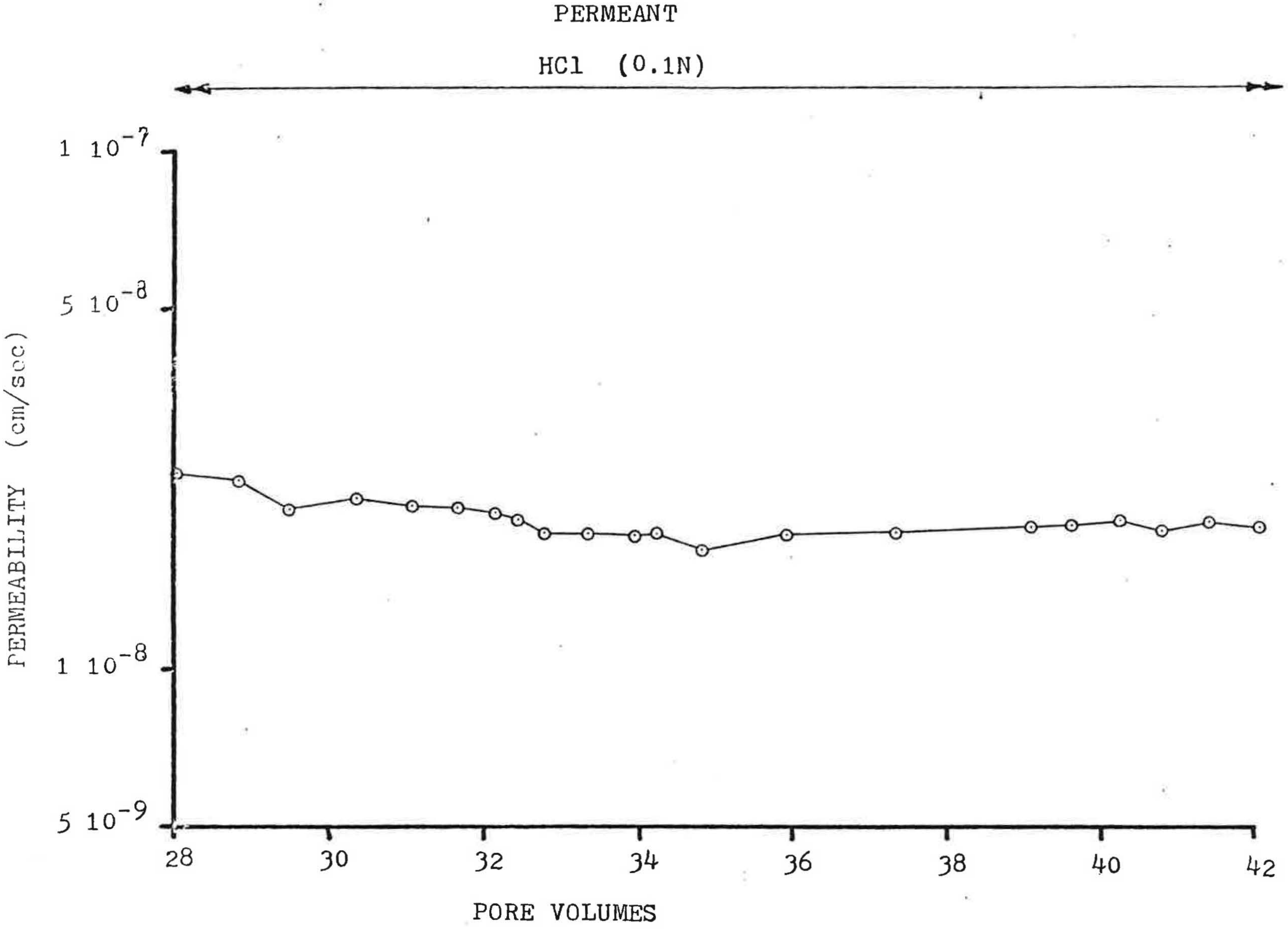


Figure 7. Permeability Vs. Pore Volumes (Test 3)

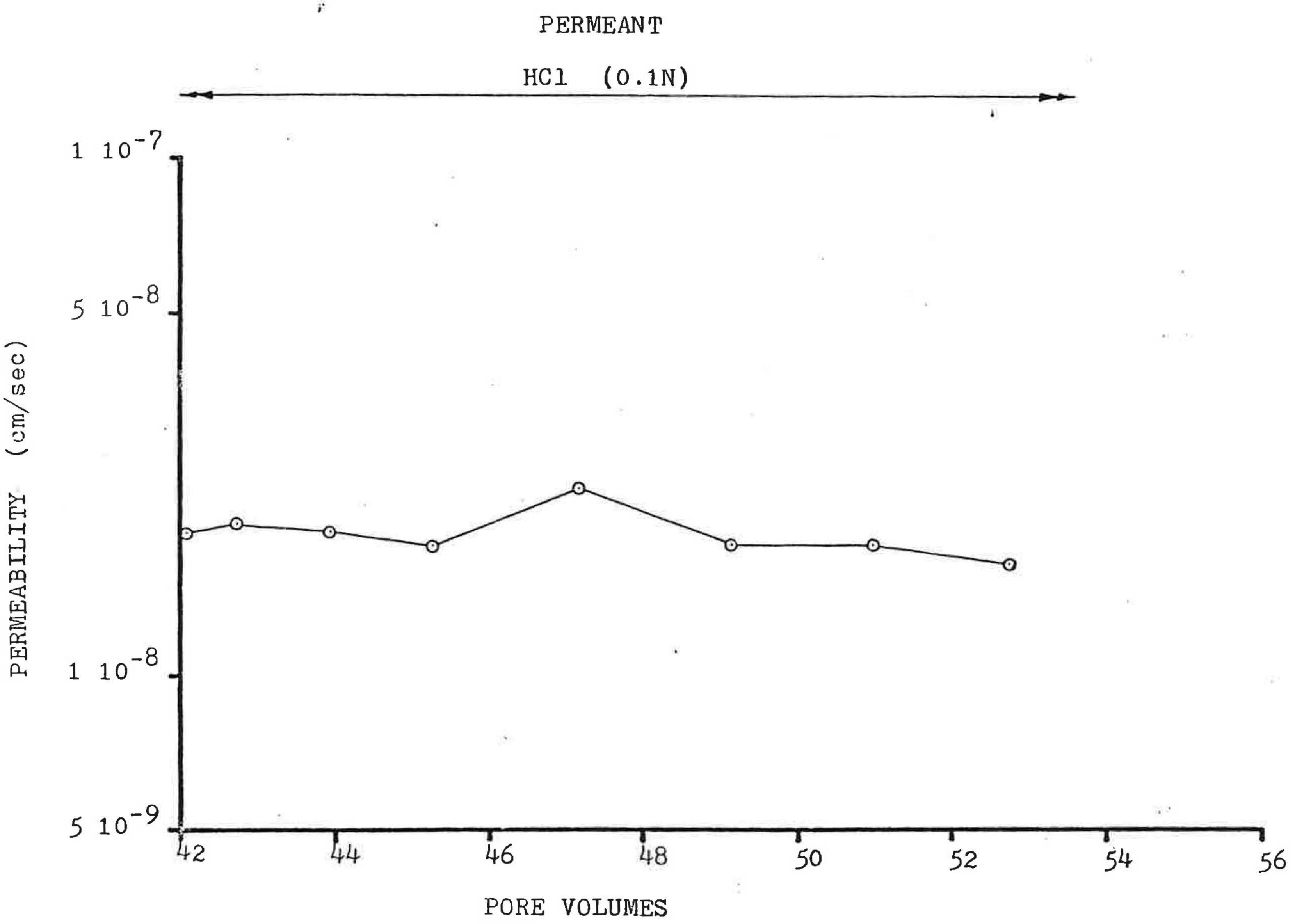


Figure 8. Permeability Vs. Pore Volumes (Test 3)

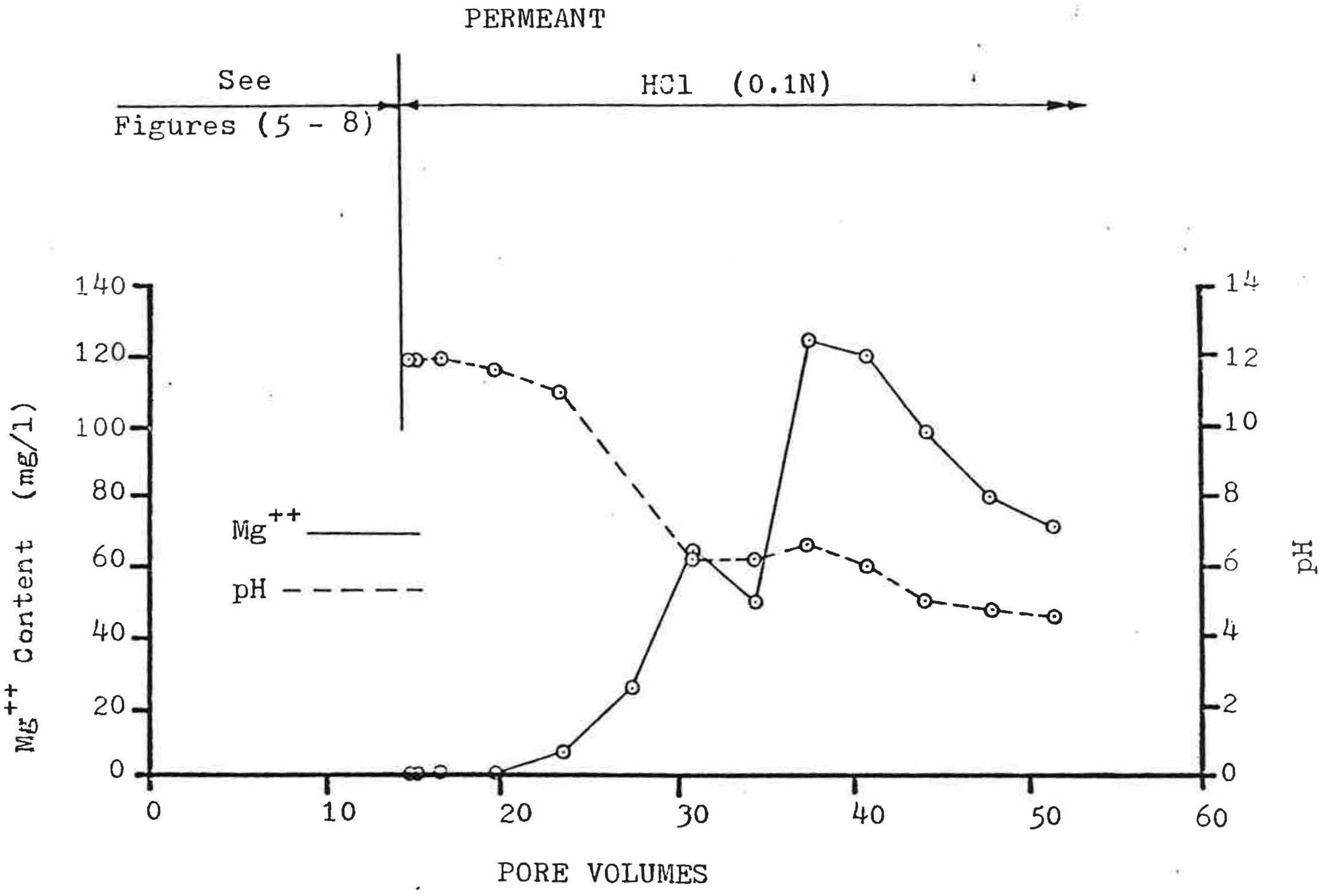


Figure 9. pH Vs. Pore Volumes, and Mg^{++} Vs. Pore Volumes (Test 3)

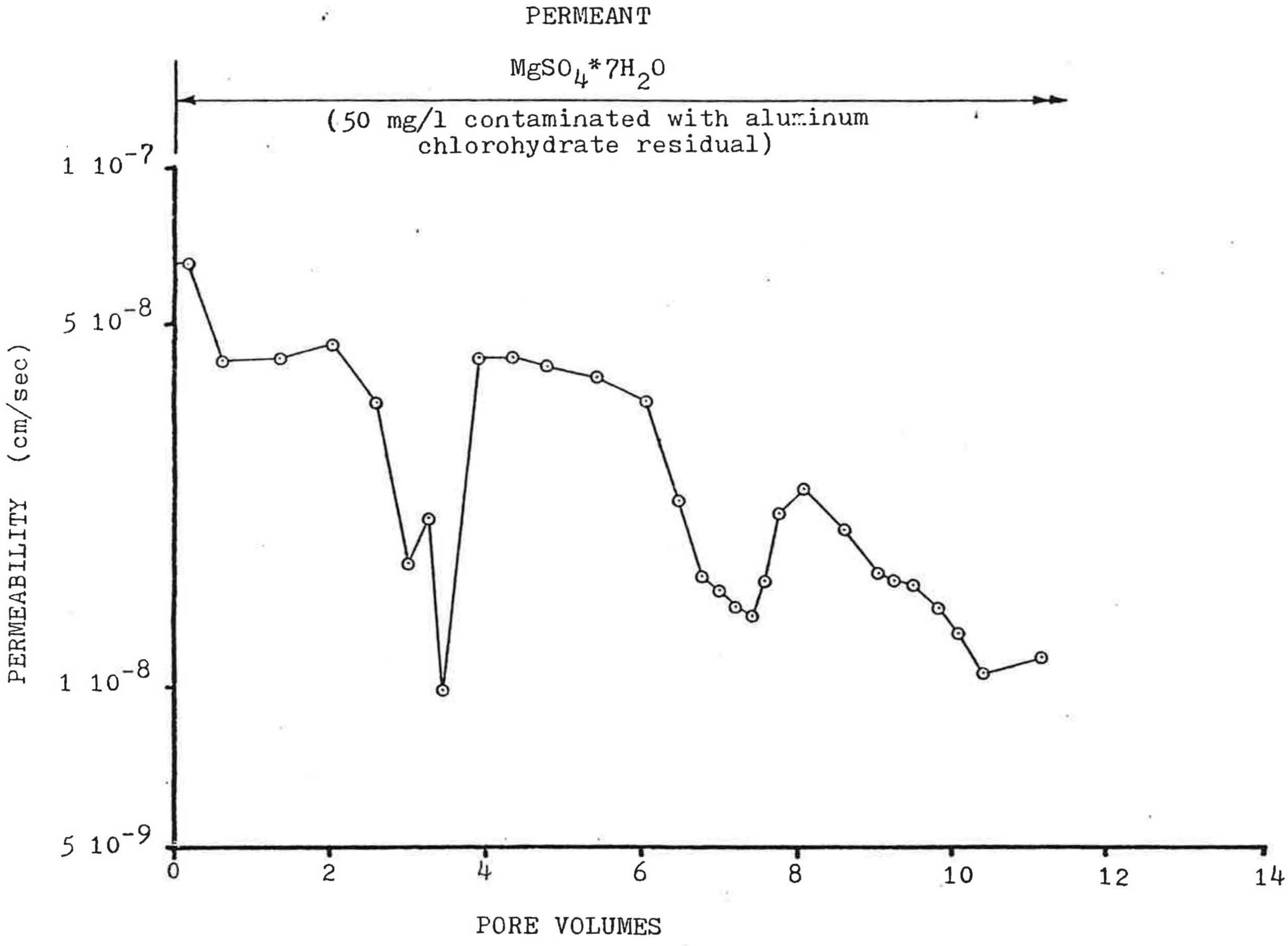


Figure 10. Permeability Vs. Pore Volumes (Test 7)