

6-1950

The effect of added substances on the volume change of cement

Owen Eugene Brown
Union College - Schenectady, NY

Follow this and additional works at: <https://digitalworks.union.edu/theses>

 Part of the [Chemistry Commons](#)

Recommended Citation

Brown, Owen Eugene, "The effect of added substances on the volume change of cement" (1950). *Honors Theses*. 1721.
<https://digitalworks.union.edu/theses/1721>

This Open Access is brought to you for free and open access by the Student Work at Union | Digital Works. It has been accepted for inclusion in Honors Theses by an authorized administrator of Union | Digital Works. For more information, please contact digitalworks@union.edu.

THE EFFECT OF ADDED SUBSTANCES ON THE VOLUME CHANGE
OF CEMENT

BY
OWEN EUGENE BROWN

UC
↑
UC 1950

A thesis presented to the Department of Chemistry
of Union College in partial fulfillment of the require-
ments for the degree of Bachelor of Science in Chemistry.

by Owen Eugene Brown

approved by Charles B. Hurd

Date July 19, 1950

UNION COLLEGE
LIBRARY

9
UN92
B879v
1950

This work, carried out under the direction of
Mr. H. F. Kichline of Catskill and Dr. Charles B. Hurd
and Dr. Jermain D. Porter of Union College, was
sponsored by the North American Cement Corporation
fellowship established at Union College in 1948.

Gift of Author, January 9, 1963

206940⁷⁶

INDEX

	Page
Introduction	1
Historical	2
Experimental Introduction	9
Apparatus	12
Experimental Results	15
Effects of Some Electrolytes	
Group I	
1. Sodium Chloride	18
2. Calcium Chloride	20
3. Aluminum Chloride	22
Group II	
1. Sodium Chloride	18
2. Sodium Sulfate	24
3. Potassium Ferricyanide (iron III)	26
4. Potassium Ferrocyanide (iron II)	29
Effects of Some Non - Electrolytes	
Group III	
1. Methanol	31
2. Ethylene Glycol	33
3. Glycerol	35
4. Acetone	37

Group IV

1. Formaldehyde	39
2. Levulose	41
3. Pentaerythritol	43
4. d- Mannitol	45
5. d- Sorbitol	47
6. Sucrose	49

Group V

1. Calgon	51
2. Versene	53

Discussion	57
Summary	60
Bibliography	62

INTRODUCTION

There are many substances which effect the volume change of cement during setting, but the lack of time has limited the number and kind of substances used during this research.

The effect of salts, or electrolytes, is shown, varying not only the valence of the cation, but also the valence of the anion. A relatively small portion of the existing salts was employed in this work, but they were so chosen as to give a complete picture of their effect on the volume change of cement.

The use of organic compounds was limited chiefly to those containing - OH groups, in any combination and quantity, although other compounds were examined in lesser detail. Although the effect of these compounds is not too clearly understood as a whole, the information obtained is of great importance.

This indicates the purpose of this research and the content of this thesis.

HISTORICAL

When water is added to Portland cement, there follows a series of reactions, the explanations of which have been sought by chemists for a great many years. Many theories have been developed, each contributing to a fuller understanding of the processes involved.

Serious consideration about the nature of the hardening process following the reactions of hydration was not given until the studies of Le Chatelier (22). He believed that setting and hardening of cements are due to:

1. The solution in water of an anhydrous or partially hydrated salt.
2. Reaction of the dissolved salt with water, to form a higher hydrate.
3. The precipitation of this hydrate due to its lower solubility and consequent development of a super-saturated solution.
4. The formation of very small but elongated crystals during precipitation which favors interlacement and large contact surface.
5. The specific properties of high cohesive and adhesive qualities on the part of the precipitated crystals.

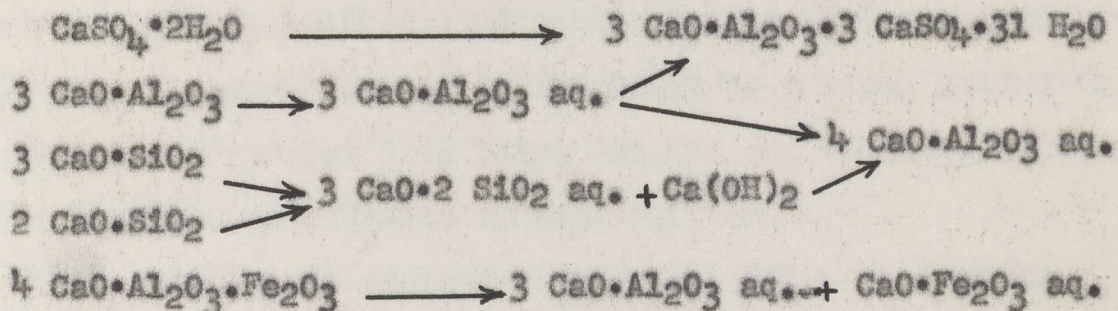
Michaelis (28) developed a theory that the hardening of cements was due almost exclusively to the formation of colloidal hydration products. This colloid theory may be summarized as follows:

The action of water on cement brings about two types of reaction. First the solution of lime, aluminates, sulfates and other compounds in the cement. From this solution there are precipitated various crystalline products, as calcium aluminates, calcium sulfoaluminates and calcium hydroxide. This gives a material possessing some strength but not at all resistant to further disintegrating action of the water. As soon as the limewater has reached a definite concentration it acts on the calcium-impooverished silicates and forms the hydrated calcium silicate. Because of the low solubility of the silicate it forms a gel which fills the pores of the cement and makes the latter impermeable to water. The gel is soft, but the inner mass of the cement grains eagerly withdraws the water from the gel and in that way the surface becomes hard. The great strength and water resistance of the cement are thus explained as due almost entirely to this gel formation and its drying out by the inner suction of the cement grains.

Both theories have had their champions and likewise

difficulties have arisen. The tendency today seems to be in favor of the crystallization theory, although the important part played by amorphous materials, as shown by Michaelis, is also recognized. This has been supported by Maeda and Yamane (24).

The reaction of Portland cement with water is essentially the sum of the reactions of the individual constituents, modified perhaps by the interaction of the compounds or their products. The reaction, according to present knowledge, may be shown schematically as follows:



As a result of the various theories, Meyer (27) came to the following conclusions:

1. The initial set is attributed to the hydration and crystallization of the tricalcium aluminate.
2. The final set is caused by the beginning of the decomposition of the tricalcium silicate. The tricalcium silicate also contributes to the major part of the strength.

3.

3. Hardening is caused by:

- a). Continuation of the decomposition of the tricalcium silicate,
- b). Crystallization of hydrated dicalcium silicate,
- c). Slow transformation of hydrated dicalcium silicate into anhydrous calcium silicate and lime.

An abnormal type of set which occasionally takes place is known as false set. The causes for this condition have been variously explained. Bogue and Lerch (4) observed that the hemihydrate of calcium sulfate is capable of introducing a condition of rigidity in cement pastes by hydrating to gypsum. Whitworth (34) also observed that this false set was due to the formation of fine crystals of hydrated calcium sulfate.

Quick setting, as explained by Roller (31), is brought about by a deficiency in calcium hydroxide, permitting the formation of the sulfoaluminate.

A theory, also developed by Roller, was that of retardation of set. The direct hydration of tricalcium aluminate proceeds with formation of the hydrated calcium aluminate. In the presence of a high concentration of calcium hydroxide, the hydrated tetracalcium aluminate will form and deposit as a film

on the grains of the tricalcium aluminate. This formation then slows down the normally rapid hydration to calcium aluminate hydrate and so retards the set. Thus calcium hydroxide is the primary retarder of the set of Portland cement and any agent which will bring about the formation of calcium hydroxide in the paste acts as a retarder. Most soluble lime salts function in this manner.

The effect of substances on the setting of Portland cement has lead to a great deal of investigation. Rohland (30) attributes all changes in the time of set to the formation of catalysts, which may be either positive or negative. The retarding action of gypsum is explained as due to a neutralizing of the positive catalytic action of the alkalies. Yamane (37) also explains the action of calcium sulfate.

Other retarders than the various forms of calcium sulfate have been suggested and used (5). Calcium chloride has been investigated by Dautrebande (7), Ferrari (10) and others (25), (29), (32), (36). A dilute solution of calcium chloride functions to retard the set, but in concentrated solutions, crystalline calcium chloraluminate is formed which hastens the set. This is due to its hastening of hydrolysis and consequent increase of calcium ion concentration.

Burchartz (6), Eklund (8), and others (12), (18) claimed that sugar delays crystalline formation during hydration, and therefore retards the processes of setting and hardening.

Other organic substances (2), (33), (35) have been found to retard the setting of cement.

Alkali compounds, however, react with calcium hydroxide and so remove it from solution. Therefore they accelerate the set.

The function of alkalies was studied by Erdahl (9) and Grimm (15). Alkali sulfates and silicates have but little accelerating action, whereas the alkali carbonates tend to produce a flash set.

The action of sodium chloride was found by Lerch (23) to be similar to that of calcium chloride but to a lesser degree, while Grün (16), (17) showed that the chlorides of magnesium, iron (III), aluminum, and barium accelerate the setting of Portland cement. The effect of other admixtures has also been studied (19), (20).

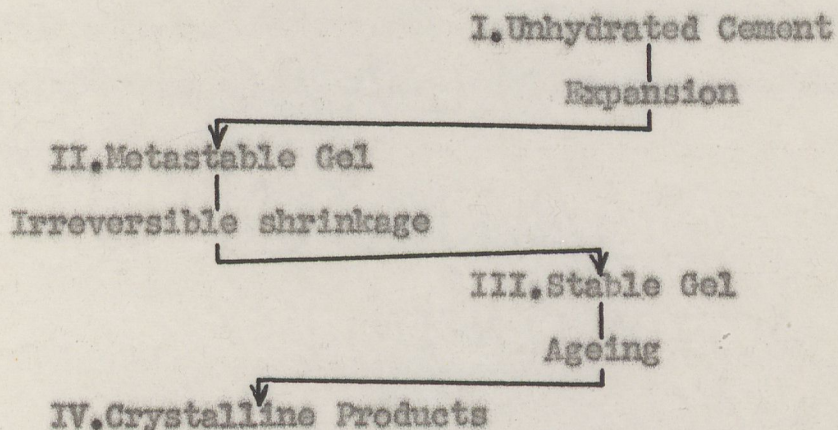
Lerch (23) confirmed the accelerating action of alkali hydroxides and found that the effects were due to the action of the alkali hydroxides on the gypsum with the formation of alkali sulfates. The effects of the alkali hydroxides would

then be similar to the effects of the alkali sulfates. The effect of sodium carbonate was also found to be similar, with the precipitation of calcium carbonate and the formation of an alkali sulfate.

EXPERIMENTAL INTRODUCTION

Portland cement exhibits certain physical properties such as its volume change (14), (13), (26). The cement grains are acted upon by water and increase in volume forming an amorphous or gelatinous mass containing some crystalline products. If Michaëlis' view is adopted the gel is formed by the coagulation of material which has first dissolved forming a supersaturated solution, while another view is that it is directly formed by swelling of the cement to form a gel as water acts on it. Swelling can be produced by crystal formation alone and is not necessarily a sign of gel formation. The gel mass probably remains unchanged in volume for a long period if kept wet, but on drying it undergoes a contraction and reduction in water content which are both irreversible. The cement gel may therefore be regarded as initially formed in an unstable condition, occupying a greater volume and containing more water than in its stable state. The gel thus has an inherent tendency to shrink and give off some of the water it contains. When the cement, which has set, begins to dry, the gel is changed into an apparently stable condition and with prolonged ageing, with growth in size of the individual silicate gel particles, an approach towards true crystal formation occurs.

This process diagrammatically is as follows:



In order to obtain the results wanted, it was necessary to control the above process. These results were the increase in volume of the cement, meaning that the irreversible shrinkage to form a stable gel had to be hindered. This shrinkage, which is caused by drying, was reduced by the addition of excess water. The cement - water ratio which was considered adequate was four parts - six parts by weight. This mixture was to be used for each subsequent run to act as a control sample.

The system, cement plus water, as a whole undergoes a diminution in volume, while the volume of the solid matter present increases. The final total change of volume increase, as found by Gessner (11) was fifty percent. The work of Anderegg and Hubbell (1) showed a similar change.

The total increase in volume of the control sample, which

is evident from any one of the succeeding graphs, is almost fifty percent, agreeing rather closely with the historical findings.

APPARATUS

It was necessary, to prevent the cement from setting, to construct a piece of apparatus which would continually keep the mixture in motion.

A wheel, twelve inches in diameter, welded to a pulley, four inches in diameter, was mounted vertically on a steel bar held in place by means of two clamp holders mounted on ring stands.

Another pulley, one inch in diameter, attached by a rawhide belt to the first pulley, was part of the driving system. This system, consisting of a variable three hundred sixty - one (361) ohm resistance connected in parallel to a one - fiftieth ($1/50$) horse power worm - geared motor, turned the wheel at the approximate rate of one revolution per second. This was controlled by varying the amount of the resistance placed in the circuit.

The containers were ten milliliter graduated cylinders, from which the bases had been removed. The volumes were corrected in order to allow the readings to be consistent. When in use, these cylinders, corked, were easily and quickly held to the mixing wheel by spring clamps. The wheel was equipped to hold twelve of these cylinders at once, so placed that the wheel was in balance.

The compatibility of the readings was further enhanced with the use of a hand centrifuge, also capable of holding twelve of the cylinders. The cement was thus thrust to the bottom of the cylinders as they were rotated at the rate of twelve hundred revolutions per minute, for one minute.

The readings, which were taken at convenient time intervals and plotted are to follow, but briefly I shall outline a complete run, which required forty - eight hours.

For convenience, I shall discuss only the use of one sample, the control.

1. 4.00 grams of regular Portland cement are placed into each of two cylinders, A and B, which are then corked to prevent the collection of moisture from the air by the cement.
2. Into cylinder A, 6.00 milliliters of distilled water is placed, shaken by hand, and placed on the mixing wheel.
3. The cylinder is removed at frequent intervals (every fifteen minutes for the first three hours, then every half hour for the next five hours) rotated in the centrifuge for one minute, the volume is read, and then the cement in the cylinder

is shaken loose. The tube is then replaced on the wheel.

4. Cylinder B, with its 4.00 grams of cement and 6.00 milliliters of water, is placed on the wheel eight hours after the start of cylinder A. This permits the obtaining of continuous readings over the forty - eight hour period with the exception of only six hours each day.
5. The volume readings are then taken every one or two hours for the remaining forty hours.
6. Upon plotting the volume readings against time, the graph is obtained.

EXPERIMENTAL RESULTS

The following table shows the effect of sodium chloride on the volume change of cement during the process of hydration.

TIME		VOLUME OF CEMENT				
hr.	min.	H ₂ O	0.10 M NaCl	0.20 M NaCl	0.50 M NaCl	1.00 M NaCl
0	15	3.40	3.40	3.30	3.35	3.45
0	30	3.38	3.38	3.25	3.30	3.43
0	45	3.32	3.35	3.25	3.30	3.40
1	0	3.30	3.35	3.25	3.30	3.40
1	15	3.30	3.35	3.25	3.30	3.40
1	30	3.30	3.40	3.30	3.32	3.43
1	45	3.30	3.40	3.35	3.35	3.45
2	0	3.30	3.45	3.40	3.40	3.50
2	15	3.30	3.50	3.45	3.50	3.53
2	30	3.35	3.55	3.55	3.60	3.56
2	45	3.35	3.65	3.60	3.70	3.60
3	0	3.40	3.68	3.65	3.75	3.75
3	30	3.45	3.80	3.80	3.90	3.95
4	0	3.50	3.90	3.93	4.05	4.15
4	30	3.55	4.00	4.05	4.20	4.30
5	0	3.60	4.10	4.15	4.30	4.50
5	30	3.70	4.15	4.20	4.40	4.60

hr.	min.	H ₂ O	0.10 M NaCl	0.20 M NaCl	0.50 M NaCl	1.00 M NaCl
6	0	3.80	4.25	4.30	4.45	4.65
6	30	3.85	4.30	4.35	4.50	4.70
7	0	3.90	4.40	4.40	4.50	4.78
7	30	3.95	4.45	4.45	4.55	4.85
8	0	4.00	4.50	4.50	4.60	4.90
15	0	4.65	4.75	4.95	5.05	5.30
16	0	4.75	4.85	5.00	5.10	5.30
17	0	4.85	4.95	5.05	5.15	5.35
18	0	4.95	5.00	5.10	5.20	5.40
19	0	5.05	5.10	5.15	5.25	5.50
20	0	5.10	5.10	5.15	5.30	5.50
21	0	5.15	5.20	5.20	5.35	5.55
22	0	5.20	5.25	5.20	5.35	5.55
23	0	5.20	5.25	5.25	5.40	5.60
24	0	5.25	5.30	5.25	5.40	5.60
25	0	5.25	5.30	5.30	5.40	5.60
26	0	5.25	5.33	5.30	5.43	5.62
27	0	5.30	5.35	5.30	5.43	5.65
28	0	5.30	5.37	5.35	5.45	5.65
29	0	5.35	5.40	5.35	5.45	5.65

hr.	min.	H ₂ O	0.10 M NaCl	0.20 M NaCl	0.50 M NaCl	1.00 M NaCl
30	0	5.35	5.43	5.35	5.50	5.70
31	0	5.40	5.45	5.35	5.50	5.70
32	0	5.40	5.45	5.40	5.55	5.70
33	0	5.40	5.45	5.40	5.55	5.70

The previous table shows the actual measurements which were obtained for one complete set of runs involving one added salt, namely sodium chloride. The results of all the other runs will not be shown in the form of this table, for reason of convenience and economy. The succeeding graphs will suffice to show the effects of added substances on the volume change of cement.

EFFECTS OF SOME ELECTROLYTES

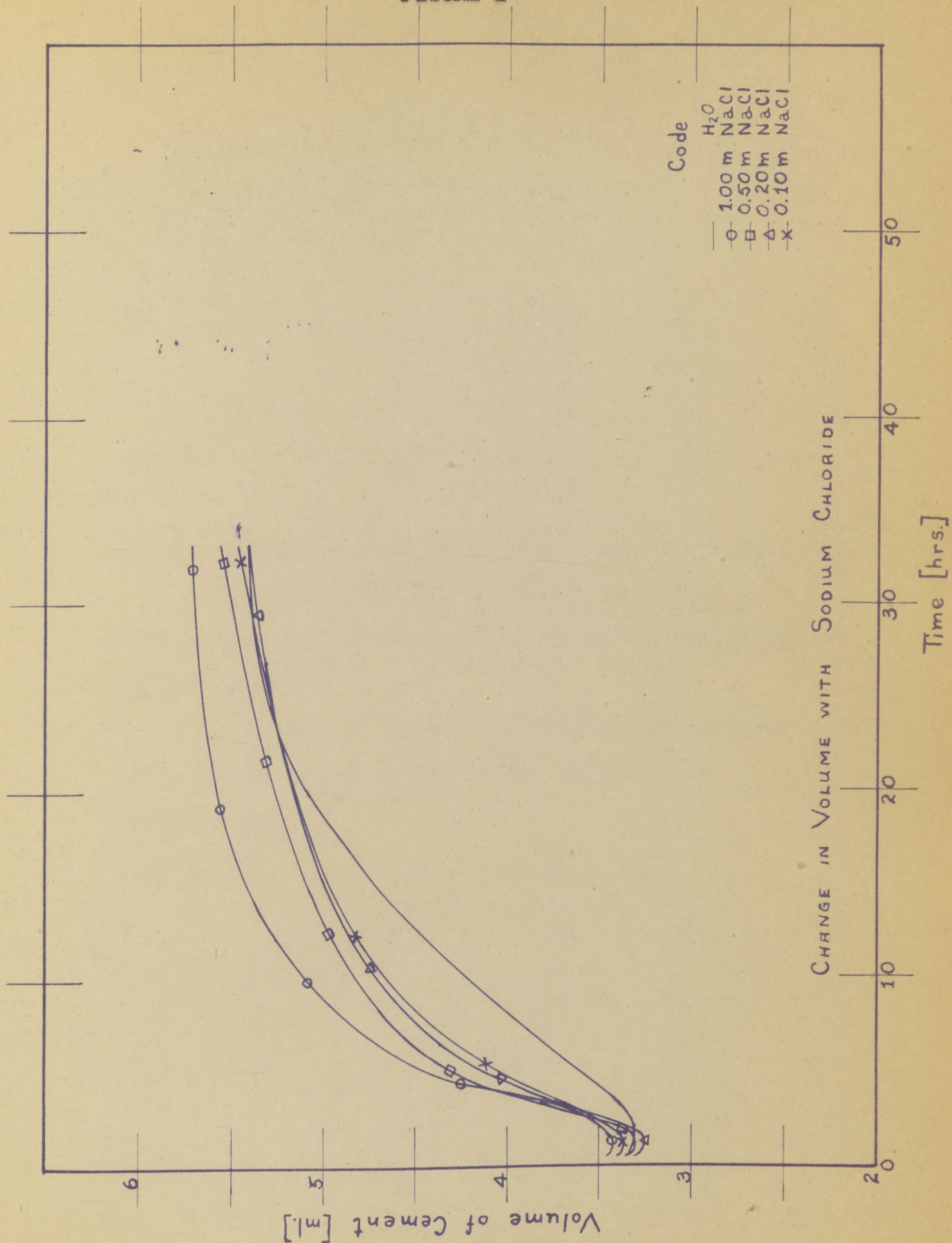
GROUP I

1. The effect of sodium chloride ----- NaCl

The table on pages 15, 16, and 17 and figure I on page 19 show the effect of sodium chloride on the volume change of cement.

The use of sodium chloride in Portland cement shows that the salt acts as an accelerating agent for the setting of cement.

FIGURE I

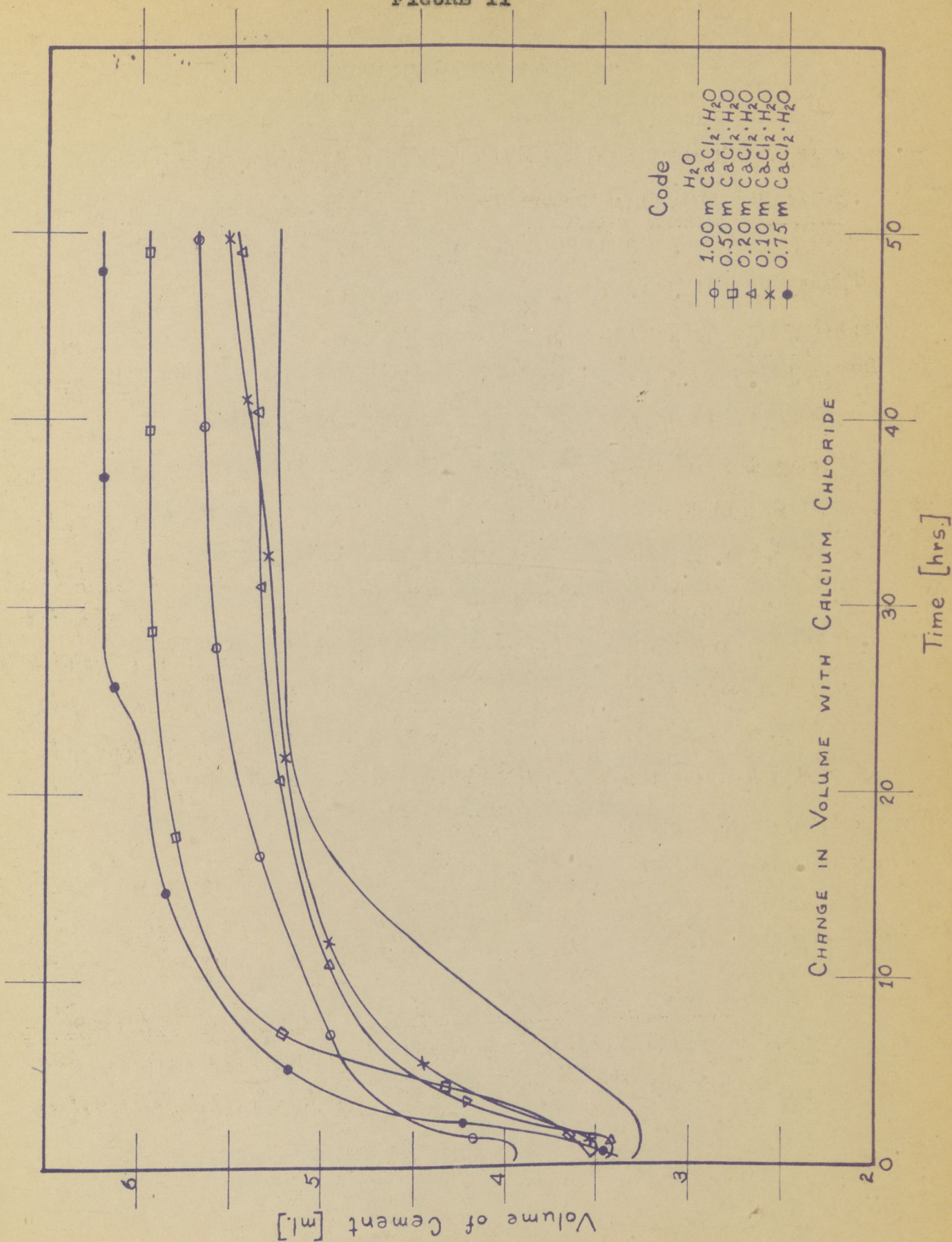


2. The effect of calcium chloride ----- $\text{CaCl}_2 \cdot 2 \text{H}_2\text{O}$

Figure II on page 21 shows, in graphical form the effect of calcium chloride on the volume change of cement.

The action of calcium chloride on the setting of Portland cement can be shown to be one of acceleration.

FIGURE II



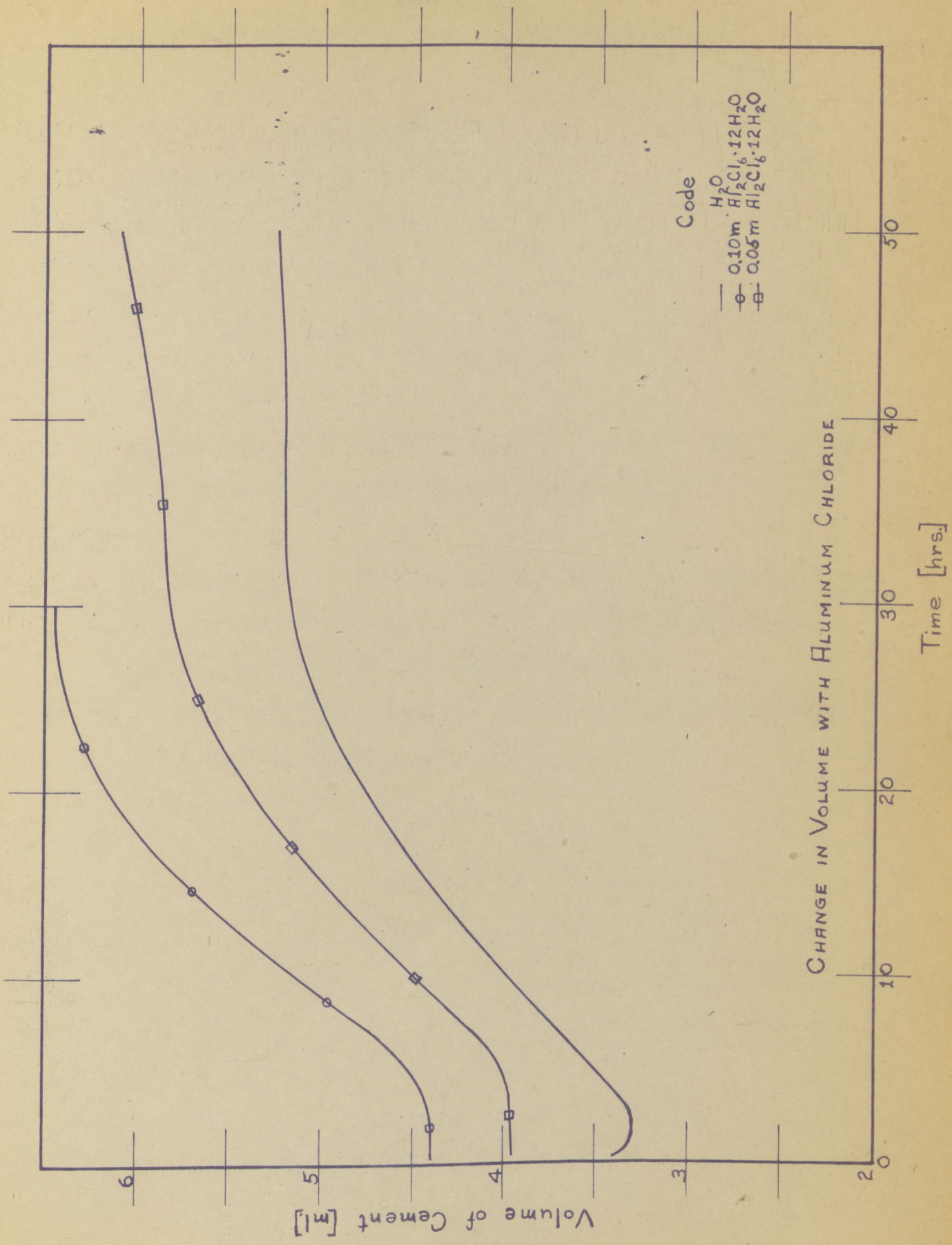
3. The effect of aluminum chloride ----- $\text{Al}_2\text{Cl}_6 \cdot 12 \text{H}_2\text{O}$

Aluminum chloride has similar accelerating action on the setting of cement as the salts previously mentioned.

The setting of the cement is accelerated to such an extent that the concentrations employed had to be very small. A concentration greater than 0.10 M caused quick setting due to the formation of gelatinous aluminum hydroxide.

Figure III on page 23 shows the effect of aluminum chloride on the volume change of cement.

FIGURE III



GROUP II

1. The effect of sodium chloride ----- NaCl

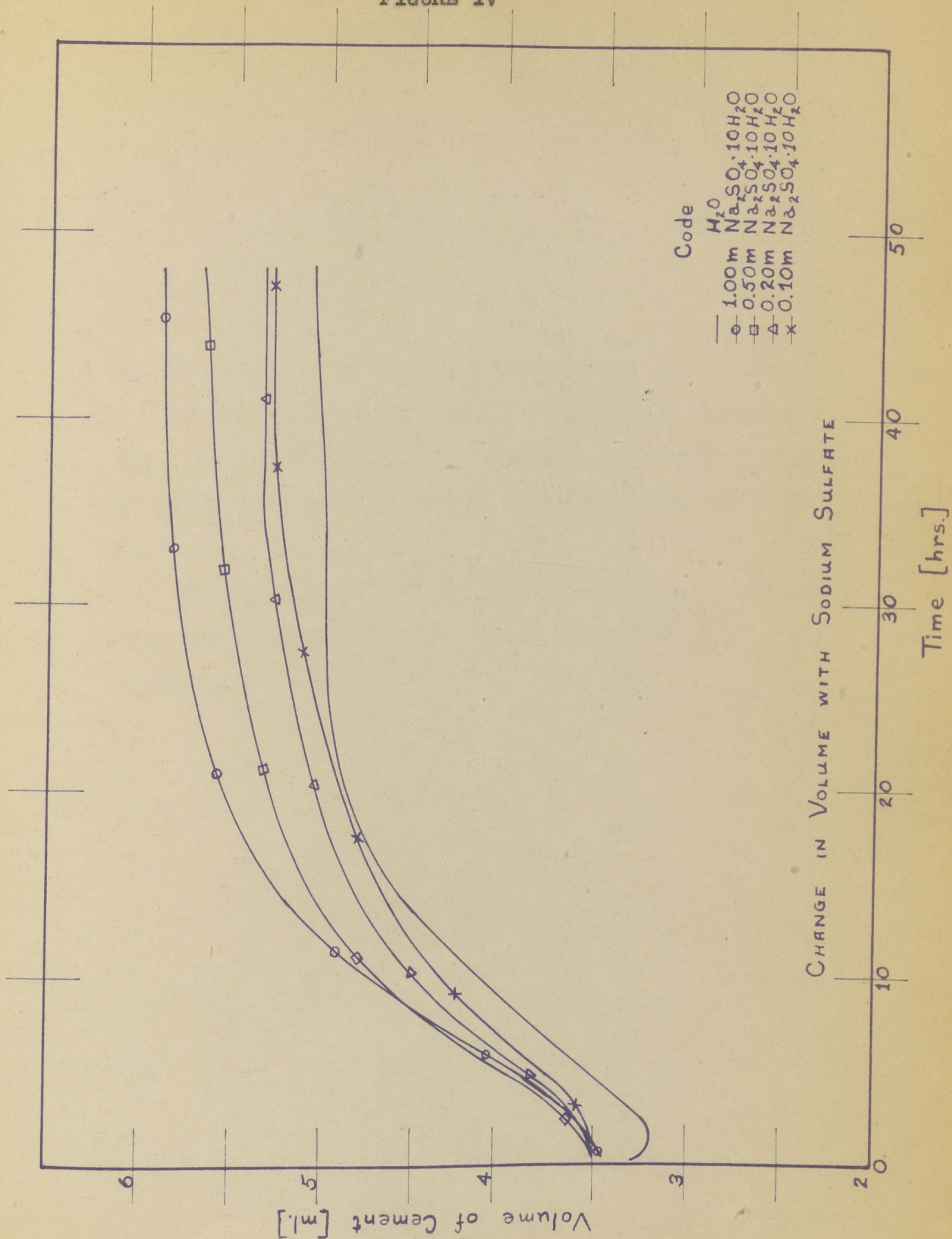
This has been shown on pages 18 and 19

2. The effect of sodium sulfate ----- $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$

Figure IV on page 25 shows the effect of sodium sulfate on the volume change of cement.

The addition of sodium sulfate has an accelerating action on the setting of cement.

FIGURE IV



3. The effect of potassium ferricyanide -- $K_3Fe(CN)_6$

The addition of potassium ferricyanide (potassium iron (III) cyanide) and its effect on the volume change of cement is shown in figures V and VI on pages 27 and 28.

The type of curves obtained here was not evident from the other salts which were employed in this research.

FIGURE V

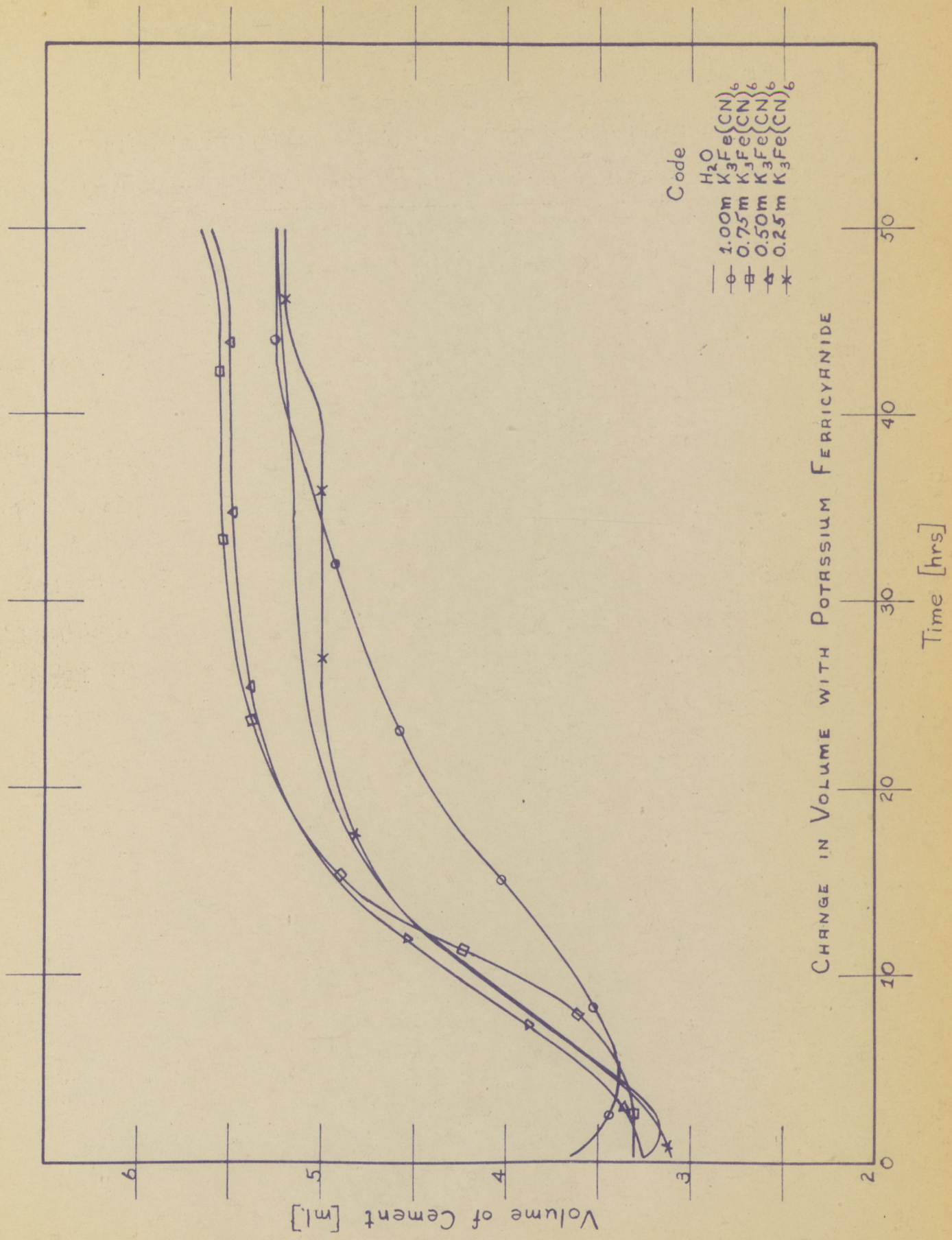
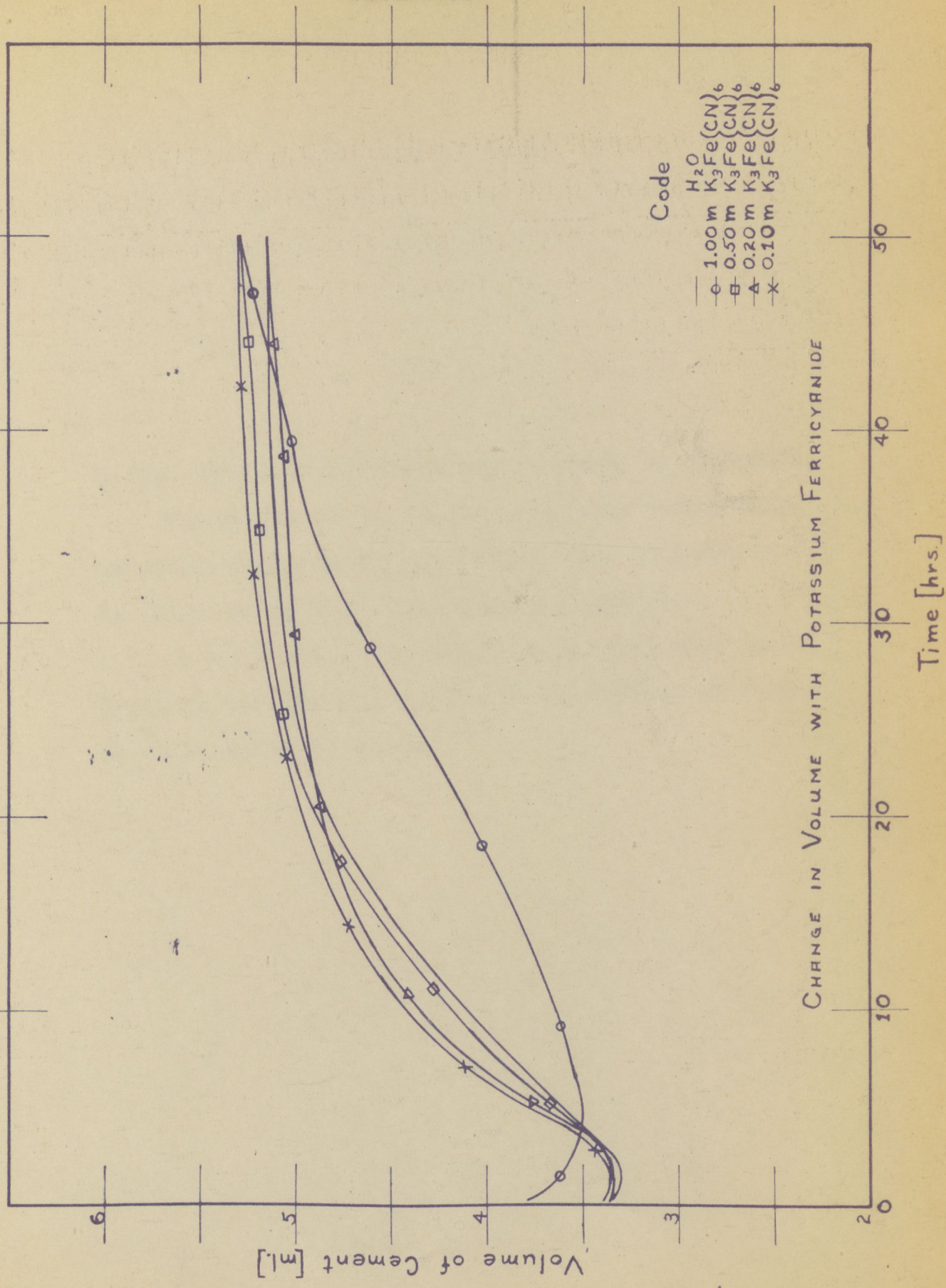


FIGURE VI

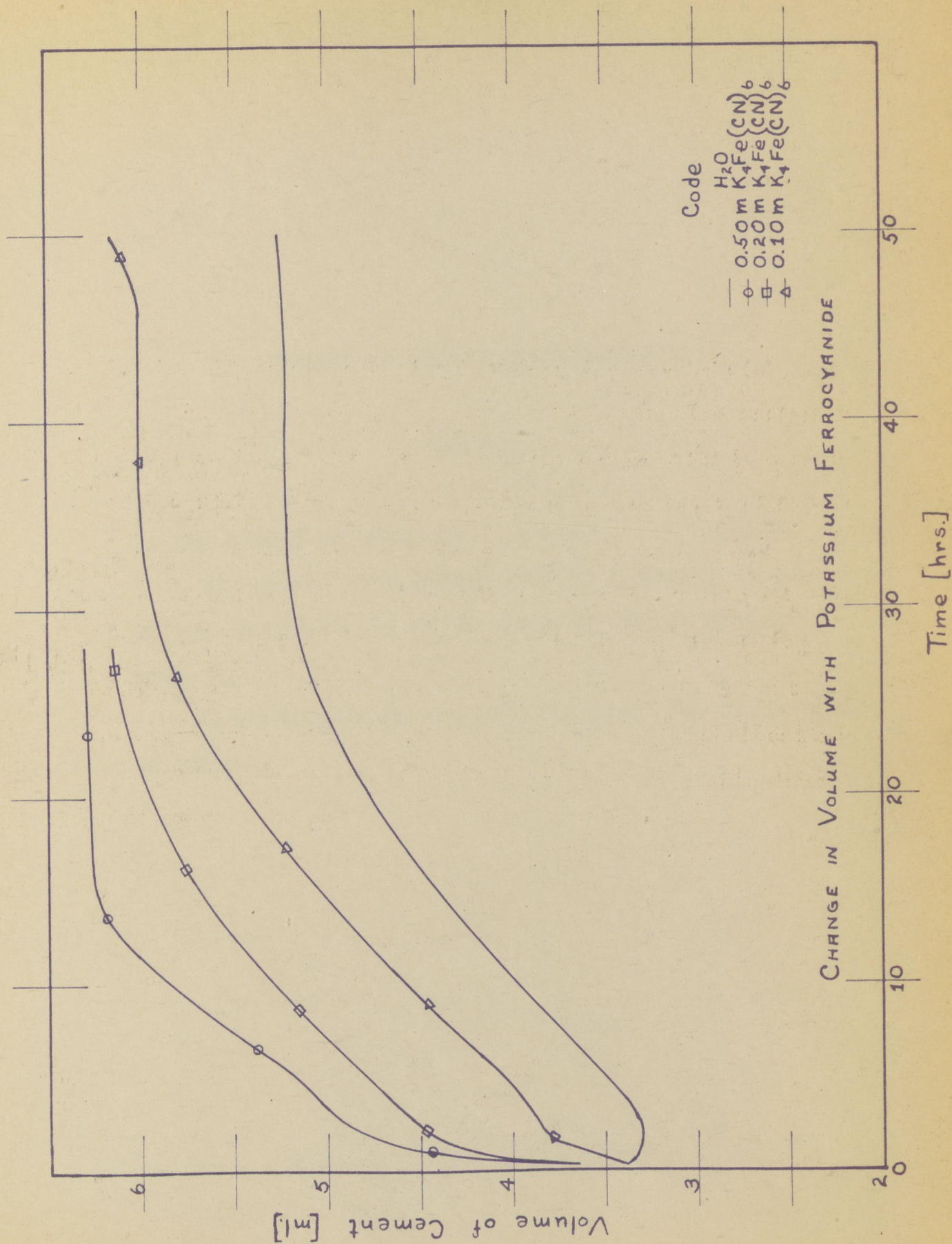


4. The effect of potassium ferrocyanide -- $K_4Fe(CN)_6$

The effect on the volume change of cement when potassium ferrocyanide (potassium iron (II) cyanide) is added is shown in figure VII on page 30.

It is evident that potassium ferrocyanide is as great an accelerating agent for the setting of cement as is aluminum chloride.

FIGURE VII



EFFECTS OF SOME NON-ELECTROLYTES

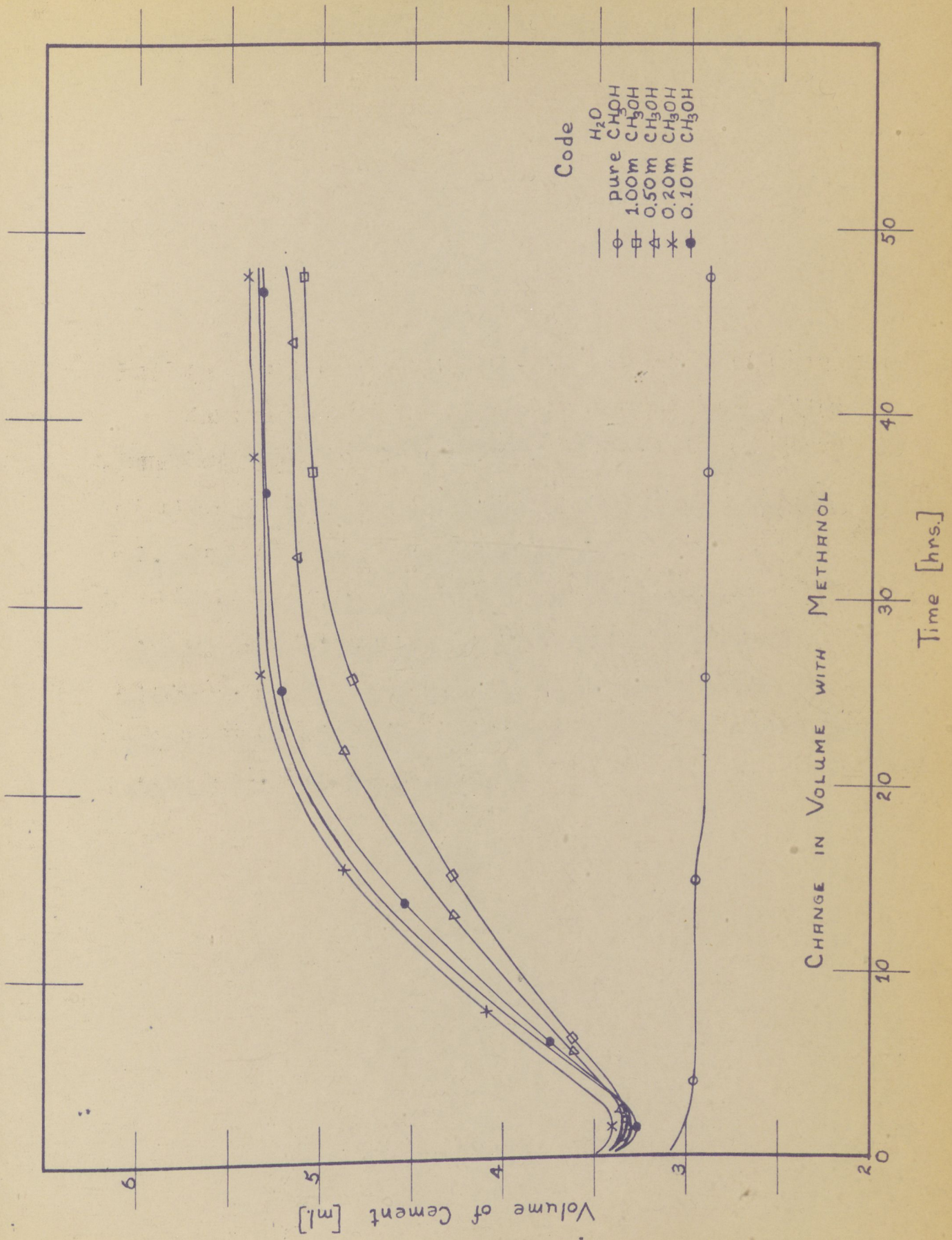
GROUP III

1. The effect of methanol ----- CH_3OH

The effect of methanol (methyl alcohol) on the volume change of cement is shown in figure VIII on page 32.

Methanol acts as a retarding agent for the setting of cement.

FIGURE VIII

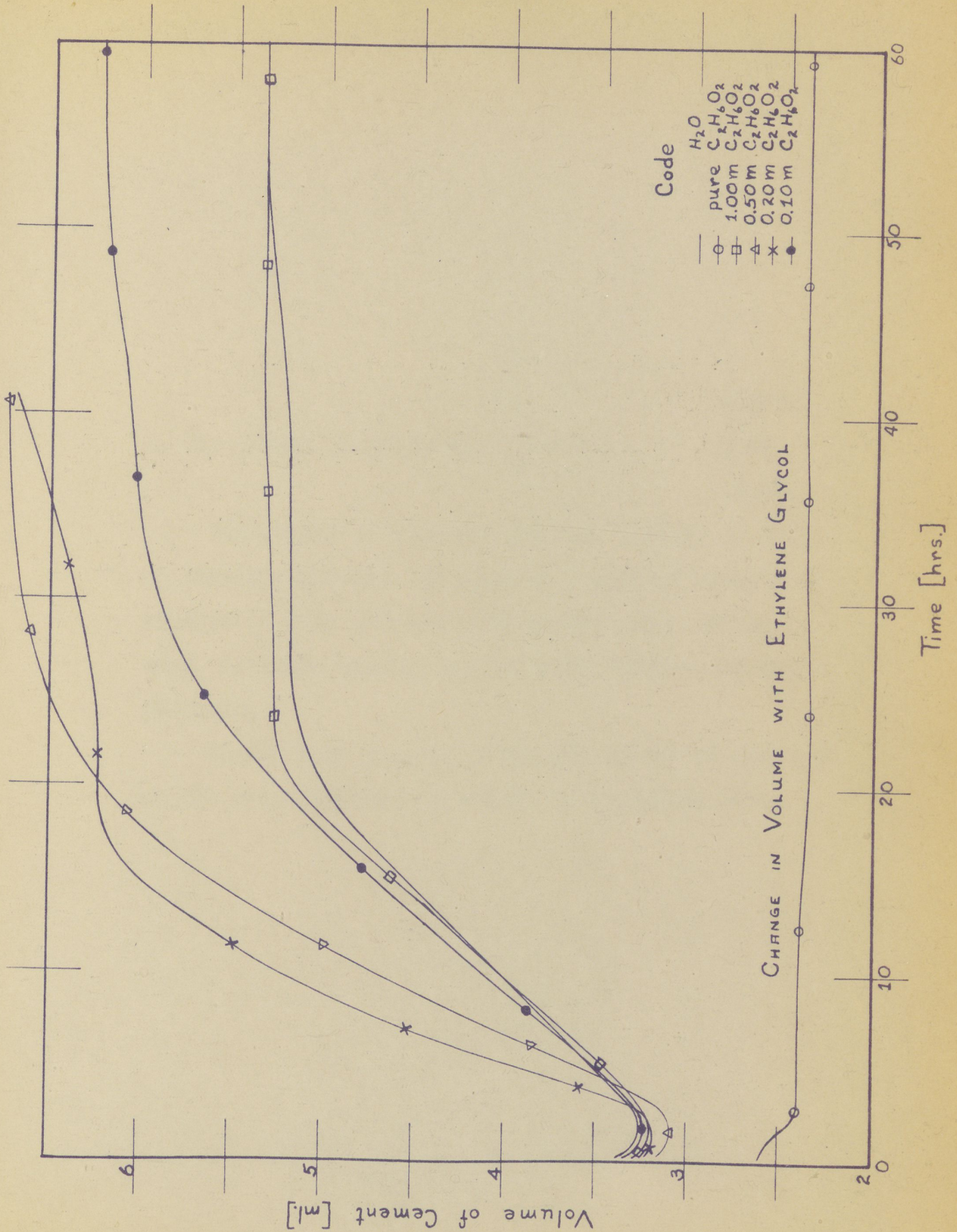


2. The effect of ethylene glycol ----- $\begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{CH}_2\text{OH} \end{array}$

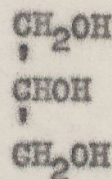
Figure IX on page 34 shows the effect of ethylene glycol on the volume change of cement.

From this research it appears that ethylene glycol has an accelerating action on the setting of cement in dilute solutions, but a retarding action in concentrated solutions. This latter effect is especially evident with the pure material.

FIGURE IX



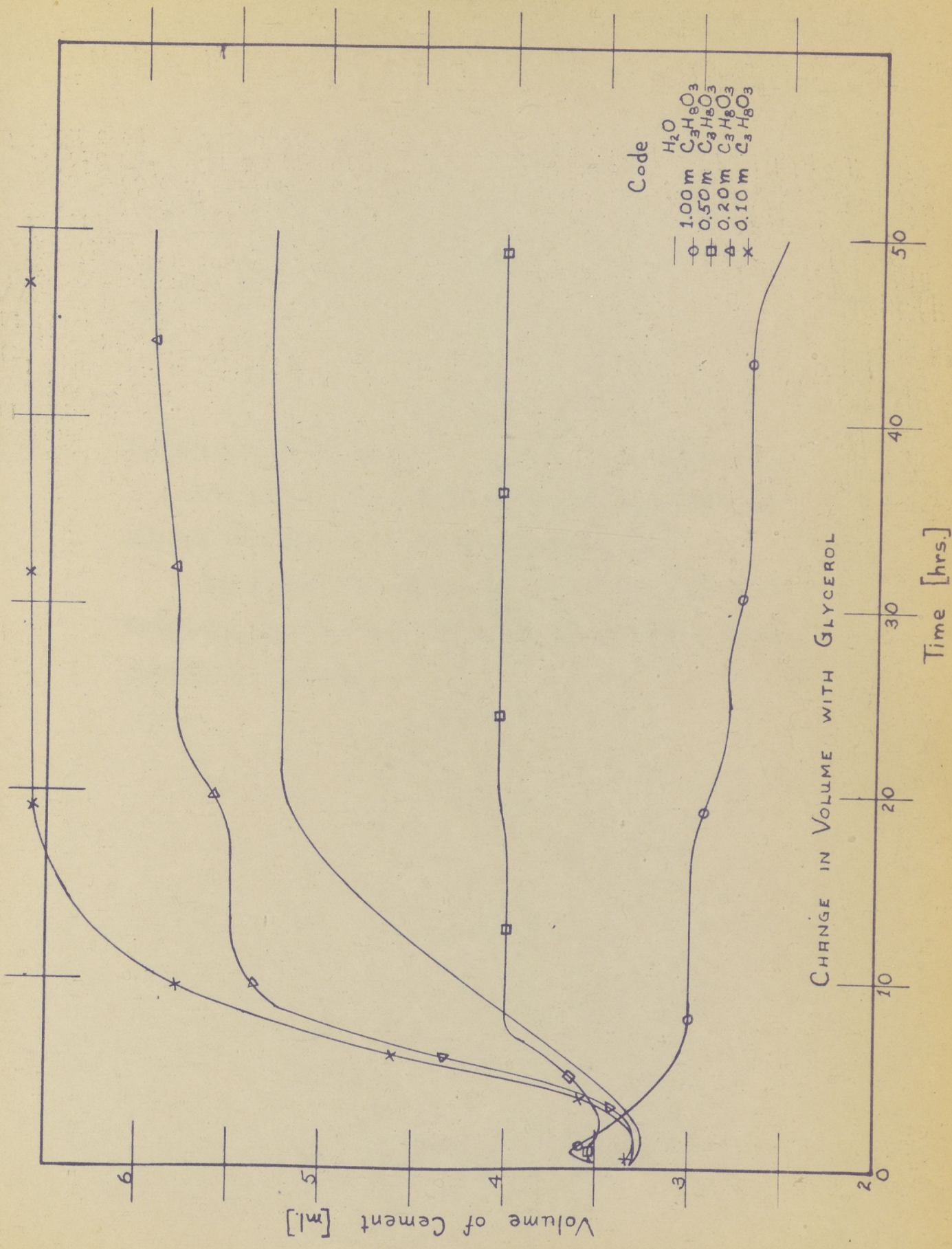
3. The effect of glycerol -----



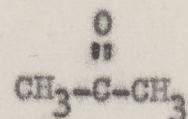
The effect of glycerol is very similar to that of ethylene glycol, but even to a greater extent. A mixture of pure glycerol and cement could not be used, however, because of the very viscous mixture produced.

Figure X on page 36 shows the effect of glycerol on the volume change of cement in graphical form.

FIGURE X



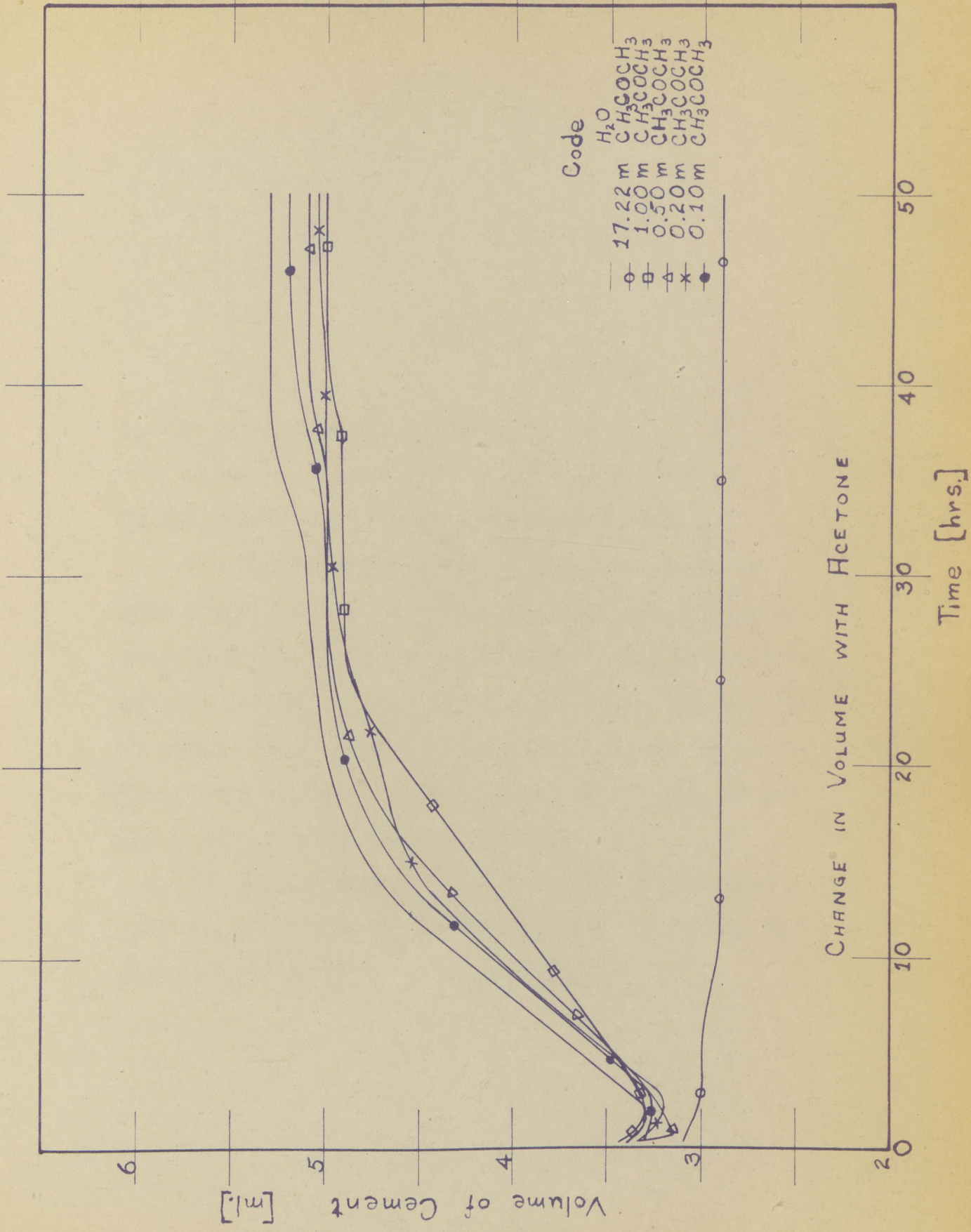
4. The effect of acetone -----



The effect of acetone on the volume change of cement is shown in figure XI on page 38.

The effect of acetone resembles the effect of methanol, in that both have retarding action on the setting of cement.

FIGURE XI



GROUP IV

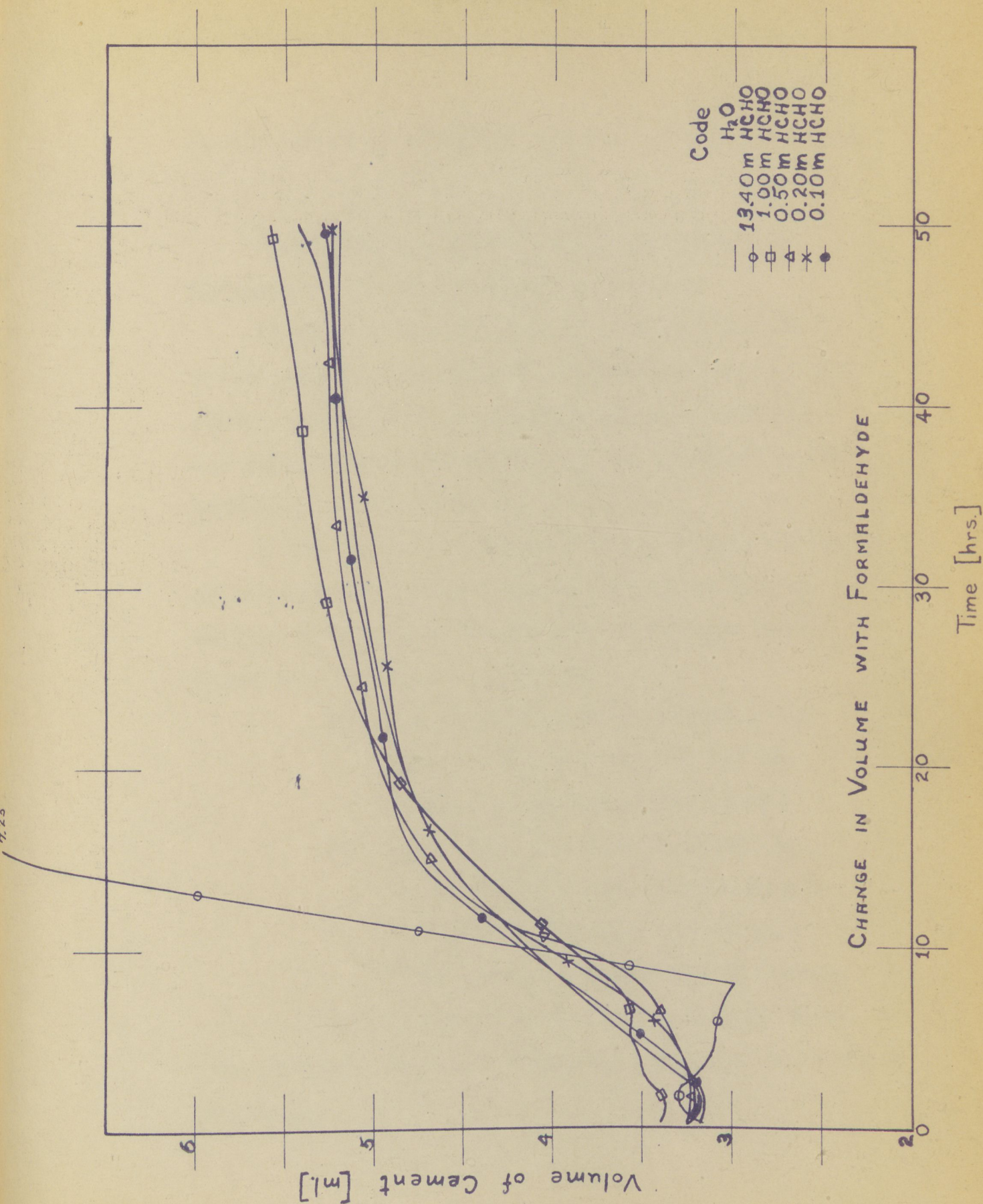
1. The effect of formaldehyde ----- $\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{H} \end{array}$

Figure XII on page 40 shows the effect of formaldehyde on the volume change of cement.

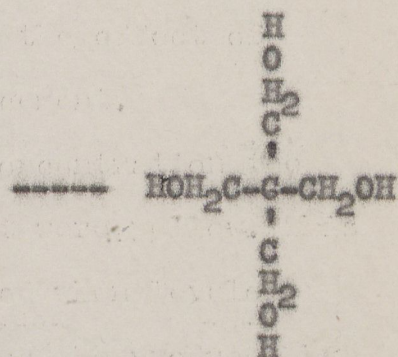
Formaldehyde in dilute solutions appears to have a slight accelerating action on the setting of cement. These lower concentrations produced a white material on the sides of the containers, increasing in amount with decreasing concentration of formaldehyde. This material did not burn, decompose, or give any visual appearance of changing.

The 13.4 M solution of formaldehyde produced a very great accelerating action, which is due to the probable formation of calcium formate.

FIGURE XII



3. The effect of pentaerythritol

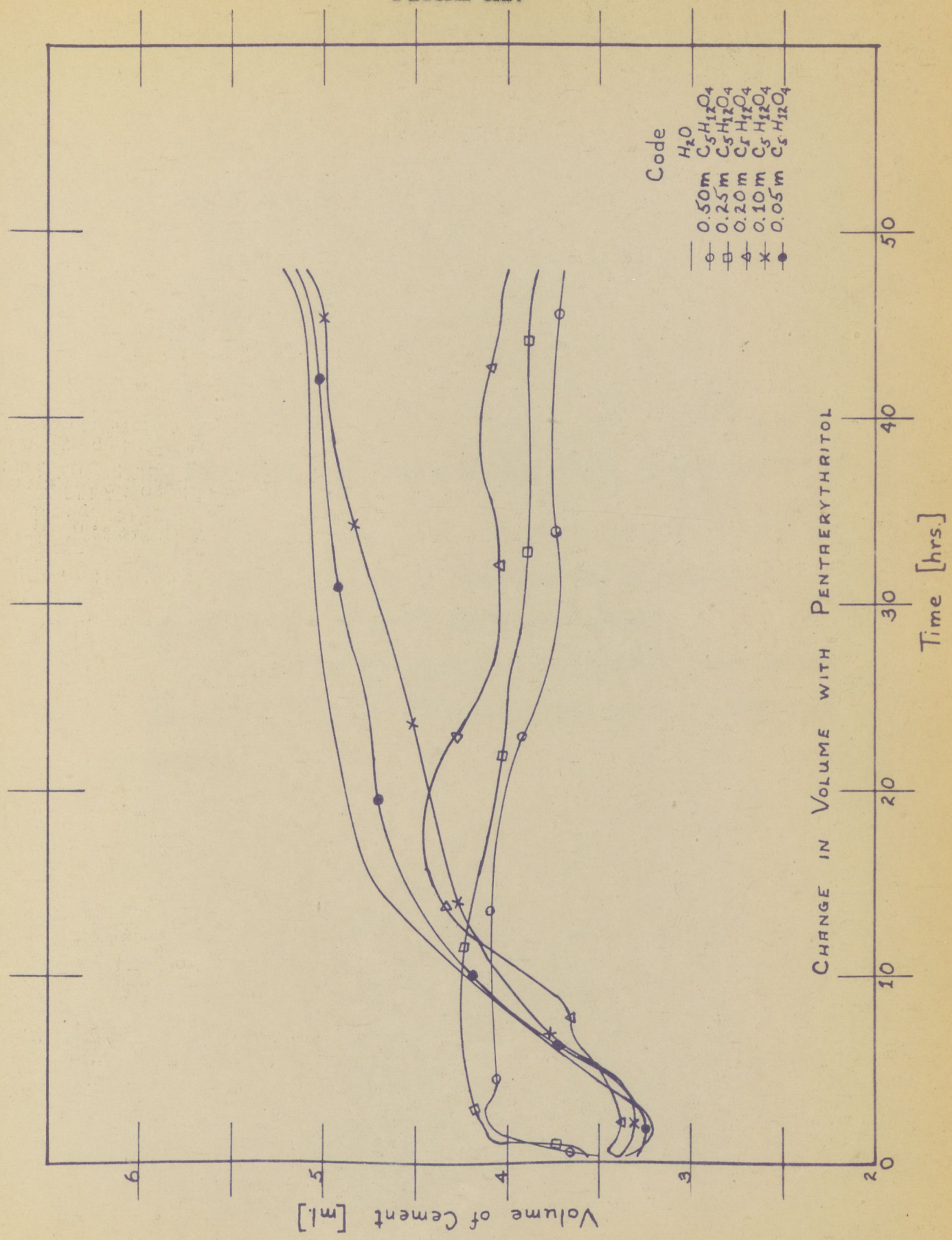


The effect of pentaerythritol on the volume change of cement is not too well understood. Figure XIV on page 44 shows the effect in graphical form.

As a whole pentaerythritol appears to act as a retarding agent for the setting of cement.

In the higher concentrations a phenomenon similar to false setting occurs, but not as pronounced as in the case of levulose previously mentioned.

FIGURE XIV



4. The effect of d- mannitol

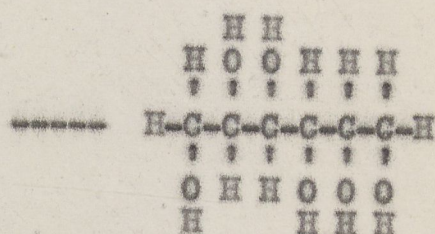
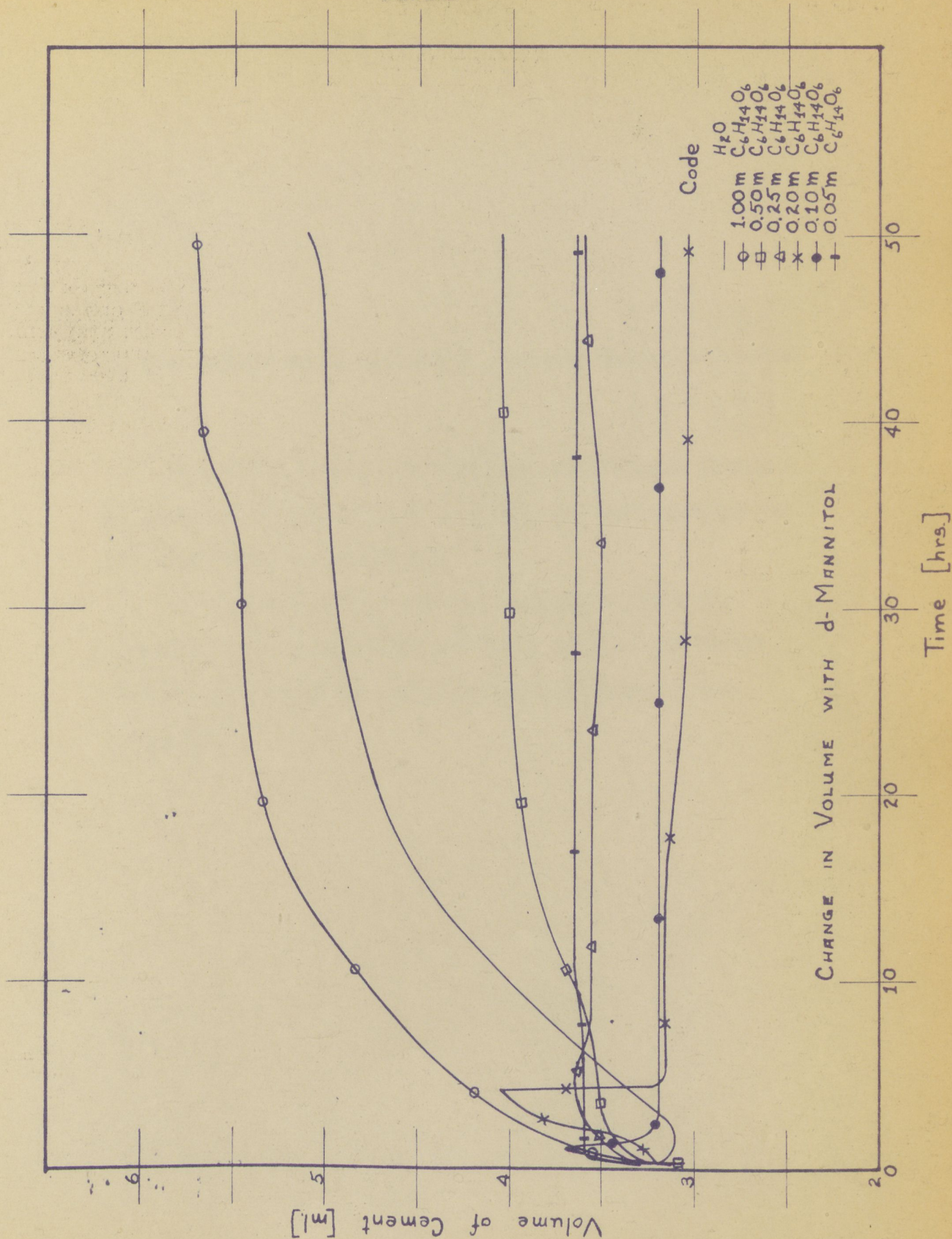
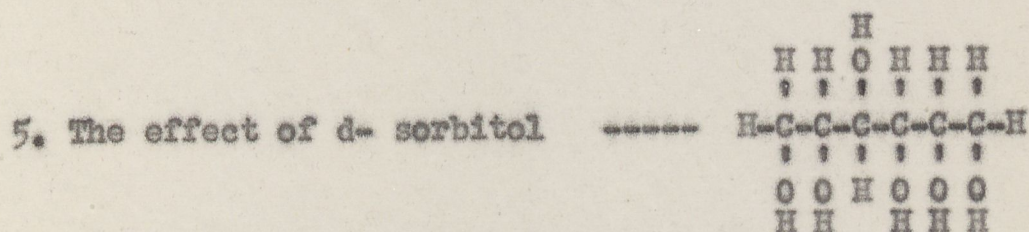


Figure XV on page 46 shows the effect of d-mannitol on the volume change of cement.

Except for the 1.00 M concentration d- mannitol appears to have a retarding action on the setting of cement.

FIGURE XV

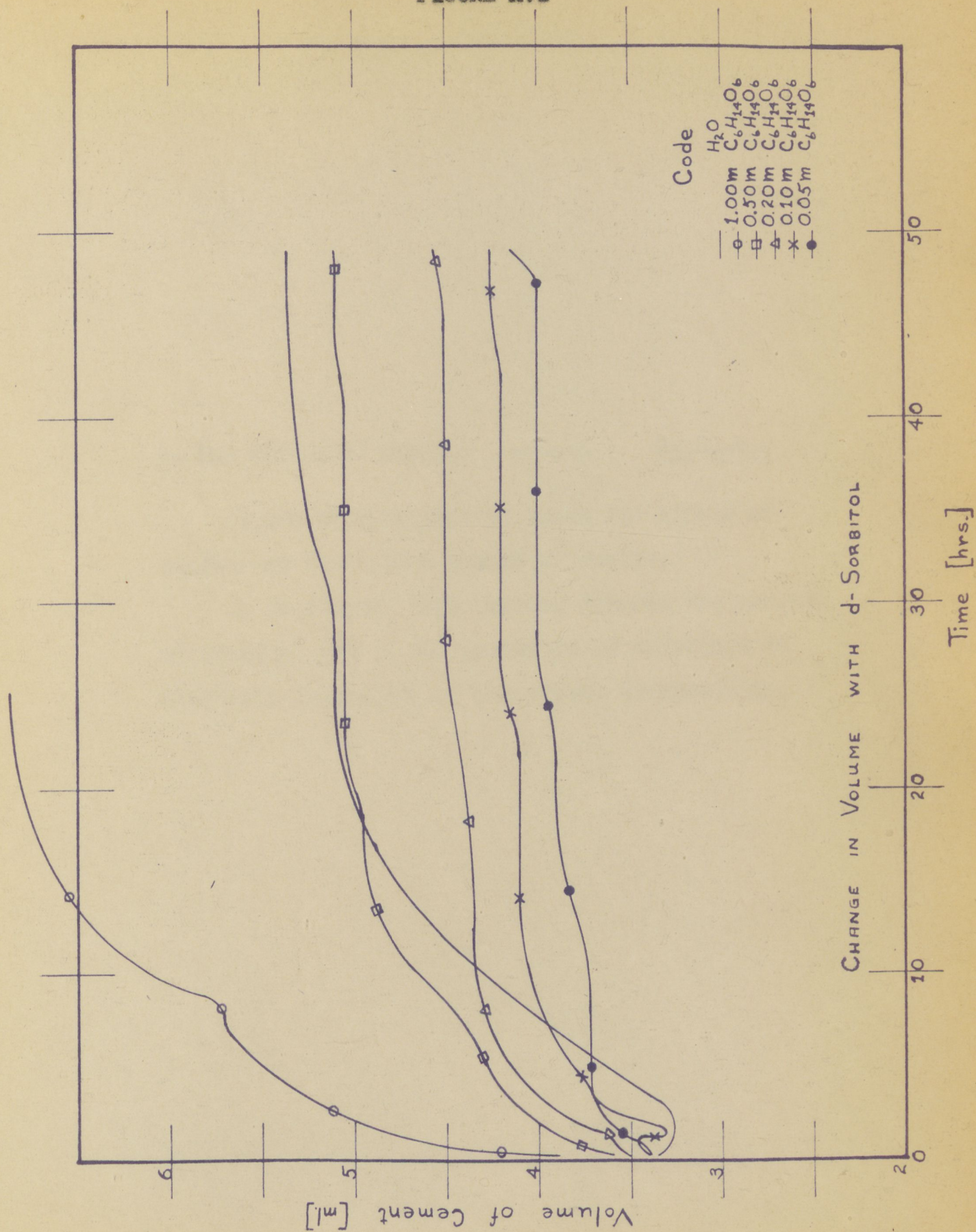




The effect of d- sorbitol on the volume change of cement, figure XVI on page 48, is very similar to the effect of d- mannitol.

This similarity would be expected since d- mannitol and d- sorbitol are very similar in their structure, differing only in the position of one -OH group.

FIGURE XVI



6. The effect of sucrose ----- $C_{12}H_{22}O_{11}$

Figure XVII on page 50 shows the effect of sucrose on the volume change of cement.

It is evident that sucrose retards the process of setting, and in the concentrated solutions it decreases the volume of the cement tremendously.

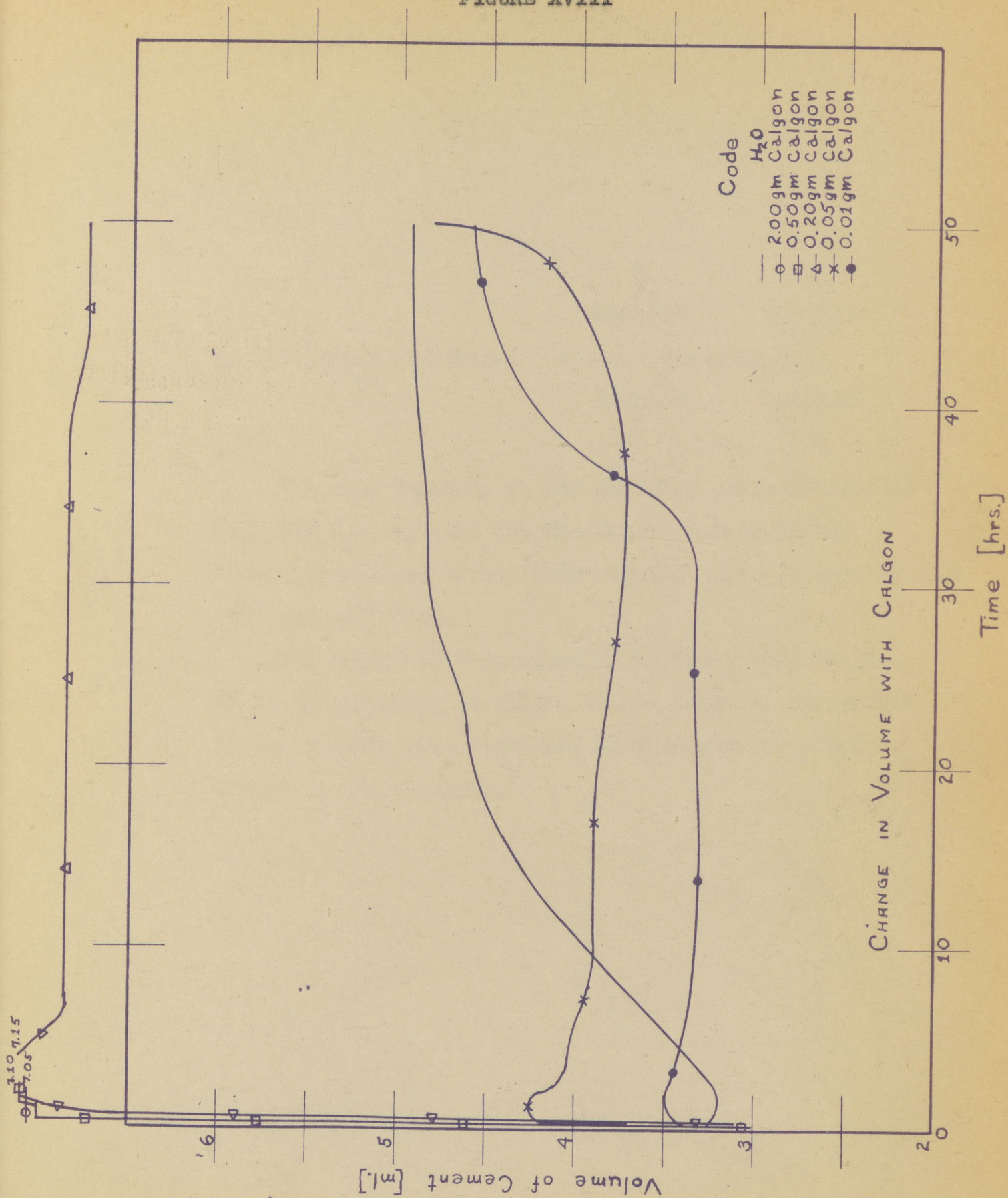
GROUP V

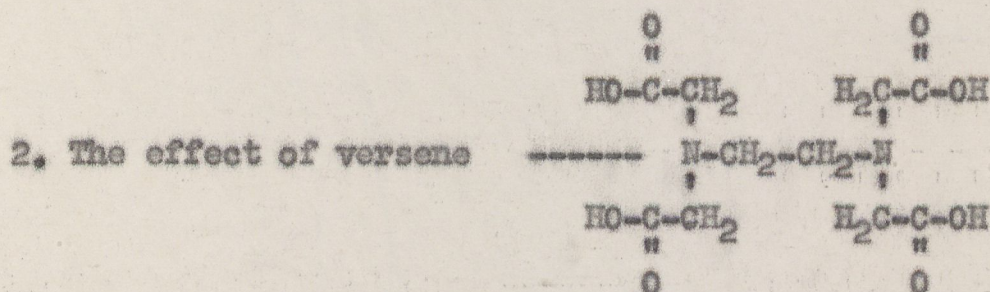
1. The effect of calgon ----- $\text{Na}_6(\text{PO}_3)_6$ (?)

Figure XVIII on page 52 shows the effect of calgon, a water softener, on the volume change of cement.

The action of this material on cement is not at all understood.

FIGURE XVIII

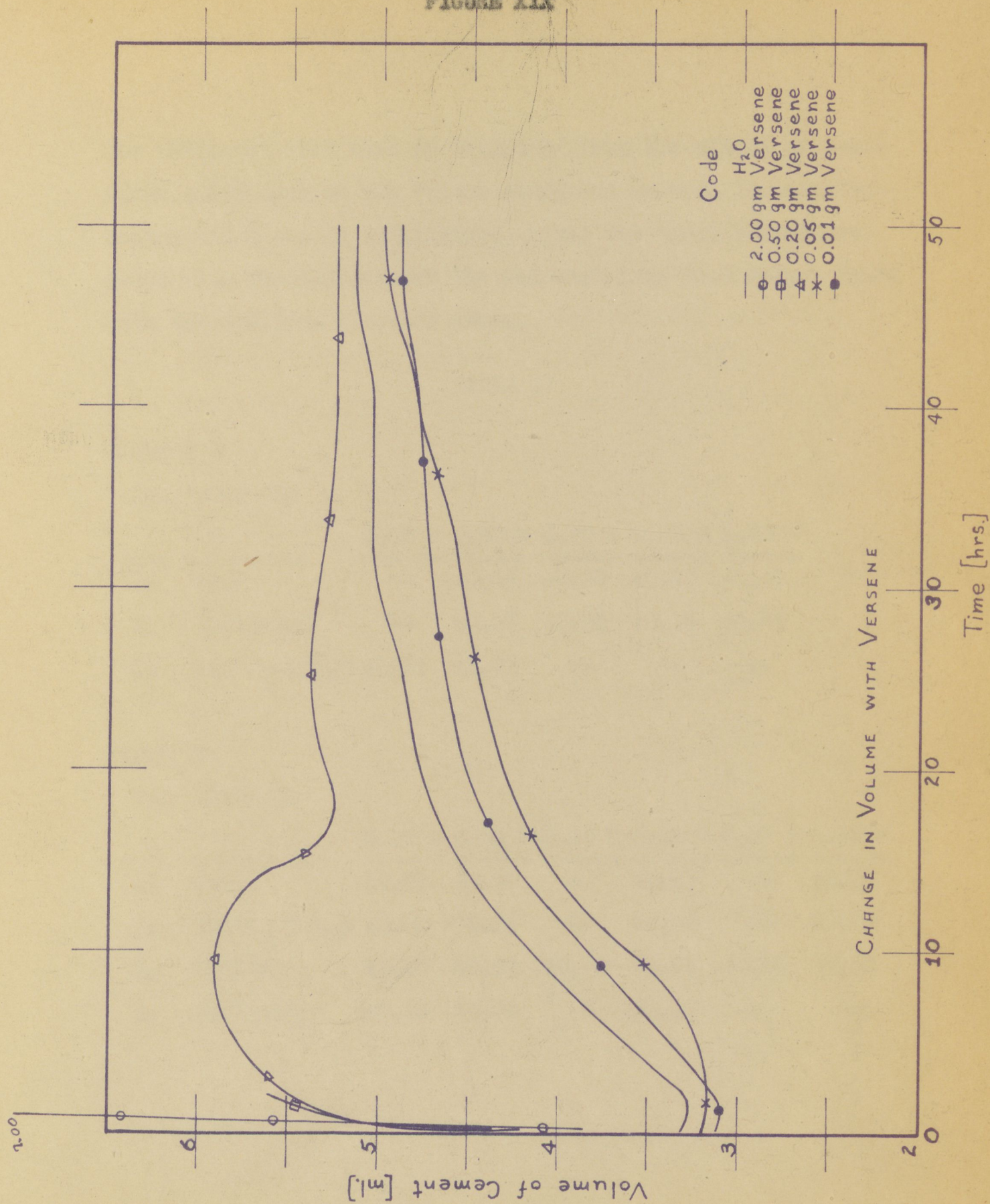




The acid versene, or the disodium salt abbreviated $\text{Na}_2\text{H}_2\text{Y} \cdot 2 \text{H}_2\text{O}$, is used for the determination of the total hardness of water. This material forms a complex with Ca^{++} and Mg^{++} ions.

The effect of this material on the volume change of cement is shown in figure XIX on page 54. The action is not clearly understood and an explanation of its effect is not possible.

FIGURE XIX



The following will show in tabulated form the effect of these added substances on the volume change of cement. The measurements, which are in milliliters, equal the final volume produced with the addition of the material less that volume found with the addition of water alone.

TABLE II

GROUP I

NO.	COMPOUND	0.05 M	0.10 M	0.20 M	0.50 M	1.00 M
1.	NaCl	--	+0.05	+0.00	+0.15	+0.30
2.	CaCl ₂ ·H ₂ O	--	+0.25	+0.20	+0.70	+0.45
3.	Al ₂ Cl ₆ ·12H ₂ O	+0.85	+1.20	--	--	--

GROUP II

NO.	COMPOUND	0.10 M	0.20 M	0.25 M	0.50 M	0.75 M	1.00 M
1.	NaCl	+0.05	+0.00	--	+0.15	--	+0.30
2.	Na ₂ SO ₄ ·10H ₂ O	+0.20	+0.25	--	+0.60	--	+0.80
3.	K ₃ Fe(CN) ₆	+0.15	+0.00	+0.00	+0.25	+0.40	+0.10
4.	K ₄ Fe(CN) ₆	+0.90	+0.90	--	+1.05	--	--

GROUP III

NO. COMPOUND

		0.10 M	0.20 M	0.50 M	1.00 M	PURE
1.	CH_3OH	+0.00	+0.05	-0.15	-0.25	-2.45
2.	$(\text{CH}_2\text{OH})_2$	+0.90	+1.30	+1.35	+0.00	-2.97
3.	$(\text{CH}_2\text{OH})_2\text{CHOH}$	+1.33	+0.63	-1.27	-2.72	--
4.	CH_3COCH_3	-0.10	-0.25	-0.20	-0.30	-2.40

GROUP IV

NO. COMPOUND

		0.05 M	0.10 M	0.20 M	0.25 M	0.50 M	1.00 M	PURE
1.	HCHO	--	+0.10	+0.05	--	+0.25	+0.40	+2.05
2.	$\text{C}_6\text{H}_{12}\text{O}_6$	-1.95	-1.75	-1.45	--	-0.85	+1.48	--
3.	$\text{C}_6\text{H}_{12}\text{O}_4$	-0.05	-0.10	-1.20	-1.35	-1.50	--	--
4.	$\text{C}_6\text{H}_{14}\text{O}_6$	-1.45	-1.90	-2.05	--	-1.05	+0.60	--
5.	$\text{C}_6\text{H}_{14}\text{O}_6$	-1.20	-1.10	-0.80	--	-0.25	+1.50	--
6.	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	-1.40	-1.40	-0.70	--	-4.00	-4.00	--

GROUP V

NO. COMPOUND

		0.01 gm.	0.05 gm.	0.20 gm.	0.50 gm.	2.00 gm.
1.	Calgon	-0.35	-0.10	+1.80	+2.15	+2.10
2.	Versene	-0.25	-0.15	+0.10	+0.45	+1.85

DISCUSSION

The effect of the electrolytes in group I, page 55, on the setting of Portland cement has been explained heretofore (7),(10),(25),(29),(32),(16),(17),(23). It was found that the accelerating action which they had on the setting of the cement was greatest for aluminum chloride, followed by calcium chloride and then sodium chloride. This indicates that the higher the positive valence of the cation, the faster will the material accelerate the set.

The results of this research show the same relative effect. The cation with the highest positive valence shows the greatest increase in volume of the cement, and the cation with the lowest positive valence the smallest increase.

The electrolytes in group II, page 55, also have an accelerating action on the setting of cement. This acceleration is greatest for the salt with the anion of the highest negative valence and least for the salt with the anion of the lowest negative valence. The action of potassium ferricyanide is not in correct order, the reason for which is not known.

With respect to this research, the anion with the highest negative valence produces the largest increase in volume of the cement, and the anion with the lowest negative valence the smallest increase.

The reason why these electrolytes have the effect which they do on the volume change of the cement, is probably because of the amount of water which is held by ionic hydration. The greater the valence, the larger the number of water molecules held due to this attraction, and therefore the greater the increase in volume of the cement.

The effect of the non - electrolytes does not appear to be as easily explained as does the effect of the electrolytes.

The overall effect of those non - electrolytes in group III, page 56, is one of solubility or dehydration. The pure materials do not permit the cement to hydrate and thereby decrease the swelling of the cement tremendously.

Yamane (35) explains this retarding effect for methanol as being due to the difference between the supersaturated solubility and the normal solubility of calcium sulfate. This difference is smaller in methanol than in water. The same might be the case for ethylene glycol, glycerol and acetone.

Acetone and methanol, in any concentration, decreases the volume of the cement, acting entirely as a dehydrating agent. The other materials, however, increase the volume of the cement in the lower concentrations.

The non - electrolytes in group IV, page 56, present the

main problem. The addition of formaldehyde indicated the presence of a chemical reaction with the probable formation of calcium formate.

When levulose was added to the cement, a false set occurred. The reason for this is not clear but probably is the result of a complex formation. A chemical reaction also was noticed, the oxidation of the levulose producing a yellow color.

The addition of sugars to Portland cement has been known for many years to retard the setting. It has been claimed by Burchartz (6), and others (8), (12), (18), that this retarding action is caused by the delay the sugar produces in the crystalline formation during the hydration.

The addition of the salts in group V, page 56, have not been investigated thoroughly enough for a conclusion to be accurately drawn. One would have expected the volume of the cement to decrease, since both salts are used to form complex Ca^{++} ions. This, however, was not the case and the theory involved is disproven.

SUMMARY

From the results of this research, there are certain points which are clearly brought out.

With the addition of electrolytes to Portland cement, the following conclusions are drawn:

GROUP I

1. The higher the positive valence of the cation the more rapidly the setting is accelerated, and the greater is the increase in volume of the cement.

GROUP II

1. The higher the negative valence of the anion the more rapidly the setting is accelerated, and the greater is the increase in volume of the cement.

Note: Potassium ferricyanide appears to be the exception, as might other uni - tri valent salts.

With the addition of non - electrolytes to Portland cement the conclusions are as follows:

GROUP III

1. Acetone and methanol act as dehydrating agents. Yamane's (35) explanation also gives reason for the effect of these materials resulting from the solubility of calcium sulfate.

GROUP IV

1. The addition of formaldehyde produces a chemical reaction with the formation of calcium formate.
2. Levulose causes false gel formation, and oxidation produces a yellow color.
3. Sugars retard the setting and decreases the volume of the cement because they delay crystalline formation during hydration.

The effect of the salts in group V is not understood and more investigation is necessary.

BIBLIOGRAPHY

- (1) Anderegg and Hubbell; Proc. Amer. Soc. Test Mat., 29, II,
554 (1929)
- (2) Bensen, H.H., Newhall, C.A. and Tremper, E.; J. Ind. Eng.
Chem., 6, 795 (1914)
- (3) Bogue, R.H.; "The Chemistry of Portland Cement" (1947)
- (4) Bogue, R.H. and Lerch, W.; Res. Reports P.C.A.F., Sept (1933)
- (5) Brown, L.S.; U.S. 2,374,581 Apr. 24, 1945
- (6) Burchartz, H.; Zement 13, 11; 509 (1924)
- (7) Dautrebande, J.; Le Ciment, 26, 291 (1921)
- (8) Eklund, K.I.A.; Brit. 480,681 Feb. 25, 1938
- (9) Erdahl, B.F.; Concrete, C.M.S., 15, 17 (1919)
- (10) Ferrari, F.; Atti. Cong. naz. chim. pura app., 294 (1923)
- (11) Gessner; Kolloid Zeit., 46, 207 (1928) ; 47, 65; 160 (1929)
- (12) Gonell, H.W.; Zement, 18, 372 (1929)
- (13) Gonnerman, H.F.; Proc. Amer. Soc. Test Mat., 36, Pt. I,
225 - 51 (1936)
- (14) Graf, O.; Beton u. Eisen, 20, 72 - 4 (1921)
- (15) Grimm, R.; Zement, 15, 775 (1926)
- (16) Grün, R.; Z. Angew Chem., 43, 496 (1930)
- (17) Grün, R. and Mancke, H.; Tonind Ztg., 58, 264 - 6;
276 - 8 (1934)
- (18) Hundeshagen, F.; Z. Angew. Chem., 36, 53 - 4 (1923)

- (19) Jolibois, P. and Nicol, A.; Rev. matériaux construction
trav. publ. 2, 1948, 169 - 73
- (20) Jumper, C.H. and Kalousek, G.; Rock Products 45, No. 6,
58 - 9; No. 7, 64 - 5 (1942)
- (21) Lea, F.M. and Desch, C.H.; "The Chemistry of Cement and
Concrete" (1940)
- (22) Le Chatelier, H.; Compt. rend., 94, 13 (1881)
Trans. Faraday Soc., 14, 9 (1919)
- (23) Lerch, W.; Res. Reports, P.C.A., Apr. 1944
- (24) Maeda, T. and Yamane, S.; Assoc. Japan Portland Cement Engrs.,
Rev. 26th. General Meeting A - 26,
60 - 72 (1941)
- (25) Mc Intosh, G.H.; Iowa State Coll. J. Sci., 10, 85 - 6 (1936)
- (26) Mc Millan, F.R.; Intern. Assoc. Testing Materials, London,
April 1937, 401 - 3
- (27) Meyer, A.; Baumaterialienkunde, 6, 141; 159; 181; 212; 232;
248; 293; 309; 326; 347; 368 (1901)
Z, 75; 111; 140; 156 (1902)
- (28) Michaelis, W.; Tonind Ztg., 16, 105 (1892)
Chem. Ztg., 982 (1893)
Baumaterial, 11, 333; 352; 366; 381 (1906)
J. Soc. Chem. Ind., 28, 836 (1909)

- (29) Newman, A.J.; Concrete Construction Eng., 38, 159 - 67 (1943)
- (30) Rohland, P.; Baumaterialienkunde, 5, 116; 134; 321; 361 (1900)
Z. anorg. Chem., 21, 28
Kolloid Z., 4, 223 (1909); 8, 251 (1911)
- (31) Roller, P.S.; Ind. Eng. Chem., 26, 669; 1077 (1934)
- (32) Simons, H.F.; Oil Gas. J., 41, 48; 50 (1943)
- (33) Swayze, M.A.; U.S. 2,374,628 Apr. 24, 1945
- (34) Whitworth, F.; Cement & Cement Manuf., 4, 756 - 62 (1931)
- (35) Yamane, S.; Sci. Papers Inst. Phys. Chem. Research (Tokyo)
16, 276 - 83
- (36) Yamane, S.; J. Soc. Chem. Ind., Japan 43 Suppl. binding
28 - 9 (1940)
- (37) Yamane, S.; J. Soc. Chem. Ind., Japan 43 Suppl. binding
97 - 8 (1940)