A STATISTICAL STUDY ON FACTORS AFFECTING SULFATE ATTACK

THESIS

BY

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-SYNOPSIS-

The sulfate resistance of two currently produced Turkish portland cements, Bartin and Darica and the contribution to this effect of four additives, namely, Kayseri pozzolana, Tunçbilek fly-ash, Karabük blast-furnace slag, and ground brick are studied; and the significance of factors influencing sulfate resistance are determined. Methods of measuring sulfate resistance are compared and discussed in view of the literature survey.

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CHAPTER I

INTRODUCTION

1.1 Introduction

Sea-water and ground waters containing sulfate ions are known to have caused deterioration on concrete structures. The binding component that is the set cement is subject to this deterioration. The behaviour of concrete in sulfate-bearing soils and in sea-water attracted attention as far back as the latter years of the nineteenth century. The records of laboratory and field studies since then are numerous. Early studies were concentrating on the relative effect of various components of cement on its resistance to the chemical action of sulfates. Soon specifications for sulfate resisting cements were developed.(1,2).

Another object was the development of a testing method, possibly a quick one, for the determination of sulfate susceptibility of cements(3,4).

Later on the effect of substitution of certain materials, i.e. , pozzolanas and slags for a part of cement on its sulfate resistance were studied. To these studies, investigation of certain physical requirements for long-time concrete durability against sulfate exposure were added(5,6,7).

In Europe and America, the problem was realized, studied and certain precautions reducing the problem to an in significant level were proposed, though still certain points exist for investigation and clarification(3,4).

In Turkey, the realization of the problem is recent(8).Only some case-histories and very limited research exist at the present. Since the sulfate attack itself was investigated extensively abroad for quite a long period of time, the study presented here was directed mainly towards the possible preventive measures easily applicable in Turkey.

For this, four materials obtainable in Turkey (one natural, three artificial) as additives to cement and two currently produced cements were studied. Three methods of quantitiative measurement of sulfate attack were employed along eith certain quantitative approachs.

Being one of the first studies on this subject in this country, this research concentrates in putting a hypothesis forward to guide the further studies and presenting a basis for such investigations as far as materials, measurements and methods are concerned.

1.2 The Statement of the Problem

Concrete is a composite material which consists essentially of a binding medium (matrix) within which are embedded particles or fragments of a relatively inert mineral filler (aggregate). The sulfates of sodium, magnesium and calcium present in alkali soils and waters are known to have caused deterioration of many concrete structures. Binder is the component of concrete which is subject to this deterioration. The sulfates of sodium, magnesium and calcium may be Na_2SO_4 (Glauber's salt), $MgSO_4$ (Epson salt), $CaSO_4$ (gypsum or selenite).

The sulfates react chemically with the hydrated lime and hydrated calcium aluminate in the cement paste to form calcium sulfate and calcium sulfoaluminate respectively, these reactions being accompanied by considerable <u>expansion</u> and <u>distruption</u> of concrete((9). The destruction is caused by <u>disintegration</u> of the cement and by the considerable crystallization pressure. During the hardening of cement hydrated lime is freed in large quantities and this enables the formation of soluble aluminates.

Therefore, specimens in sulfate solutions deteriorate by the action of two distinct processes namely: by <u>expansion</u> and subsequent <u>distruption</u> and by <u>destruction</u> of the silicate hydrates due to chemical action. The second process causes a disintegration (10). These reflect the two aspects of sulfate deterioration on concretes: physical and chemical.

A mortar attacked by sodium or calcium sulfate ultimately becomes more often of hard granular particles. Concretes which are mildly attacked by sulfate have a whitish appearance. After further attack, they expand, crack, and spall but pieces remain hard. In later stage they become friable and finally reduce to a soft mud.

1.3 Background of the Problem

The presence of gypsum beds and undesirably high concentrations of sulfate in most of the ground waters in Turkey is a source of problem in many structures constructed by various agencies i.e. The Ministry of Puplic Works, State Hydraulic Works... The foloowing are the districts where major occurences of attack were observed by the State Hydraulic Works Directory (8):

a) Mamasin Dam Derivation Tunnel:

The sand used in this tunnel, built in 1958, was obtained from Kireçlik Creek where the water contains gypsum dissolved in large quantities. The sand which was similar in appearance to a clean construction sand had about 20% $CaSO_4.2H_2O$ in its composition. During the construction period, nothing notable was observed, but soon after with the action of drainage waters leaking, the reactions have started and in three months time cracks and swellings were observed. Dry parts of the tunnel, on the other hand, showed no indication of attack. The concrete sections of the construction had to be reneved with the use of a different sand.

The piers of the Uluirmak Bridge at the same side, made of the Kireçlik sand, rapidly disintegrated, even before the deck of the bridge was casted.

b) Aksaray Irrigation System:

At certain sections of this canal system the ground water contains sulfate at a concentration of approximately 1650 ppm. At these sections the ground water table was kept below the level of canal bottom-lining in order to prevent the contact of water with concrete. No attack has been observed yet.

On the other hand, the flood beds where the main canal passes contain gypsum carried from the upstream. At these sections, soon after entering the operation, a drop of 60 cm to 120 cm was observed. This was attributed to the fact that waters drained from the bottom of canal dissolved the sulfate ions in the underlying strata and carried them down to the under ground leaving holes behind and caused the collapse of the bottom of canal. Sulfates couldn't attack the concrete since they didn't came into contact.

c) Sarayköy - Yenice Irrigation Canal:

A branch of this canal goes through gypsum beds, about 500m. in length. There is not ground water at the bottom of canal. The lining is concrete, but not attacked by sulfates. The problem is the same as occured in Aksaray Irrigation System, i.e. pits form under the bottom of canal; canal collapses and water is lost through these holes.

Only in a secondary branch of this canal, the ground water is above the level of canal bottom in all seasons and is saturated with sulfate. Concrete linings of this canal disintegrated two years after the construction.

d) Yüregir Plain Irrigation Network:

The ground water in this area, containing large amounts of sulfate dissolved attacked the piers of Karaömerli and Zagerli Bridges.

e) Çifteler Irrigation - Sakaryabaşi Regulator:

Because of the high concentration of sulfates in the ground water in this area, the site of regulator contruction was changed.

f) Manavgat - Ulualan - Muş Irrigation

The ground water, containing much sulfate deteriorated the bottom of canals.

Many other discrete examples can be added to the ones given above, like Konya irrigations system... Ground water, in the plains where irrigation structures made without proper drainage may rise up to concrete sections and containing sulfates, deteriorate these structures.

The sea-water action on sea-front structures, particularly the chemical attack of magnesium sulfate is also of high importance in a country like Turkey surrounded by seas.

In general waters containing sulfates more than 150mg/L usually deteriorate the concrete sections of the structures in contact.
The cheapest means to protect concrete from sulfate attack is to use cements resistant to sulfate. Taking this fact into consideration the

auther made a survey of various cements currently produced in Turkey.

At present, only the NCP-350 (corresponding to Type I) Portland cement is normally being produced in Turkey and its composition may vary from one mill to another and it may be close to various types. A study of the analysis of 13 different mills" products in 1962 was made by DSI Research Center and the results on Table I (pg 6) were obtained (8). Only these compositions occured temporarily, that the composition of a particular mill's cement doesn't remain constant, but is apt to change at any time. Nevertheless if the source of the raw material doesn't change, a degree of consistency may be expected. The Table II (pg. 6) gives the changes in Ankara mill's cements with the years (8).

In the Research Laboratories of the State Hydraulic Works Directory some studies concentrating on cements resistant to sulfate were undertaken (8). In general these researches were directed to be the studies of clinker composition and behaviour in sulfate solutions of normal portland cements produced in Turkey.

In 1960 and 1962, samples of all types of cements produced in Turkey were obtained and analized; and particularly their C_3A percentages were determined. Also mortars of these cements were stored in $MgSO_4$ solutions and controlled for 18 months.

These researched led to the following conclusions (8):

1- The clinker composition of Turkish cements are not constant.

2- Storage of mortars made of these cements, in $MgSO_4$ solutions revealed the relationship between tricalcium aluminate content and degree of attack.

3- It was not possible to derive general conclusions.

4- It was realized that the production of a sulfate-resisting cement was indispensible for the State Water Works Projects.

Since there is no type of Turkish cement which is resistant to sulfate attąck and since our portland cements normally contain high amount of tricalcium aluminate, the importance of sulfate corrosion increases.

Turkish Portland Cements Clinker Compositions§

Cement Mill	Mineralogic Composition of Clinker, as percentages								
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	Free CaO	MgO	Ignition Loss	Closest Type
Afyon	52	21	10	7	2,9	0,4	3,1	2,2	I
Ankara	41	32	8	11	2,0	0,5	2,6	1,9	II
Balikesir	41	29	11	10	2,5	0,4	2,7	1,4	I
Çorum	52	16	9	15	2,8	0,2	1,2	1,4	III
Çukurova	50	21	10	11	3,1	0,1	2,3	1,1	I
Darica	56	23	8	7	2,1	0,2	1,5	1,1	II
Elaziğ	46	24	14	9	2,6	0,1	3,3	0,8	I
Eskişehir	50	21	12	10	2,6	0,1	2,1	1,4	I
Gaziantep	51	17	13	12	2,6	0,3	1,8	1,3	III
İzmir	62	13	11	7	2,0	0,1	2.6	1.0	III
Pinarhisar	21	46	15	7	2.9	0.5	4.8	212	IV
Sivas	44	27	11	10	3.0	0.4	1.5	1.3	I
Zeytinburnu	27	43	15	6	2.2	0.1	3.9	1.3	IV

§DSI Research Reports

TABLE I

The Clinker Composition of the Products of Ankara Cement Mill 1962 - 1966§

Production Years	% C_3S	% C_2S	% C_3A	% C_4AF	Closest Type
1962	42	36	4	14	II
1963	26	47	6	14	IV
1964	30	44	4	14	IV
1965	50	21	4	16	II
1966	29	43	3	16	IV

§DSI Research Reports

TABLE II

1.4 Purpose, Scope and Limitations

1.4.1 Purpose

Under the light of the preceding sections, the major purposes of the study were determined as follows:

1- The determination of the effects of certain additives, which are producable (obtainable) in Turkey, on the qualities, particularly on the resistance to sulfate attack, of ordinary cements.

2- The determination of the effect of sulfates on concretes made with ~~various~~ cements currently being produced in Turkey. More emphasis is attached to the first item, since the studies on various cements in Turkey were made previously by some other agencies; and it was revealed that their clinker composition showed no reliable consistency from one mill to another with time. Two cements only, were studied and compared under item two.

For the study of additives, four different materials were selected. The natural additives used are native of Turkey and the artificial ones are always obtainable, in Turkey.

1.4.2 Scope

The scope of the study covers the assessment of the resistance of the above mentioned cements and the effect of the additives to sulfate attack through the following tests and observations:

1- Dynamic Modulus Determinations by the sonometer;
2- Expansion Measurements by the length comparator;
3- Tensile and compressive strength tests;
4- Visual Examinations.

1.4.3 Limitations

Four different additives were chosen for this study: Kayseri pozzolana, Karabük blast furnace slag, Tunçbilek flyash, and ground brick. These additives were blended with an ordinary, widely used Turkish Portland Cement, namely, Eskihisar-Darica cement. Bartin cement, which is known to have blast furnace slag in its clinker, was compared with Eskihisar-Darica cement for its resistance to sulfate attack.

In these evaluations, certain statistical methods were employed. A statistical design of experiments was made, and accordingly the necessary specimens were prepared.

In testing the additives, the additive type and percentage, the concentration of the sulfate solution in which the specimens were stored, and the water-cement ratio of the specimens were chosen as the variables.

In testing the relative resistance of Bartin and Eskihisar cements, all factors were held constant while the type of cement was kept as the only variable.

CHAPTER II

THEORY

2.1 Historical Review

As early as 1908 in Canada there were reports of destructive action on concrete of salts present in ground water. Little was then known about the scientific design of concrete mixes, and the few cases of deterioration reported were usually ascribed to poor concrete. Ten years later, however, when expensive and well-designed structures in the area became affected, engineers became alarmed (3).

In Saskatoon, Canada, in 1919, Dr. C.J. Mackenzie of the Engineering Department of the University of Saskatchewan began some field exposure testing. Soon, the head of the Chemistry Department of the same university Dr. T. Thorvaldson became interested in the broader problem and started an investigation of his own. His basic plan was to study the action of alkali waters on the chemical components of portland cement. From the beginning of his work Dr. Thorvaldson recognized the need to develop a method for a more direct correlation of the chemical and microscopic results with the behaviour of concrete when exposed to sulfate solutions. In 1924 he began to use the mortar bar for length change measurements with time (3).

In the United States, in 1926 the portland Cement Association Fellowship at the National Bureau of Standards began an extensive investigation of the volume stability of 1:2 mortar bars made with pure compounds, cements prepared in a small experimental kiln, and commercial cements stored in water and in solutions of sulfates. The results of these studies were published in several papers and were summarized by Boque (11). Miller and Manson determined the sulfate resistance of 119 commercial cements when exposed as mortar bars in sulfate solutions in the laboratory and in the water of Medicine lake in South Dakota (12,13).

Miller and Manson also had these commercial cements analized completely and used the data to compare the resistance on the basis of the calculated compound compositions ofthe cements. In 1935, the Technical Committee on Cement, Lime, and Plaster of the U.S. Federal Executive Committee, under the leadership of P.H. Bater, Undertook the preparation and revisions of the then current specifications for normal portland cement; this included a new specification, namely, sulfate-resisting cement (14). In 1940, the portland Cement Association undertook an extensive investigation of the performance in the field of concrete in various types of structures and exposures (15).

In France, as early as 1812, L.J. Vicat began his experiments on destructive action of sea-water on concrete and published his first results in 1818 (16). It was first realized by Vicat that the chemical action of sea-water on concrete was mainly due to the presence of magnesium sulfate. W. Michaelis also carried out much pioneer work on the action of sea-water on cements in Germany (17). F. Ansett, with his well known sulfate resistance test, is one of the early European investigators studying the sulfate attack. The work of the Laboratoire des Ponts et Chaussees at Boulogne on concrete in sea-water commenced in 1886 and has continued over a long period of years. In reports published in 1922 and 1924-1925 Feret stated that in general the behaviour of the Portland cements was relatively bad, but that quite favorable results should be obtained from the addition of suitable pozzolanas, or by the use of cements containing granulated slag (5).

In 1929 a large series of tests were commenced in Great Britain. These tests also conformed with the above mentioned results.

From a partial review of the literature (18), it can be concluded that (a) no cement or concrete can be totally resistant to sulfate attack under all possible conditions; and (b) the degree of sulfate attack depends upon: (i) the type of cement used; (ii) the quality of concrete (iii) sulfate concentration in contact with the concrete; (iv) surface protection of concrete.

Research-work is still being done on sulfate attack, and there exist many points for investigation and explanation.

2.2 Effect of Sulfates on Portland Cement and Involving Mechanisms of Attack

2.2.1 Early Studies on Sulfate Resistance

When T. Thorvaldson started the Canadian studies on sulfate resistance, he prepared and studied the behaviours of the pure cement minerals in water and in solutions of calcium and magnesium and sodium sulfates, $CaSO_4$, $MgSO_4$ and Na_2SO_4. Thorvaldson, Vigfusson, and Larmour (19) studied mortar bars of the following compositions:

I. 1 part C_3S + 5 parts sand;
II. 1 part C_2S + 5 parts sand;
III. 1 part C_3S + 0.25 parts C_3A + 5 parts sand;
IV. 1 part C_2S + 0.25 parts C_3A + 5 parts sand;
V. 0.53 parts C_3S + 0.26 parts C_2S + 0.21 parts C_3A + 7.5 parts sand.

In 2 and 8 per cent solutions of Na_2SO_4, bars of I and II expanded no more than did similar bars stored in water. However, in solutions of $MgSO_4$ of about the same concentrations, bars of I and II expanded gradually. The incorporation of C_3A with the silicates, bars III, IV, and V, destroyed the high resistance to sulfate observed for bars of I and II. The increased rate of expansion was more marked for bars of III and V made with C_3S than for bars of IV made with C_2S.

Bars containing C_4AF and C_2F were later introduced into the series. The results with those bars showed that the subtitution of either C_4AF or C_2S for C_3A markedly increased the resistance of the bars to attack by solutions of $MgSO_4$. This is shown by the results for 1:10 mortars given in Table III, (pg. 12). No calcium sulfate was added to the pure compounds, as is the case with portland cement. It may be unsafe, therefore, to conclude that the behaviours of the compounds in these specimens might be identical with their behaviours in portland cements containing calcium sulfate.

In 1926 the Portland Cement Association Fellowship at the National Bureau of Standards began an extensive investigation of the volume stability of 1:2 mortar bars made with pure compounds, cements prepared in a small experimental kiln, and commercial cements stored in water and in solutions of sulfates. These studies differed from those of Thorvaldson and associates in that 1:2 mortars were used instead of the very lean mortars

Expansions and Tensile Strengths of 1:10 Mortar Bars in
0.15 Molar Magnesuim Sulfate Solutions§

Composition of cement per cent by weight								Expansion (percent)	Exposure (days)	Strength (psi)
C_3S	BC_2S	C_3A	C_5A_3	CA	C_3A_5	C_2F	C_4AF			
100								1.12	200	65
	100							1.26	200	38
50	50							1.05	325	42
80		20						4.86	26	low
80			20					4.69	26	low
80				20				6.27	10	very low
80					20			5.50	10	very low
80						20		1.48	200	48
80							20	2.04	160	bar firm
40	40	20						3.08	11	low
40	40		20					3.58	10	very low
40	40			20				3.00	45	fairly firm
40	40				20			3.32	16	low
40	40					20		1.11	450	86
40	40						20	+1.22	200	60
	80	20						3.05	35	fairly firm
	80		20					+2.10	210	60
	80			20				+0.85	300	81
	80				20				200	87
	8o					20				no test
	80						20	0.85	1100	no test

§Data from Thorvaldson, Wolochow, and Vigfusson (20)

TABLE III

used by the latter. Accordingly the expansion and deteriorations proceeded at slower rates(11).

One object of the study was to determine the effect of C_3S content when the C_3A and C_4AF contents were relatively constant. An increase from 40 to 50 per cent in the C_3S content appeared to have no significant effect upon the expansion. Another object was to determine the effect of increasing the C_4AF content at the expense of the C_2S content. The data show that this increase of C_4AF and decrease of C_2S increased the expansions.

The results of these and other studies clearly indicated that cement with relatively high resistance to sulfate could be prepared by increasing the F/A ratio of the clinker, either by decreasing the alumina content of the kiln feed or by adding additional iron-bearing material to it, both of which reduce the potential C_3A content of the clinker. European investigators also had reached the conclusion that C_3A was the least resistant of the cement minerals to attack by sulfates. Miller and Manson (12,13) determined the sulfate resistance of 119 commercial cements when exposed as mortar bars in sulfate solutions in the laboratory and in the water of Medicine Lake in South Dakota. As a result of the findings of Thorvaldson and others, Miller and Manson had their cements analized completely and used the data to compare the resistance on the basis of the calculated compound compositions of the cements. This showed a definite relationship between calculated C_3A content and sulfate resistance. They then arranged for 19 of the cement mills to modify the compositions of their kiln feeds so as to decrease the potential C_3A contents and to increase the potential C_4AF contents. These cements showed a resistance to sulfate much improved over that of the unmodified cements.

2.2.2 Calcium Sulfoaluminates and Solid-Liquid Reactions

According to Lerch, Ashton, and Bogue (21), Candlot appears to have been the first to establish the formation a definite compound by the interaction of aqueous solutions of calcium aluminates and calcium sulfate. A number of investigators restudied this system and confirmed the existence of such a compound. Lerch, Ashton and Bogue made a thorough study of the system and established the existence of two compounds: a high sulfate compound with the composition $C_3A \cdot 3CaSO_4 \cdot 31H_2O$ and a low sulfate coupound with the composition $C_3A \cdot CaSO_4 \cdot 12H_2O$. The high sulfate form occurs naturally and has been given the same ettringite. There is not complete agreement as to the water content of this compound, but it seems likely that the crystals in equilibrium with the mother liquor contain 32 moles instead of the 31 as reported by many investigators. Because of its formation in large quantities in concrete attacked by sulfates, this compound has been called "cement bacillus". Midgley and Rosaman (22) believe that the ettringite phase in hardened cement pastes may be a solid solution phase in which some sulfate ions are replaced by hydroxyl ions.

A number of investigators have attributed the deterioration of concrete in sulfate-bearing water to the formation of ettringite. It appears that most investigators have assumed that, since this highly hydrated salt occupies much more volume than the C_3A from which it fromed, its formation by a <u>through-solution</u> process in pores of the concrete would cause <u>expansion</u> and <u>destruction</u> of cement paste. According to Blondiau (23), however, Le Chatelier concluded that expansion was caused primarily by the reaction of the dissolved calcium sulfate with C_3A to produce solid ettringite in situ. That is, in this reaction the C_3A does not dissolve in the water but reacts directly with ions of calcium sulfate and water to yield a solid product. Such reactions have been referred to as <u>solid-liqued</u> and <u>topochemical</u> reactions and have been discussed in some detail (24). Apparently Le Chatelier also believed that hydrated aluminates, such as C_4A.aq. and C_3A.aq., could also undergo this solid-liquid reaction because he decided that the most effective test procedure for determining the sulfate resistance of a cement would be to measure expansions of specimens prepared from fully reacted pastes.

Those who support the solid-liquid reaction, and there appears to be an ever encreasing number, probably accept the principle that a crystal cannot enter the solution phase as ions or molecules, without first reacting with the solvent in a manner that overcomes the energy by which the atoms or ions in the crystal are bonded to one another. Van Arkel (25) has discussed this process in some detail for the dissolution of NaBr, which forms the hydrate $NaBr.H_2O$. According to Van Arkil, NaBr dissolves complętely in an excess of water but forms $NaBr.H_2O$ in a limited amount of water. When a crystal of NaBr is exposed to water, the first water molecules are taken up in a regular manner in the lattice of the crystal and surround the positive ions. When additional molecules of water are taken up, the ions are loosened from the structure and each ion goes into solution with its portion of the water molecules attached to it. This take-up of water furnishes the energy required to break the ionic bonds in the crystal and thus allow the dissolution of the crystal. It seems evident from this mechanism that relatively insoluble compounds should form as solids on the surfaces of the reacting crystals at higher rates than those at which they can dissolve. If the reacting crystals are in contact with one another, except possibly for a thin layer of adsorbed water, this formation of the reaction product as a solid on the surface could cause the crystals to exert pressure against each other and, in a rigid paste, cause it to expand.

Chatterji and Jeffery (26), suggest that conversion of C_4AH_{13} to the low sulfate sulfoaluminate might be a solid-state reaction, which could cause expansion in concrete. They point out that the crystal structure of C_4AH_{13} is such that sulfate ions can replace two hydroxyl ions, by an ion exchange, as illustrated in the following equation:

$$\underset{277.37}{C_4AH_{13}} + SO_4^{2-} + \text{water} = \underset{313.68}{C_3A.CaSO_4.H_{12}} + 2(OH^-)$$

The numbers 277.37 and 313.68 are the volumes of the two solids which show that the volume of the solid phase increases about 14 per cent if this reaction occurs. There appears to be no reason why this reaction should not occur as a solid-liquid reaction if the compound C_4AH_{13} is present as a component of the hardenend cement paste and sulfate ions diffuse into the paste.

It was pointed out in 1952 (27) that certain surface reactions explained why portland cement products continued to expand over long periods of time when stored in water. Later (28) an attempt was made to show by means of an idealized model that these expansions should never be very large and accordingly, should not destroy the cement paste.

Gonnerman, Lerch, and Whiteside (3) gave expansions for neat cement specimens of 418 commercial cements stored in water for 15 years. All of the cements passed ASTM pat test for soundness. The range of expansions for the 15-year period was 0.0095 to 0.379 per cent.

When C_3A combines with water an $CaSO_4$ to form ettringite, 1 volume of C_3A yields 8.2 volumes of reaction product.

2.2.3 Through-solution Reactions

Burke and Pinckney (29) were among the early investigators of the causes of the deterioration of concrete in sulfate waters. They treated powdered hardened cement pastes with water and solutions of sulfates and from the results of chemical analyses of the filtrates and residues concluded that the reactions causing deterioration were double decomposition reactions as illustrated by the following equations:

$$Ca(OH)_2 + MgSO_4 + 2H_2O = CaSO_4.2H_2O + Mg(OH)_2$$

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O = CaSO_4.2H_2O + 2NaOH$$

They calculated that on volume of $Ca(OH)_2$ yielded 3.13 volumes of $CaSO_4.2H_2O + Mg(OH)_2$. On the assumption that the reaction products tended to be deposited in the space occupied by the $Ca(OH)_2$, they concluded that this increase in space required by the reaction products was responsible for the disruption of the cement paste, causing the specimens to bulge, crack, and crumble. This might be true if the solid $Ca(OH)_2$ reacted as a solid with dissolved sulfate and water to yield the reaction products. However, this cannot be true if the $Ca(OH)_2$ dissolves and reacts with dissolved sulfate and water. One theory appears to be that sodium sulfate, for example, diffuses into a pore in the hardened paste and there reacts with $Ca(OH)_2$ as the latter dissolves to form gypsum which occupies a greater volume than the $Ca(OH)_2$ because on mole of $Ca(OH)_2$ occupies a volume of 31.6 cc compared with 74.2 cc for one mole of $CaSO_4.2H_2O$.

It seems that concrete cannot be caused to expand and crack by the simple mechanism of filling pores with solids by a through-solution process. This can be demonstrated with some volumetric calculations(30). After a while, it appears that the reactions will stop for lack of water before any expansion occurs. This result will be the same for a pore of any size. The double decomposition reactions of equations 1 and 2 can destroy concrete by dissolving the cementing phases and precipitating noncementing phases such as $Mg(OH)_2$. Later a mechanism will be described to explain the expansion of concrete caused by the formation $Mg(OH)_2$.

Results by Thorvaldson, Wolochow, and Vigfusson (20) demonstrated the inability of the crystallization of gypsum in mortar bars to cause expansions and disintegration of mortar bars made with calcium silicates as the cements.

The authors point out the possibility of the strengths having been affected because microscopical examination of the bars showed the presence of large quantities of gypsum. It seems, however, that their results indicate that Na_2SO_4 reacted with $Ca(OH)_2$ and converted the latter into gypsum without causing expansions of the specimens. On the other hand, the data indicate that the reaction of $MgSO_4$ with $Ca(OH)_2$ caused large expansions of the bars made with calcium silicates in relatively short periods of time. The strength tests showed that the strengths were not harmed by the crystallization of gypaum in the specimens. It appeared from such data that the C_3S content of a sulfate-resisting cement should be as low as is consistent with satisfactory strength, and the first U.S. specification for such a cement (14) placed a limit on the SiO_2 content which was equivalent to placing a maximum limit on the C_3S content.

With respect to strength, Miller and Manson (13) pointed out that strengths were not satisfactory as measures of the deterioration because in many cases compressive strengths of cubes stored in sulfate solutions were higher than those of cubes stored in water. In other words, precipitation of salts in the hardened cement paste seemed to augment the strength. Nevertheless tensile strength reflects the deterioration.

2.2.4 Crystal Growth as a Source of Expansion

Portland cement concrete or mortar, if porous enough, could be disintigrated by the mechanical force exerted by the crystallization of almost any salt in its pores. This type of disintegration is seen in such places as the area immediately above the waterline on concrete structures which are partially immersed in salt-bearing water or soils and on the surfaces of dams, retaining walls, and so forth from which water is evaporating as it migrates through the concrete(31)

With a diagram, Taber (32) explained the action of crystallization and resulting distruption. He concluded from his work that a crystal will grow in the direction in which external forces oppose growth if the surfaces on which the forces are acting are in contact with a solution that is supersaturated with respect to it, and if the growing crystal is composed of a substance the solubility of which increases with pressure. Then for any increase in the forces opposing growth a corresponding increase in the concentration of the solution is necessary.

Taber also studied the behaviour of water and solutions in porous materials and found that solutions in subcapillary pores are not readily nucleated.

Suppose that the concrete depicted in Figure 1 (pg.18), is partially immersed in and is saturated with a solution of a salt at a given temperature. If water evaporates from the surface of the structure, crystals will form in the larger pores A and D but will not form in the smaller pores B and E. This crystallization of salt in pores A and D reduces the concentration of salt below that in pores B and E. Solute molecules or ions will diffuse from the solutions in the smaller pores into the larger pores and the crystals in the larger pores will grow. As pores A and D become filled with crystals, the crystals, because of their weight, will exert pressure on one another, will dissolve at the interfaces, and grow at other faces. This will cause then to grow into a single crystal, the bottom face of which is in contact with the solution in the smaller pore. If the larger pore is open, as depicted for A in Figure 1 below, solute molecules adding onto the bottom of the crystal will cause the crystal to grow above the surface as was observed by Griffin and Henry(33).

If the larger pore is connected to the surface by a smaller pore C, as depicted for pore D, the growing crystal, being unable to grow into pore C, will exert pressure on the bottom shoulders of pore C. If the pressure is sufficient to overcome the tensile strength of the concrete, the concrete immediately surrounding pore C will spall from the surface of the structure. If the concrete does not spall, the pressure exerted against the shoulders of pore C can cause the concrete to expand and crack.

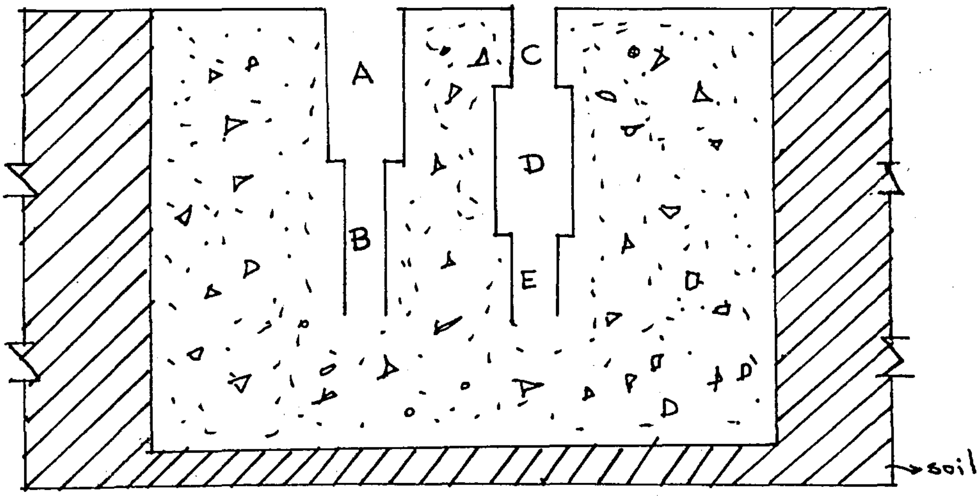


FIGURE 1. Diagram depicting a section through a concrete slab containing large pores A and D and smaller pores B, C, and E.

2.2.5 Reactions of Magnesium Ion with Hardened Cement Paste

As pointed out earlier, Thorvaldson, Wolochow, and Vigfusson (20) found that mortars made from C_3S and C_2S, as the cements, expanded in solutions of $MgSO_4$. This indicated that the chemical composition of the solid particles of the hardened cement paste probably plays little part, if any, in the expansion of cement products by magnesium ion. The liquid phase in a gel pore is saturated with respect to $Ca(OH)_2$. When magnesium ion diffuses into this solution it will, because of the very low solubility of $Mg(OH)_2$ cause the precipitation of $Mg(OH)_2$ in accordance with the following equation:

$$Ca(OH)_2 + MgSO4 = Mg(OH)_2 + CaSO_4.$$

Also because of its low solubility, $Mg(OH)_2$ precipitates as extremely fine or colloidal particles. As already pointed out, the water in the gel pores, shells of adsorbed water, is in equilibrium with the surface forces of the colloidal reaction products. Precipitation of colloidal $Mg(OH)_2$ in the gel pore introduces new surface forces that upset this equilibrium, In order to re-establish equilibrium between the surface forces and water, additional water will be drawn into the gel pore. This can be accomplished only by enlargement of the pore by "osmotic pressure".

Thorvaldson, Wolochow, and Vigfusson found that specimens made with mixtures of C_3S and C_2S containing various amounts of calcium aluminates behaved differently in solutions of Na_2SO_4 than they did in solutions of $MgSO_4$. Bars exposed to Na_2SO_4 shed their surfaces continuously with the hard cores expanding as much as 2 per cent before they fell to pieces. In $MgSO_4$, the bars did not crumble but retained their shape and remained fairly firm until they reached a very high expansion. This indicates that sulfate and magnesium ions produce expansions by different mechanisms. However, in the case of $MgSO_4$ both mechanisms are operating, whereas in the case of Na_2SO_4 only the sulfate ion is producing expansion. It must be recognized also that bars made with the pure minerals did not contain sulfate as portland cement does.

In exposure to sea-water, Bryant Mather (34) summarizes the chemical reactions involved in the attack on concrete by magnesium sulfate as follows:

(a) The magnesium sulfate reacts with hydrated C_3A:

$2(3CaO.Al_2O_3.12H_2O) + 3(MgSO_4.7H_2O) =$

calcium aluminate hydrate — magnesium sulfate

$3CaO.Al_2O_3.3CaSO_4.31H_2O + 2Al(OH)_2 + 3Mg(OH)_2 + 8H_2O$

calcium aluminum sulfate hydrate (ettringite) — aluminum hydroxide — magnesium hydroxide

(b) The magnesium sulfate also reacts with calcium hydroxide:

$Ca(OH)_2 + MgSO_4.7H_2O = CaSO_4.2H_2O + Mg(OH)_2 + 5H_2O$

calcium hydroxide — calcium sulfate (gypsum)

(c) The gypsum formed in (b) or (d) also reacts with hydrated C_3A:

$3CaO.Al_2O_3.12H_2O + 3(CaSO_4.2H_2O) + 13H_2O =$

$3CaO.Al_2O_3.3CaSO_4.31H_2O$

(d) The magnesium sulfate also reacts with calcium silicate hydrate:

$3CaO.2SiO_2.nH_2O + 3MgSO_4.7H_2O + 3CaSO_4.2H_2O + 3Mg(OH)_2 =$

calcium silicate hydrate

$2SiO_2,nH_2O + 12H_2O$

silica gel

(e) The magnesium hydroxide formed in (a) or (b) reacts with the silica gel formed in (d):

$4Mg(OH)_2 + SiO_2.nH_2O = 4MgO.SiO_2.8.5H_2O + n-4.5\ O_2$

magnesium silicate hydrate

Hansen and Offutt (35) have shown the following reactions of C_3A, calcium sulfate (gypsum), and water, depending on which form os calcium aluminum sulfate hydrate is formed:

$3CaO.Al_2O_3 + 3CaSO_4.2H_2O + 25H_2O = 3CaO.Al_2O_3.3CaSO_4.31H_2O$
88.8 222.3 450 714.7 (46.4)
1 8

$3CaO.Al_2O_3, + CaSO_4.2H_2O + 10\ H_2O = 3CaO.Al_2O_3.CaSO_4.31H_2O$
88.8 74.1 180.0 319.6 (23.3)
1 3.6

The numbers in the first line below the equations are participating volumes. The number in parenthese at the right is the volume added to that on the right side of the equation to make its volume equal to the sum of those on the left; thus both of these reactions involve a net reduction in volume of the reactants. The second line of numbers compares the relative volume of anhydrous C_3A and the volume of calcium aluminum sulfate formed from it by sulfate reaction. In one case, the increase in volume is eightfold; in the other nearly fourfold.

In sulfate attack on concrete in sea-water, the sulfate is predominantly magnesium sulfate in a solution that contains such more chloride ion than sulfate ion. Lea (4) has suggested that the presence of the chlorides retards or inhibits the expansion of the concrete by sulfate attack but does not reduce the degree of reaction. He cited work attributing this effect to increased solubility of calcium sulfate and calcium aluminate sulfate in chloride solution.

Lea and Desch (4) give the equations for the chemical reactions anticipated to take place in the cement paste on the sulfate attack as follows: With Na_2SO_4, for example,

(i) $Ca(OH)_2 + Na_2SO_4 . 10H_2O = CaSO_4 . 2H_2O + 2NaOH + 8H_2O$

(ii) $3CaO.Al_2O_3.12H_2O + 3(CaSO_4.2H_2O) + 13H_2O = 3CaO.Al_2O_3.3CaSO_4.31H_2O$

(iii) $2(3CaO.Al_2O_3.12H_2O) + 3(Na_2SO_4.10H_2O) = 3CaO.Al_2O_3.3CaSO_4.31H_2O + 2Al(OH)_3 + 6NaOH + 17H_2O$

With calcium sulfate only reaction (ii) occurs. In Equation (i) $CaSO_4 . 2H_2O$ is the gypsum cristal. Magnesium sulfate has a more far reaching action than other sulfates. It both decomposes hydrated calcium silicates in addition to reacting with the aluminates and calcium hydroxide.

(iv) $3CaO.2SiO_2.aq. + MgSO4 . 7H_2O = CaSO_4.2H_2O + Mg(OH)_2 + SiO_2.aq.$

As seen from the equation (i) the sulfate salt first changes the hydrated lime of the concrete to gypsum. This causes what is so called "Gypsum Swelling". And the gypsum produced reacts with the lime aluminate of the concrete producing the so called "Calcium sulfoaluminate" which crytallizes with 30 molecules of water.

Michaelis (36) has anticipated the formula of calcium sulfoaluminate as follows: $Al_2O_3 + 3CaO + 3CaSO_4 + 30\ H_2O$

As seen from this formula, this crystal has much more crystal water in its content and i.e. greater volume. Thus causes considerable crystallization pressure.

During the hardening of cement hydrated lime is freed in large quantities and this enables the formation of soluble aluminates.

Van Aardt (37) explains the influence of equilibrium condition on the nature of hydrated cement compounds: "When anhydrous cement compounds are brought into contact with water, reaction and decomposition take place with the formation of hydrates. Super satured and unstable solutions are formed which slowly tend to equilibrium. However, when the mass sets and hardens the mobility of ions is reduced and attainment of equilibrium is very slow. When anhydrous aluminates react with water, metastable equilibrium conditions prevail and plate like metastable aluminate hydrates are formed. On prolonged storage under appropriate conditions, the metastable compounds alter to stable materials. It is conceivable that stable and metastable compounds will react differently in an aggressive environment.

The reaction of hydrated cement compounds with varous chemical media is of considerable importance with respect to corrosion of hydraulic cement, but since many of compounds are metastable, and their formation depends on the conditions of hydration, it is difficult to predict with absolute certainly the behaviour of cement of known composition for different conditions of use". The action of sulfates on cement compounds is dependent not only on the compound composition but also on the type of sulfate. Also the speed and nature of reaction is modified by the physical state of the cement product. Although the alumina content of a cement is of considerable importance the state of equilibrium after hardening with respect to $C_3A.3CaSO_4.3H_2O$ will influence vulnerability to sulfate ions. On the other hand, it has been shown that the cations in the solution have a marked influence on the nature and speed of reaction during attack by sulfate.

Distruption occurs if substances are present which can yield $CaSO_4.2H_2O$ and $C_3A.CaSO_4.32H_2O$ at a <u>rapid rate</u>.

2.3 Protection Against Sulfate Attack and Sulfate Resisting Cements

2.3.1. By controlling the composition of the cement clinker

At present, the principal approach to the production of sulfate-resisting concrete is to limit the allowable tricalcium aluminate (C_3A) content of the cement to progressively lower limits as the sulfate concentrations that are expected to come into contact with the concrete in service increase. The Corps of Engineers and the U.S Bureau of Reclamation, for example, require (38,39) that, where sulfate concentrations exceed 0.20 per cent as water-soluble SO_4 in soil or 1000 ppm as SO_4 in water Type V (sulfate-resisting) cement will be used; where concentrations are in the range 0.10 to 0.20 per cent in soil or 150 to 1000 ppm in water, Type II portland cement or Type IS (MS) portland blast-furnace slag cement will be used, Where the concentrations are lower than 0.10 per cent in soil or 150 ppm in water, no special precautions are needed. So far as is known, no significant deterioration of concrete due to sulfate attack has been encountered when these precautions have been taken and the estimated sulfate contents have not been sigficantly exceeded.

In 1966 the British Standards Institution issued a specification for sulfate-resisting portland cement in which it is stated that "a considerable degree of sulfate resistance is conferred on portland cement if the tricalcium aluminate is limited to 3 1/2 per cent". This may be compared with the limits of 5 and 8 per cent respectively on Type V and Type II in specifications used in the United States.

The limitation on C_3A content of cement involves a calculation of C_3A content based on the results of chemical analysis using the formula:

$$\text{Per cent } C_3A = 2.650 \times \text{per cent } Al_2O_3 - 1.692 \times \text{per cent } Fe_2O_3.$$

2.3.1.1 Tricalcium Aluminate and Tetra Calcium Alumino Ferrite Content (C_3A and C_4AF)

In many localities Type V portland cement containing 5 per cent or less C_3A calculated from chemical analysis is not readily available. The question has been asked whether some cements which, upon chemical analysis, yield values for percentages of Al_2O_3 and Fe_2O_3 that cause the calculated C_3A to exceed 5 per cent, might not be as sulfate-resistant as others whose calculated C_3A content is 5 per cent, or less, because of possible incorporation of some of the Al_2O_3 in constituents of the cement other than C_3A, in ways not contemplated by the phase equilibria relations upon which the calculations are based. In 1956 a sample of cement was received for study from the U.S. Army Engineer District, Los Angeles. An attempt was made to compare its C_3A content estimated from X-ray diffraction data with that of other cements that had been studied by the light microscope, chemical analysis, and X-ray diffraction (40).

The cement submitted for test did not have a peak at 2.70A that was well enough developed to scale; it had 3.9 percent Al_2O_3 and 2.6 per cent Fe_2O_3 and hence 6 per cent calculated C_3A. It was concluded that, had it been examined as clinker by microscope methods, it would have been found to contain less than 5 per cent C_3A. It was assumed that the 5 per cent limit on C_3A applicable to Type V cements was intended to refer to C_3A that could, under optimum conditions of crystallization of the cement clinker, be found by microscope examination. The potential sulfate resisting qualities of this cement were therefore expected to meet the requirements of the specification for Type V cement.

Miller and Manson (41) set the extreme upper limit of C_3A permissible for a cement of high sulfate resistance as 5.5 %.
Most resistant is 4.4 %, least resistant is 11.9%. "Although there are exceptions 5.4% C_3A seems to be optimum." Among the factors known to affect both the sulfate resistance and the amount of C_3A and C_4AF in the clinker is the glass content. Bogue (11) concluded that "Crystalline C_3A is less resistant to sulfate attack than a glass rich in C_3A, but crystalline C_4AF is more resistant than a glass rich in C_4AF and the the proportion of C_4AF should not exceed 15% and that glasses of low A:F ratio are more resistant to sulfate action than those of higher A:F ratio". Crystalline C_4AF is vulnerable to sulfate action although much more resistant than crystalline C_3A.

2.3.1.2 Tricalcium Silicate and ß-Dicalcium Silicate Content (C_3S and ß-C_2S)

Davis, Hanna and Brown (42) reported that "Portland Cements having the same C_3A content, the lower the C_3S content, the greater the resistance of the cement to the action of Sodium Sulfate solutions". The storage of mortars made with pure C_3S and β-C_2S in sulfate solution indicated complete immunity to the action of solutions of sodium sulfate and calcium sulfate. But after long exposures (18years) it becomes evident that they are vulnurable.

2.3.1.3 Calcium Oxide (free) (CaO) and Magnesium Oxide (MgO)

CaO should not be present in cement in appreciable amounts. MgO as crystals of periclase may cause serious expansion.

As shown in Table IV, the C_3A and C_4AF are both relatively low in cement Type V, the sum of the aluminates being lower than for any of the other types. This combination of low C_3A and C_4AF and accompanying high C_3S and C_2S produces a cement having exceptional resistance to sulfate attack in comparison with other tqpes of cement. Type II cement can be considered next to Type V in sulfate resistance.

ASTM Classification of Portland Cements§

Cement Type	Mineralogic Composition of clinker, as percent.							
	C_3S	C_2S	C_3A	C_4AF	$CaSO_4$	Free CaO	MgO	Loss on Ignition
Type I	49	25	12	8	2.9	0.8	2.4	1.2
Type II	46	29	6	12	2.8	0.6	3.0	1.0
Type III	56	15	12	8	3.9	1.3	2.6	1.9
Type IV	30	46	5	13	2.9	0.3	2.7	1.0
Type V	43	36	4	12	2.7	0.4	1.6	1.0

§Concrete Manual, Bur. Reclamations, 7th ed. 1966.

TABLE IV

2.3.2 By the Use of Pozzolanas

Before it was discovered that cements with high resistance to attack by sulfates could be produced by controlling the composition of the cement clinker, considerable effort was made to find a pozzolana that could be used with any portland cement to increase the resistance to attack by sulfate (43). The results of these studies usually shoved that some pozzolanas increased significantly the sulfate resistance without them, but had little, if any, effect with cements that showed relatively high resistance. In some cases, pozzolanas had an adverse effect(44)

The theory upon which these investigators were working was that uncombined $Ca(OH)_2$ produced during the reaction of the cement with water would combine with silica and alumina of pozzolanas to produce colloidal hydrated calcium silicates and aluminates similar to the reaction products of cement with water. It was believed that: (a) uncombined $Ca(OH)_2$ had no cementing properties and could, by reaction with a pozzolana, be converted to products with cementing properties; (b) uncombined $Ca(OH)_2$ was more readily dissolved and, therefore, more readily leached from the concrete than was the combined $Ca(OH)_2$ from the reaction products-a higly questionable assumption; and (c) the colloidal products produced by the reaction of $Ca(OH)_2$ with pozzolanas would decrease the porosity of the hardened cement paste.

In a relatively recent study, Polivka and Brown (45) found, in tests in which 25 per cent of the cementin ingredient was a pozzolana, that no improvement in the sulfate resistance of the cement in which the calculated C_3A and C_4AF contents were 11.7 and 8.2 per cent, respectively, the sulfate resistance of the cement was improved by the pozzolanas but did not approach that of the cement with the low C_3A content.

Since crystals of $Ca(OH)_2$ can be readily identified microscopically in hardened cement pastes, it has generally been assumed that all of the free $Ca(OH)_2$ is present as relatively large crystals. Such crystals having low specific surfaces compared with those of the colloidal reaction products, would have inferior cementing properties. Brunauer, Kantro, and Copeland (46), however, from x-ray diffraction analysis of the reaction of C_2S and C_3S with water, concluded that significant amounts of the $Ca(OH)_2$ released when these compounds react when water is present in an amorphous form. In the mechanism previously described for the reaction of cement with water, it seems logical to expect that much of the $Ca(OH)_2$ released during this reaction would remain in the hardened paste as colloidal and possibly amorphous crystallites. These might have relatively good cementing properties. The well-formed and relatively large crystals of $Ca(OH)_2$ found in the cement paste were certainly formed by the dissolution and recrystallization of such crystallites.

Most, if not all, of the reaction products in a hardened cement paste decompose in water and liberate $Ca(OH)_2$ to the solution. The rate of liberation of $Ca(OH)_2$ by these products probably is about as rapid as the rate of dissolution of $Ca(OH)_2$ crystals. Hence from the standpoint of the rate of leaching of $Ca(OH)_2$ from concrete products, the absence of crystalline $Ca(OH)_2$ in the hardened paste probably would not significantly affect this rate.

It is possible to make calculations (22) that qualitatively show whether one could expect the use of pozzolana with portland cement to decrease the porosity.

It appears that for the same water-cement ratio, the porosity of the portland-pozzolana cement concrete made with a highly siliceous pozzolana would be somewhat greater than that of a concrete made with the portland cement. On the other hand, these calculations indicate that the use of pozzolanas containing both alumina and silica might reduce the porosity of the concrete.

Malquori points out that it has been repeatedly stated that pozzolanic cements do not possess any intrinsic, specific, chemical resistance to attack by sulfates because the alumina of the pozzolanic materials is found in the hardened cement paste in the form of potentially vulnerable calcium aluminates. It is true that ettringite forms only in solutions saturated with respect to $Ca(OH)_2$ and that pozzolanas are supposed to combine with the free $Ca(OH)_2$ of the cement paste. It seems likely, however, that the $Ca(OH)_2$ concentration of the liquid phase of portland-pozzolana cement concrete will be that of a saturated solution and sufficient for the formation of ettringite. Eitel (47) discusses the formation of ettringite in lime-pozzolanic mortars containing gypsum. It appears from this brief review that the sulfate resistance of a cement that will meet ASTM specifications for a sulfate-resistant cement will not be improved by the use of a pozzolana with it and that it might be harmed because of either increased porosity or the presence of aluminate phases that can react with sulfate.

Turriyiani, Rio and Co-workers (22-48) showed that for any given clinker, including ones high in C_3A, high resistance to attack by calcium sulfate could be obtained by selecting a suitable mixture of pozzolanas and especially by employing one of sufficiently high silica content.

The effect of the pozzolana is mainly related to the amount of tobermorite gel which is formed from it by reaction with the lime liberated from the cement; the results appear to support Lea's suggestion (4) that the enhanced resistance is partly caused by formation of a protective film of this product.

Evidence was also obtained that ettringite is less stable when excess silica is present. If ettringite is treated with high-silica pozzolanas in aqueous solution, it hydrolizes almost completly; at a pozzolana ettringite weight ratio of 20 the decomposition occurs within a few minutes. Hydrolysis occurs most effectively in water but also proceeds in saturated gypsum solution, when a very stable, supersaturated solution results. It is largely prevented in saturated lime water. The reaction is very dependent on the reactivity of the pozzolana and the fineness of grinding, The lowered stability of ettringite may therefore be an additional reason for the enhanced calcium sulfate resistance of pozzolanic cements.

This shows that pozzolanic cements have potentially a wide technological application with cements of high C_3A percentages.

Expansion of Cement Mortars in Sulfate Solution[§]

Cement			Time in weeks to expand 0.1 %	
Percent Portland Cem.	Percent Pozzolana	Pozzolana	5% Na_2SO_4	5% $MgSO_4$
100	0	None	18	10
80	20	Burnt Clay	52	20
60	40	" "	200	220
60	40	Burnt shale	200	200
80	20	Trass	50	14
60	40	"	200	170
60	40	Ground sand	22	9
60	40	Ground brick	44	21

[§] Lea and Desch, Chem. of Cement

1:3 Cement: Standard sand Mortars W/C about 0.5. Immersed in sulfate solution at 18 at 7 days old.

TABLE V

Data such as these are only relative and in fact tests on mortars tend to overestimate the benefit gained in concrete, but they nevertheless illustrate the increased chemical resistance obtained with pozzolanas in concrete, a substitution of 30 to 40 % Pozzolana will considerably increase the resistance to 5% sodium sulfate and to 0.5 % magnesium sulfate solutions, but is less effective against 5 % magnesium sulfate.

Parker (49) reported that cements high in glass showed the greatest response to pozzolanas in increased sulfate resistance. The increased resistance to sulfate and sea-water attack obtained by the addition of pozzolanas has long been the subject of discussion. Although in part it is attributable to removal of the free calcium hydroxide, formed in the hydration of Portland cements, by combination with the pozzolana. This however, cannot be the sole explanation and many theories were advanced on the subject, as presented in the preceding paragraphs.

The other advantages secured by the addition of pozzolanas in optimum proportions to Portland cements.

1) Smaller temperature rise and thermal volume change in massive structures.
2) Saving in cement cost.
3) Lessens also the permeability.
4) Improved workability in lean mixes used in mass concrete.
5) Reduced bleeding and segregation.
6) Reduced Alkali-Aggregate reaction.

2.3.3. By the Use of Slag Cements

The sulfate resistance of blended cements has not been studied to the extent of that of portland cements, even though reports have been available in increasing numbers for over 100 years that indicate that most of the materials used together with portland cement clinker to produce blended cements have themselves been used as admixtures to improve the sulfate resistance of concrete. In an investigation of portland blast-furnace slag cements, it was found (50) that, when tested according to the procedure by which mortar bars are made with added sulfate and observed for length change during water storage, the indicated sulfate resistance appeared to be primarily influenced by the calculated C_3A content of the portland cement clinker constituent of the blended cement.

Since the products of hydration of portland, portland blast-furnace and supersulfate cements are very similar, differences in their behaviour towards aggressive chemicals arise principally from the differing amounts of the various hydrates which are formed during setting and hardening, and especially from the differing amounts of $Ca(OH)_2$.

The incorporation of slag with portland cement increases the resistance to decomposition by sulfates. With up to 50 % of slag the effect is very slight, but thereafter resistance increases rapidly with slag content. Too great a fineness has an adverse effect on sulfate resistance. The chemical resistance of blast-furnace type cements is, of course, markedly dependent on the C_3A content of the Portland component. Supersulfate cement resists sulfates well because of the absence of $Ca(OH)_2$ in the set cement and because of the combination of much of the alumina as ettringite. It is attacked by strong solutions of $MgSO_4$ and $(NH_4)_2SO_4$ but resists sea-water.

There are no good data comparing the behaviour of slag cements with that of sulfate-resisting Portland cements of very low or zero C_3A content from the constitutions of the set cements, it would be expected that, in the absence of ions such as Mg^{2+} or NH_4^+ which can remove OH^- from solution, sulfate solutions would attack the $Ca(OH)_2$ in the Portland cement (56):

$$Ca(OH)_2 + SO_4^{2-} + 2H_2O = CaSO_4.2H_2O + 2OH^-$$

They would be expected to have relatively little effect on the slag cements, as these contain little or no $Ca(OH)_2$. If Mg^{2+} or NH_4^+ was also present, both slag and Portland cements should be attacked to comparable extents, because these ions lower the pH and thus permit the SO_4^{2-} to attack the tobermorite gel. With long periods of exposure to such solutions, ettringite can also be attacked (56):

$$C_3A.3CaSO_4.32H_2O + 3SO_4^{2-} + 6H^+ = 6CaSO_4.2H_2O + 2Al(OH)_3 + 20\ H_2O$$

Ettringite is present in hydrated Portland cements as a product of reactions involving the gypsum added in manufacture, or as a result of initial attack by sulfate. In supersulfate cement, it is a normal product of the early setting reactions.

Various cements have been compared in their resistance to sea-water by Campus (51); all the slag cement concretes were performing well after 20 years. The chemical resistance of supersulfate cement has been studied extensively by Blodiau (52).

2.3.4 High Alumina Cement

This is a cement characterized by its dark color, high early strength, high heat of hydration and resistance to chemical attack.
Its composition roughly is:

40 % lime
10 % silica
40 % alumina
10 % ferric oxide

It has, under ordinary temperature conditions, a resistance to attack by sulfate and sea-water unequalled by any other constructional cement.

The high resistance of aluminous cement concretes to the action of sulfate solutions is again most probably due to the protective action of alumina gel and possibly also of iron-containing gels. The absence of calcium hydroxide from the hardened concrete may be a small contributory factor, particularly in the case of ammonium and magnesium sulfates, but it cannot be a major direct reason. However, it has been suggested (53) that the absence of excess $Ca(OH)_2$ allows sufficient alumina to dissolve and react in solution with the sulfate, whereas the lowered solubility of alumina resulting from the presence of $Ca(OH)_2$ would force the sulfate to react with the solid calcium aluminates, thus producing expansion.

The resistance of the various forms of cements to sulfate attack in increasing order can be listed as follows:

(1) Ordinary and rapid hardening Portland cement.
(2) Blast furnace and low heat Portland cements.
(3) Sulfate resisting and Pozzolanic cements.
(4) Super sulfated cement.
(5) High alumina cement.

2.3.5 By Improving the Physical Conditions of Concrete

Resistance to disintegration of the second type-that is by crystal growth- is best obtained by use of a dense, impervious concrete of relatively low water-cement ratio (less than 0.56; never more than 0.60) and preferably containing entrained air.

Curing conditions also have an influence on behaviour of cement products in aggressive media. High pressure steam curing has an advantageous effect against sulfate attack. Lea (4) gives optimum conditions for steam curing as 6 hours, 175°F, 120 lb/in^2. Blair and Chi-Sun Yang (54) sum up the factors contributing to the superior stability of autoclave-cured Portland cement products as follows:

1) Elimination of free calcium hydroxide,
2) Formation of a better crystallized calcium silicate hydrate,
3) Elimination of small amounts of hydrated sulfoaluminates,
4) The probable elimination of C_3AH_6 as indicated by the fact that it is not detectable by X-ray analysis.

Humid atmosphere curing is better than underwater curing. Van Aardt (37) reports that carbonation of cement products during and after curing improves their behaviour in aggressive media. Only early carbonation has an adverse effect on the quality of super sulfated slag cements.

After all, the nature and type of aggregate has an influence on corrosion resistance of cement products. It appears that not only does the acid soluble aggregate "protect" the cement in that it aids in neutralizing the acid, but it also has a retarding effect on the expansion resulting from sulfate attack in acid solutions; the carbon dioxide produced when the acid reacts with carbonate aggregate apparently reduces the formation of Tri-calcium sulfoaluminate(37).

It is possible to use some special purpose cements instead of Portland cements in structures exposed to sulfate action in order to improve their sulfate resistance, if other properties of these cements also prove suitable for the case.

CHAPTER III

EXPERIMENTAL DESIGN, PROCEDURE AND APPARATUS

3.1 Variables

Under the light of the discussion presented in previous sections the major variables controlling the sulfate attack may be summarized as follows:

1- The type and compositon of cement to be used.

2- The type and percentage of additive to be blended.

3- The type and concentration of sulfate solution with which the specimens come into contact.

4- The physical qualities of concrete, i.e. its density, porosity and permeability as a result of mixing proportions, namely water-cement ratio and aggregate-cement ratio.

5- Curing conditions and Temperature.

6- Manner of exposure to sulfate solutions (e.g. manner of immersion, continious flow of solution, etc...)

7- Time element.

According to the purpose and scope stated in Chapter I, only some of these variables and their effects on the resistance of concrete to sulfate attack were covered and studied.

More emphasis was paid to the effect and usability of various additives obtainable or producable in this country. As to the type and compositional effects of cements on sulfate resistance, only two of Turkish portland cements were selected and compared, namely Bartin and Eskihisar-Darica cements; holding every variable constant except their compositions.

Four different types of additives were selected:

a) Kayseri pozzolana

b) Tunçbilek fly-ash

c) Karabük blastfurnace slag

d) Ground brick

The percentage of blending these additives with the base cement (common to all additives) was taken as another variable, in increasing order as, 10, 20, 30 and 40 percents.

The specimens were decided to be exposed to sulfate solutions rather than sulfate soils, all in the same manner that is full immersion. The sulfate solutions were prepared only of magnesium sulfate ($MgSO_4$) at different concentrations, specifically 0.5, 1.8, 5, and 10 percent solutions.

One part of cement to two parts (in weight) of fine sand of constant gradation was used in all specimens as the cement-aggregate ratio.

The water-cement ratio, on the other hand was taken as another variable to be investigated, having an important bearing on the over all quality of concrete and also on its resistance to sulfate attack, at levels of 50, 55, 60, and 65 percents by weight.

Certainly the behaviour of specimens through out the testing period as a function of change in time was to be included in the analysis of results taking the time element as a variable.

3.2 Statistical Design

In order to evaluate the relative effects of these variables upon the resistance of concrete to sulfate attack, certain statistical methods of analysis were adopted. (Refer Appendix 2.1 and 2.2).

To study the effect of these variables, a 4x4 Greco-Latin square was constructed. A variance analysis was to be performed and significance of results to be evaluated. Also a regression and correlation was to follow if possible.

This Greco-Latin square of the arrangement of these variables is as follows:

Type of additive:

I. Kayseri pozzolana
II. Fly ash
III. Slag
IV. Ground brick

Percentage of additive:

1. 40 %
2. 30 %
3. 20 %
4. 10 %

Concentration of $MgSO_4$ Solution
in which the specimens were stored

A. 0.5 %
B. 1.8 %
C. 5 %
D. 10 %

Water/cement Ratio of Mix

α. 0.50
β. 0.55
γ. 0.60
δ. 0.65

	I	II	III	IV
1	Aα	Bβ	Cγ	Dδ
2	Cδ	Dγ	Aβ	Bα
3	Dβ	Cα	Bδ	Aγ
4	Bγ	Aδ	Dα	Cβ

TABLE VI

In this arrangement, everyone of these sixteen specimens is different than the other and unique with respect to the combination of variables and their levels. Rectangular bars and tension briquettes with certain control duplicates were prepared representing these sixteen combinations of variables.

In order to study the effects of sulfate solution concentration and water/cement ratio alone, a 4x4 balanced block was arranged and tension briquettes were prepared for the sixteen unique combinations of this block (the levels of these two variables are the same as taken in the Greco-Latin square). The results of this block can also be used to compare by incorporating this 4x4 block with the 4x4 Greco-Latin square.

Eskihisar-Darica cement was used as the base cement in all the specimens mentioned above.

4x4 Balanced Block of Variables:

$A\alpha$	$B\beta$	$C\gamma$	$D\delta$
$C\delta$	$D\gamma$	$A\beta$	$B\alpha$
$D\beta$	$C\alpha$	$B\delta$	$A\gamma$
$B\gamma$	$A\delta$	$D\alpha$	$C\beta$

TABLE VII

To compare the relative resistance of Eskihisar-Darica and Bartin cements to sulfate attack, six rectangular bars and tension briquettes were prepared from each of these cements holding everything constant, except the cements. A 1:2 cement-aggregate ratio and 0.50 water-cement ratio were adopted (by weight). The fine aggregate had the same gradation for both series. They were both exposed to & % $MgSO_4$ solution. Comparison of these two sets was to be made with a t-test, Bartin cement containing slag in its clinker composition was expected to have a higher resistance to sulfate attack. Only to compare them without having exposed to sulfate at all, six cylinders were prepared from each of these two cements to be tested for compression strength at the end of two and four weeks.

3.3 Apparatus and Methods of Test for Studying Progressive Deterioration in Concrete:

3.3.1 Tests of Visual Examination

This is a method used to follow the progressive deterioration of concrete qualitatively. The visible changes in appearance of the specimens like color, texture, etc. are observed.

3.3.2 Expansion Tests

The effect of sulfate solutions can be observed by measuring the change in length (expansion). The initial rate of expansion, i.e. after short immersion periods, can often provide an indication of sulfate vulnerability. Specimens which show considerable expansion can still be of high quality if the expansion has taken place slowly. It usually doesn't take long to identify unresisting concretes; but it takes long periods of time to prove the relative merit of comparatively resistant cements and treatments. For this reason, an accelarated test is needed. Such are developed recently by Taylor and Bogue and H.L. Flack (55) None theless expansion measurements give a good picture of physical deterioration of concrete. To measure the expansion of concrete samples, <u>length comparator</u> is used. The comparator used has an Ames dial gage with a sensivity of 1/10.000 inches mounted on invar steel stand. A specimen of concrete was prepared with contact points at the two ends to fit the receptacles of the comparator. The comparator is equipped with an invar steel reference bar for adjusting the dial gage. Confidence range of measurements with the comparator is 95 % with μ= 50.68 ± 0.652. (Refer Appendix 2.3).

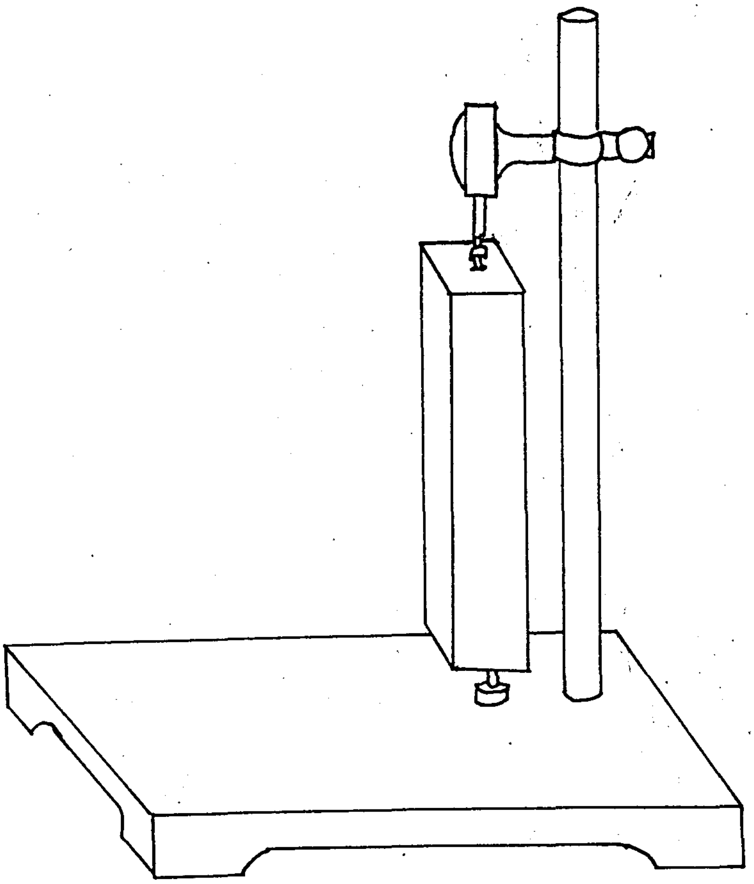


FIGURE 2. The length comparator.

3.3.3 Test for Dynamic Modulus of Elasticity

There are dynamic methods in which the response of the material to small dynamic forces is determined by measurements of the natural frequency of vibration of a specimen of known dimensions or by measurements of the velocity with which sound waves travel through the concrete. By means of established physical relations, the measured quantities may be converted into values of the modulus of elasticity or of Poisson's ratio. The value of the modulus of elasticity obtained by dynamic methods is used as an index of concrete quality. (ASTM Designation C 215-58T). This is a method well suitable to study progressive deterioration on the same sample, since it is an indestructive test. (For calculation of E refer Appen. 3)

In our investigation variation of the dynamic moduli of elasticity of concrete prisms subjected to sulfate attack is measured with the electro-sonometer, (Fg. 3, pg. 39) which works on same principle (Electro-Electronic Equipments Model 4100).

The apparatus was set up, and Young's and Shear Modulus determinations of a 3lb. concrete prisms were made. These experiments brought forward several precautions to be taken in order to minimize the experimental errors. They are:

1. Support conditions: In order to approach the theoretical support conditions, two rubber prismatic supports are necessary. Or the bars must be suspended by threads from their nodal points.

2. Interference from other vibrating bodies: Several deflections are observed on the resonance indicator meter as the frequency is varied. Most of these deflections were picked from the ground, which were due to the vibrations of other bodies in the laboratory. In order to avoid these undesirable vibrations, isolation of the oscillator-sample-pick-up system is necessary.

3. A mis-aligned placement of the driver hammer against the sample during transverse flexural vibration test, drives the sample into torsional vibrations as well as transverse vibrations.

4. Determination of the mode of vibration is only possible with the use of a cathode ray oscilloscope.

To measure the transverse frequency of concrete bars, a stand was set up, and specimens were suspended from their nodal points on this

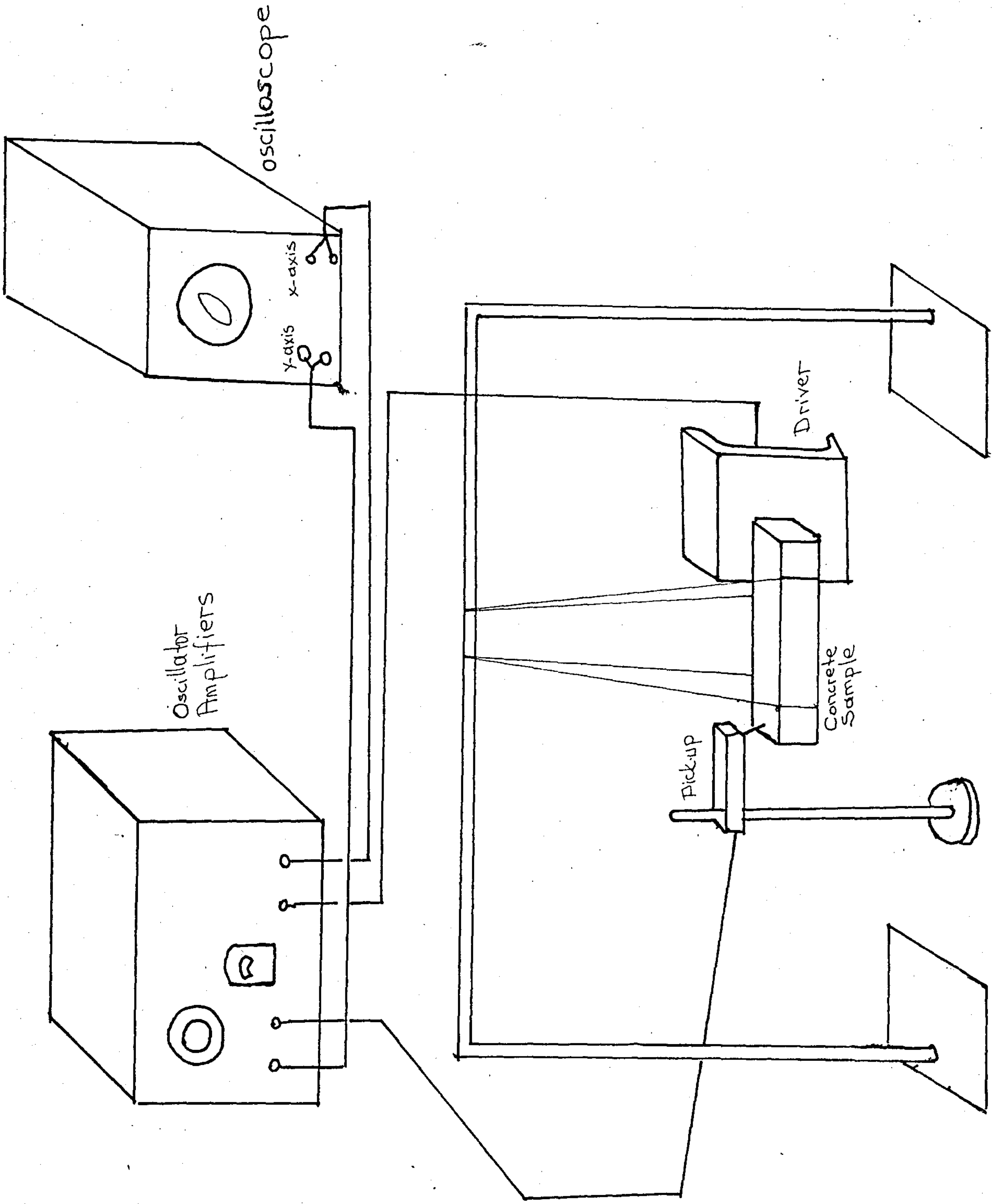


Figure 3.- Electrosonometer - Interconnection Diagram

stand. The driver hammer was placed against the side of the sample, as close as possible to the end of the side face and vertically positioned so that the depth of the bar is bisected by the position of hammer end. The pickup was placed on the top of the sample as close as possible to the end. The long dimension of the pickup cartridge was paralleled to longitudinal dimension of the bar. By use of controls of the sonometer, frequency was varied until maximum deflection was obtained on the resonance indicator. This resonant frequency was related to elastic modulus of the sample.

The confidence range of measurements with the electro-sonometer was found to be 95 % with $\mu = 2547.9 \pm 5.86$. (Refer Appendix 2.3)

3.3.4 Tension Tests

Since the deterioration of concrete under sulfate attack is mostly due to the crystals formed in the pores and the cracks caused by the pressure they exert, the tension or bending tests may give a better picture of progressive cracking and deterioration rather than the compression test. For this purpose briquettes can be performed. In our investigation, we used the cement briquette machine for determining the tensile strength of the cement mortars prepared. (Soil test Inc., Model CT-700A). The load was applied continuous at a rate of 600 ± 25 pounds per minute.

3.4 Materials to be Investigated and Their Unique Properties

3.4.1. The Cements

The properties of the cements are listed in Table VIII (pg.43) Bartin cement is known to contain slag in its clinker composition (C_3A Content 27.88 %). Eskihisar-Darica cement has a compound composition close to Type III portland cement (C_3A Content 8.18 %). It was considered as a normal portland cement with no special qualities and used as a base cement with the pozzolanas other than using in comparing Bartin cement.

3.4.2 The Additives

The general properties of the pozzolanas used as additives are listed in Table VIII (pg.43).

3.4.2.1 Kayseri Pozzolana is a natural pozzolana occuring in the area 30km. from Kayseri towards Sivas. The sample used in the research was taken from the place called Ağilmağrasi. The sample which was originally in appearance of medium to large size rocks was ground to about 5950 cm^2/gm Blaine fineness in a cement mill. Its chemical composition is close to santorin pozzolana, which may be considered as a hint for its pozzolanic activity. According to investigations undertaken at the laboratories of Istanbul Technical University on its strength development qualities, it was found out that (57):

a) At early stages, it decreases the strength of cement paste.

b) But this drop in strength diminishes as time passes, and final values of strength are the same whether some cement is substituted with pozzolanas or not.

On the whole, this material obtained from Ağilmağrasi shows pozzolanic properties. It has a brownish-red color.

3.4.2.2 Karabük slag is obtained from the blastfurnaces of Karabük Steel comlex. It is formed in the process of iron manufacture from the fusion of limestone with ash from coke and the siliceous and aluminous residue remaining in the ore after the reduction and separation of iron. The slag rises to the surface and is tapped off from time to time. Granulation is carried out in practice by a variety of methods. At Karabük the slag is tapped directly into pits kept filled with water, and granulated slag is obtained.

This granulated slag is ground to pass No. 200 sieve after oven-drying in the laboratory before blending with cement. About 40 % by weight of granulated slag has passed No. 200 sieve, and the coarser portion was discarded. It has a yellowish-white color.

3.4.2.3 Fly-ash, being an artificial pozzolana, was obtained from Tunçbilek Thermic Power Plant. State Hydraulic Works Directory, after some investigations (58), concluded that fly-ash had pozzolanic properties and the gain in strength, after 90 days, was higher when fly-ash was substituted into normal portland cement upto 20 %. Also its substitution decreases the heat of hydration.

The chemical composition of Tuncbilek fly-ash samples taken showed quite consistency for a period of eight months. The sum of SiO_2 + Al_2O_3 + Fe_2O_3 percentages change from 86 % to 90 % and this is an important indication for the pozzolanic properties. This sum is well above the 70 % requirement of ASTM specifications.

The fineness of fly-ash showed certain changes during the eight month testing period. This was due to the shifts in the plant from one unit to another. Only the fly-ash taken from underneath of the electro-filters had always the same fineness and this amounts to 100 to 150 tons of fly-ash daily. To eliminate some impurities of, usually, larger size, fly-ash was sieved through No. 200 sieve before testing. Tunçbilek fly-ash was found to be suitable for blending with portland cement in the construction of Gökçe Kaya Dam by the State Waters Works Directory.

Fly-ash was oven-dried in the laboratory before usage. It has a grayish-black color.

3.4.2.4 Ground brick was prepared in the laboratory by grinding ordinary bricks and passing through No. 200 sieve. It was considered as artificial pozzolana. It has red color.

3.4.3 Fine aggregate used in all tests was prepared according to a certain gradation from two types of sands. The Turkish standard sand has almost single size particles. An aggregate similar to ASTM graded sand was decided to be used. For this a sea-sand called "Perdah Kumu" (Finish Sand) was obtained. After washing and oven-drying it was sieved and mixed with the standard sand in appropriate proportions to obtain a graded aggregate.. The gradations of all these sands are given in the Table VIII (pg. 43)

The chemical compositions of the materials used in this research conform, in general, to the ASTM chemical requirements corresponding each one of them.

3.5 Preparation Procedure of the Samples

The additives prepared as described above were weighed out according to blending proportions and mixed with Eskihisar-Darica cement on a vibrator while constant mixing by hand was applied till the mixture came to uniformity in color and appearance.

According to 1:2 cement aggregate ratio, the prepared graded sand and the blended cements were mixed thoroughly. The mortar was prepared by adding water according to the respective water-cement ratios

Cement Designation	Oxide Composition (percent by weight) SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	Ignition Loss	Residue	Compound Comp. (percent by weight) C$_3$A	C$_2$S	C$_3$S	C$_4$AF	Blaine Fineness cm^2/gm	Spec. Grav.
Darica–Eskihisar	22.0	5.0	3.0	66.0	1.8	2.1	1.2	0.6	8.18	19.3	58.12	9.12	2711	3.17
Bartin	24.8	11.9	2.2	54.0	4.8	2.3	1.2	—	27.88	62.3	11.81	6.69	3218	3.00

PROPERTIES OF POZZOLANAS

Pozzolana Design.	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	Ignition Loss	MnO$_2$	Residue	Blaine Fineness cm^2/gm	Spec. Grav.
Kayseri Pozz.	63.8	19.3	5.1	4.5	3.0	0.01	2.9		86.0	5964	2.54
Karabük Slag	31.72	16.65	1.26	36.22	4.22	0.1		3.65	2.64	—	2.54
Tunçbilek Flyash	53.9	24.8	8.8	2.2	4.5	0.5	4.2		—	5548	1.98
Ground Brick	69.9	17.8	6.7	1.1	1.3	0.1	0.5			3184	2.73

PROPERTIES OF FINE AGGREGATE

Sand Design.	Gradation (Percent finer) No. of Sieve 16	20	30	40	50	100	Specific Gravity
Standard Sand	96.4	66.5	0.014	—	—	—	2.70
Finish Sand	—	—	71.4	38.5	15.9	—	—
Sand Used	95.0	80.0	60.0	45.0	20.0	—	—
ASTM Graded Sand	100	—	98	—	28.0	2	—

TABLE VIII

and by mixing with trowel till a uniform consistency was obtained. The mixture, then, was poured into molds which were oiled and placed on a vibrator, in three layers while compacting with an iron rod.

Molds were kept under wet rags over night. The specimens demolded were put into sulfate solutions half immersed for another day and then were fully immersed in sulfate solutions.

The plastic storage tanks were kept in a closed room and solutions were renewed everymonth for the first four months.

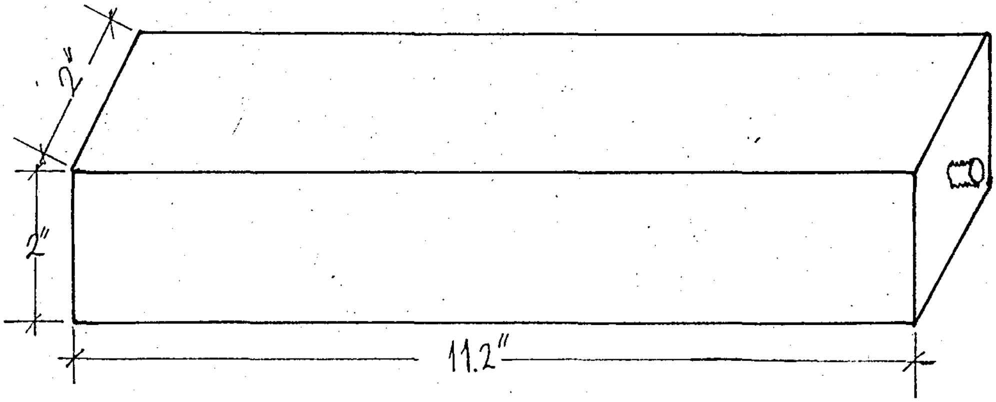
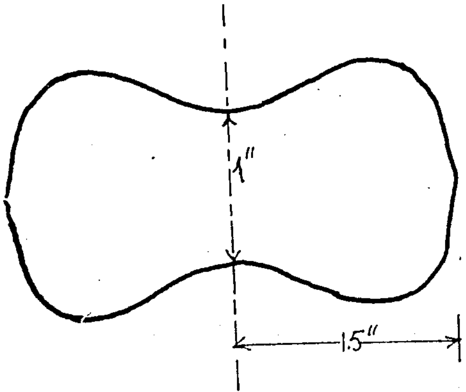


FIGURE 4. Mortar Bar.

In mortar bar preparation for the Greco-Latin square, one sample was prepared from each mix. Only certain control duplicates were prepared from a different batch. To compare the two cements sulfate resistance six samples from each were prepared. Tension briquettes were three from each batch.



Depth: 1+0.02"

FIGURE 5. Tension Briquette

CHAPTER IV

RESULTS AND CONCLUSIONS

4.1 Data

In Table IX (Appendix 1.1.1,pg. 53) the characteristics of sixteen specimens of the Greco-Latin square are given in terms of the corresponding levels of four factors.

In Table X (Appendix 1.2, pg. 54) the percent change in length of these sixteen specimens are tabulated with time up to 8 months.

The dynamic Modulus of elasticity E and percent change in E are tabulated on Table XI (Appendix 1.2, pg. 55).

The moduli and percent change in moduli are calculated by Compertar Programs One and Two, respectively (Appendix 4, pg. 70).

Table XII gives the tensile Strengths of these specimens at the end of 8 months sulfate exposure.

The data of Bartin and Darica cements are tabulated in Table XIII (Appendix 1.1.2, pg. 56). This includes 7 and 28 days compressive strength; and tensile strength, Young's modulus and percent expansion after 8 months sulfate exposure.

Table XVI (pg. 57) gives the percent expansions of Bartin, Darica (stored in 5 % $MgSO_4$) and neat cement paste (stored in water).

In Appendix 1.2 The Variance Analysis results are tabulated on the basis of percent expansions and Young's Moduli, Table XIV and XV (pg. 57).

4.2 Results and Discussion

The results of the research can be grouped under three parts:

1- Results obtained from the data of Greco-Latin square,

2- Results obtained from the comparison samples of two cements, Bartin and Darica.

3- Results obtained by comparing different methods of measuring the sulfate deterioration of concrete.

However the results are grouped in three parts, while discussing one group of results the results of other groups are also realized and incorparated.

4.2.1 Results Obtained from the Greco-Latin square

The results of the variance analysis performed on the expansions and elastic moduli data, specifically the F values of four factors (variables) are tabulated in TableXIV(pg.57) with time. The significance levels of the significant factors are also given.

The F values obtained on the basis of percent expansion values, after the first month, show complete consistency as far as the significance ranking of the factors are concerned. This is well demonstrated by the Chart I (pg.58). The significance ranking of the factors on the basis of percent expansion is as follows:

1- Type of Additive

2- Percentage of Addition

3- $MgSO_4$ concentration of the solutions in which the specimens were stored

4- Water/cement ratio of mix.

At the end of 7 months of testing period, the significance of "type of additive" factor reaches almost 0.05 probability level.whereas the other factors stay below the 0.20 probability level. This indicates that the variation from one additive to another, alone, contributes most to the total variance of results and this is true with 95 % confidence. Some of the four additives must impart much less resistance to the cement than the others.

It is also clear that the "blending proportion" is quite an important factor and have much influence on the resistance of the cement to sulfate attack.

"Type of Additive" factor appears to be of the model III[§] type and the evidence of regression of conversion with "type of additive" on the results of 7th month should be checked.

On the other hand the variance analysis performed on Young's Moduli gives the following significance ranking at the end of 8 months, which is reverse of the ranking obtained with the expansion values: (Table XV, pg.57)

1- Water/cement ratio of mix
2- $MgSO_4$ concentration of storage
3- Percentage of addition
4- Type of additive

For the 8 months testing period, it seems that the development of dynamic modulus and expansion of bars are affected differently by the four variables. This may lead to the fact that these two methods are not the measures of the same thing-that is the sulfate attack. One should speak of such conclusions with reserve for the reason that sulfate attack is a slow process and real effects of attack can be observed only after much longer periods of testing like two or three years at least.

This point is confirmed by the experiences of many investigators. As it can be followed from Table XI (pg.55), Young's modulus development still continues at the end of 7 months period. This, too, reveals the fact that the experimentation is still in an early stage to talk of sulfate deterioration on the basis of dynamic modulus values.

So, for further discussion, the expansion values and rate of expansion are taken as basis.

In Chart III (pg.59) the percent expansions of four of the specimens from the Greco-Latin square, all stored in 5 % $MgSO_4$ solutions are plotted along with the mean percent expansion of bars made with base cement Darica, stored also in 5 % $MgSO_4$ solution, and the percent expansion of a bar made of neat cement paste and stored in water, against time. All specimens exposed to sulfate solution have higher expansions

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[§] In Model III type of variance, a regression and correlation exist between the levels of factor and the data, if these levels could be expressed in terms of a series of number, can be related to the variable as an arithmatical expression.

than the normal expansion of the neat cement paste in water after the first month on. It is clear that sulfate attack cause definitely observable expansions in concrete. On this chart, it appears that three of the specimens (No. 2, 7 and 9) have larger expansions than the base cement and ground brick (No. 16) is the only one with lesser expansion in 5 % $MgSO_4$ solution. We can't conclude definitely, the adverse effect of these additives, only it is obvious that at their respective blending proportions they display an adverse effect against sulfate attack. That is when Kayseri pozzolana is blended at 30 %, fly ash 20 % and slag 40 %.

The bar diagram, Chart IV (pg.60), of 8 months expansions reveals the following observations about the four additives used (Refer Table IX, pg.53 for the characteristics of samples):

a) Three of the specimens containing slag (No. 9,11 and 12) show expansions larger than the mean of expansions of bars made of the base cement, Darica. Only No. 10 is about at the same expansion as the base cement. This is due to the lower concentration of its solution (0.5 %) compared to the 5 % solution in which the base cement specimens were stored.

This implies that the addition of Karabük slag decrease the resistance of Darica cement in any concentration of sulfate solution within the 40 % addition range. This point is further confirmed by the larger expansion mean of Bartin cement (0.0414 % expansion in 7 months) which is known to contain slag in its clinker. Also it is known, that with up to 50 % of slag, the beneficial effect, if ever exists, is slight (56).

b) Ground brick substitution proved to be consequential. All four specimens containing ground brick (No. 13, 14, 15, and 16) have expansions less than the mean expansion of the base cement stored in 5 % $MgSO_4$ solution.

c) In preparing the specimens containing fly ash, it was observed that fly ash required more water than any of the other additives. The two specimens of fly ash (No. 6 and 8) with water/cement ratios 0.60 and 0.65 show less expansions while the ones (No. 5 and 7) with 0.50 and 0.55 show more expansions than that of the base cement. No. 6 was exposed to 10 % $MgSO_4$ solution, double of base cement's. The water/cement ratio may have a more pronounced effect in the case of fly-ash substitution.

d) Kayseri pozzolana showed more expansions except one specimen (No. 4) with 10 % substitution. For resistance to sulfate attack always substantial amounts of pozzolana is required (4) (30-40 %, definitely greater than 30 %). So the lesser expansion of 10 % Kayseri pozzolana specimen than that of the base cement specimen (exposed to 5 % $MgSO_4$) can be attributed to the lower concentration of solution in which it is stored (1.8 % $MgSO_4$).

The results above could be more pronounced if we had used a cement with higher C_3A content, for example Bartin (27.8 % C_3A), than Darica's (8.2 % C_3A). It is known that pozzolanas give better results with cements high in C_3A content (44,45).

4.2.2 Results Obtained from the Comparison Samples of Two Cements, Bartin and Darica.

When the 7 and 28 days compressive strength means of these two cements compared, we observe that they have just about the same strength.

When we compare their tension, expansion and Young's Modulus values after 8 months of exposure to 5 % $MgSO_4$ solution, we observe higher resistance of Darica than Bartin cement, even though the latter is known to contain slag in its clinker. This may be due to the poor quality of slag with respect to sulfate resistance or higher C_3A content of Bartin (27.8 % C_3A) than Darica (8.18 % C_3A).

Strength-wise they show just about the same quality but the sulfate resistance of Bartin is lower than Darica. Table XIII, pg. 56

We must note that not necessarily all of the 27.8 % C_3A content of Bartin is subject to attack. In computing C_3A we might have included Al_2O_3 of the slag added in clinker. 27.8 % C_3A is an unusually high percentage.

4.2.3 Results Obtained by Comparing Different Methods of Measuring the Sulfate Deterioration of Concrete

As indicated previously, three quantitative methods of measurement were employed in this investigation:

1- Length Change Measurements;
2- Dynamic Modulus of Elasticity Measurements;
3- Tension Tests;

in order to study the sulfate deterioration of concrete.

The first two methods, being indestructive, give a picture of progressive deterioration in concrete. The last one is a destructive method and gives the last standing of samples after a period of time.

When we look at the length changes data, Table X (pg.54), we observe progressive expansion from one month to eight months. The young's moduli data doesn't show any noticable trend of decrease, Table XI (pg.55) in this period. This implies the fact that E development still continues and sulfate attack is shadowed by some other factors contributing to E development, such as further hydration, initial W/c ratio etc... On the other hand, expansions, being a result of deterioration only, give a clear picture of relative resistance. (In part 4.2.2 it was pointed that expansion of neat cement paste in water was definitely less than sulfate expansions).

This point is further confirmed by comparing the three bar diagrams of 8 months expansion, Young's Modulus and change in Young's Modulus, Chart IV, VI (pg. 60). They show almost no relation.

In Young's Modulus bar diagram, Chart VI (pg.60), almost all specimens have E less than Darica, the base cement. This is due to decrease in strength by substitution of additives in cement. This may be a good picture of relative strengths of these specimens, but not their sulfate resistance. Young's modulus determinations may give a picture of sulfate attack when employed on plain cements and only after some period to begin a trend of decrease in E due to deterioration. When used with blended cements, the relative pozzolanic action of specimens with different additives at different percentages may shadow the decrease in E due to sulfate attack.

Same argument may be extended to the tension test by observing Chart V (pg.60), there again there is not much relation with the expansion values.

When these methods compared in the case of the two cements, Bartin and Darica. They give reasonable results. Young's modulus and tension strength of Darica is higher than Bartins while Darica's expansion is less than Bartin's. This is due to the fact that there is no additive in these plain cements to shadow E and strength development.

The results of 4x4 Balanced Block are not presented here, because its testing period had not terminated at the date of submission of this thesis.

4.3 Conclusions and Suggestions

This research was intended, as previously stated, to put a hypothesis forward in order to guide the further studies in this country on sulfate attack problem. This was tried to be accomplished by giving so some general ideas and suggestions on methods and materials, rather than specific results. Because this is one of the first studies on the subject in this country; factors, materials and methods of approach are numerous; and period of testing is relatively short for a sulfate attack study (8months).

Under the light of results obtained and discussion, the following conclusions and suggestions can be made:

1- Type of additive and percentage of additive have a more significant bearing on sulfate resistance of a currently produced, normal portland cement in Turkey, namely, Darica, rather than its water/cement ratio of mix and the concentration of sulfate solution with which it comes into contact. So further studies must concentrate on type of additive and its percentage. And a study leading to a regression and correlation for these factors may be consequential.

2- Karabük slag upto 40 % blending proportion doesn't impart any sulfate resistance in cement. It is highly probable that it is not properly quenched with respect to this purpose in the steel plant and it is not suitable for sulfate resisting slag cements. However behaviour of higher percentage blends should be investigated (above 50 %).

3- Ground brick is a relatively good additive. Its optimum percentage of blending must be clearly defined (Normally lies between 20-40 %).

4- Fly ash also proves to be useful for sulfate resistance. Only optimum percentage of blending and water/cement ratio must be determined (normally 30 % and 0.65 respectively).

5- Kayseri pozzolana doesn't seem to have sulfate resistance imparting qualities; however it has pozzolanic activity and cause less decrease in strength upon substitution.

6- It is advisable to use a cement with higher C_3A content than Darica, for example, Bartin as the base cement in order to have better results of resistance.

7- Darica cement (8.2 % C_3A) has higher resistance to sulfate attack than Bartin (27.8 % C_3A), though they have about the same compressive strengths.

8- With blended cements, the tension tests (strength) and the elastic modulus determinations don't give a clear picture of attack and resistance. Expansion tests are more suitable for this purpose and in relatively shorter periods of testing.

It would be a nice idea if the suggested points could be studied further in this school, while the tests on undestroyed samples of this research still preserved in the Concrete Laboratory are carried.

APPENDIX 1

1.1.1 Tabulated Data of Greco-Latin Square Specimens

Characteristics of Greco-Latin Square Specimens

Sample No.	Type of Additive	Percentage of Addition	Concentration of $MgSO_4$ Sol'n.	Water/cement Ratio
1	Kayseri Pozzolana	40 %	0.5 %	0.50
2	"	30 %	5 %	0.65
3	"	20 %	10 %	0.55
4	"	10 %	1.8 %	0.60
5	Fly-Ash	40 %	1.8 %	0.55
6	"	30 %	10 %	0.60
7	"	20 %	5 %	0.50
8	"	10 %	0.5 %	0.65
9	Blastfurnace Slag	40 %	5 %	0.60
10	"	30 %	0.5 %	0.55
11	"	20 %	1.8 %	0.65
12	"	10 %	10 %	0.50
13	Ground Brick	40 %	10 %	0.65
14	"	30 %	1.8 %	0.50
15	"	20 %	0.5 %	0.60
16	"	10 %	5 %	0.55

PERCENT EXPANSION OF GRECO-LATIN SPECIMENS

SAMPLE No.	1 Week Reading	2 Weeks	3 Weeks	1 Months	2 Months	3 Months	4 Months	5 Months	6 Months	7 Months	8 Months
1	.811	.0040	.0065	.0140	.0330	.0350	.0425	.0430	.0395	.0395	.0445
2	.861	.0040	.0055	.0130	.0300	.0345	.0430	.0435	.0415	.0420	.0480
3	.730	.0010	.0095	.0170	.0265	.0330	.0375	.0395	.0410	.0465	.0400
4	.7535	-.0005	.0005	.0050	.0075	.0115	.0145	.0165	.0165	.0235	.0195
5	.860	.0040	.0085	.0170	.0310	.0325	.0410	.0380	.0350	.0350	.0395
6	.475	.0035	.0045	.0090	.0160	.0190	.0220	.0240	.0220	.0230	.0215
7	.452	.0015	.0040	.0125	.0230	.0290	.0330	.0340	.0330	.0350	.0350
8	.849	.0030	.0010	.0055	.0100	.0120	.0165	.0185	.0160	.0180	.0170
9	.578	.0050	.0090	.0170	.0370	.0410	.0500	.0510	.0490	.0500	.0555
10	.7775	.0030	.0005	.0150	.0160	.0215	.0260	.0270	.0270	.0335	.0280
11	.713	.0020	.0070	.0235	.0410	.0500	.0570	.0490	.0600	.0700	.0670
12	.746	.0240	.0260	.0310	.0370	.0410	.0480	.0495	.0490	.0540	.0505
13	.578	.0020	.0020	.0100	.0230	.0260	.0280	.0305	.0305	.0320	.0250
14	.468	.0030	.0000	.0085	.0120	.0130	.0160	.0175	.0180	.0235	.0190
15	.775	-.0030	.0080	.0080	.0100	.0100	.0140	.0155	.0140	.0190	.0150
16	.776	.0050	.0080	.0110	.0165	.0190	.0200	.0240	.0230	.0290	.0240

TABLE X

YOUNG'S MODULUS* AND CHANGE IN YOUNG'S MODULUS (psi)

Sample No.	1 Week	2 Weeks		3 Weeks		1 Month		2 Months		3 Months		4 Months		5 Months		6 Months		7 Months		8 Months	
	E_0	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE	E	ΔE
1	3.557	3.902	9.712	4.120	15.83	4.303	21.00	4.702	32.20	4.877	37.13	5.006	40.76	5.096	43.29	5.137	44.44	5.210	46.48	5.229	47.1
2	2.698	3.273	21.319	3.472	28.69	3.548	31.50	4.018	48.91	4.219	56.36	4.400	63.06	4.445	64.76	4.564	69.15	4.590	70.12	4.616	71.0
3	3.364	3.993	18.68	4.178	24.19	4.312	28.17	4.590	36.44	4.742	40.94	4.939	46.81	5.028	49.46	5.109	51.86	5.206	54.76	5.044	49.9
4	3.008	3.472	15.420	3.608	19.93	3.864	28.44	4.262	41.69	4.325	43.77	4.534	50.71	4.513	50.03	4.705	56.42	4.714	56.71	4.610	43.8
5	2.841	3.452	21.514	3.516	23.75	3.648	28.39	3.998	40.72	4.125	45.2	4.166	46.65	4.249	49.57	4.244	49.37	4.328	52.32	4.308	51.6
6	2.874	3.241	12.756	3.534	22.96	3.570	24.20	3.911	36.07	3.988	38.77	4.146	44.27	4.166	44.94	4.227	47.06	4.254	48.02	4.358	51.7
7	3.795	4.112	8.35	4.424	16.55	4.490	18.30	4.776	25.83	4.887	28.77	5.019	32.23	5.087	34.02	5.221	37.56	5.311	40.73	5.260	38.7
8	3.172	3.486	9.89	3.824	20.52	3.866	31.87	4.353	37.20	4.566	43.92	4.652	46.63	4.779	50.62	4.824	52.06	4.959	56.31	4.830	52.2
9	3.099	3.491	12.66	3.661	18.15	3.703	19.48	4.464	44.06	4.493	44.98	4.621	49.13	4.648	49.98	4.707	51.90	4.842	56.25	4.764	43.8
10	3.042	3.271	7.52	3.620	18.99	3.767	23.81	4.302	41.41	4.552	49.61	4.631	52.22	4.675	53.67	4.824	58.56	4.851	59.45	4.815	58.4
11	2.307	2.789	20.92	3.003	30.18	3.276	42.03	3.604	56.26	3.888	68.55	3.980	72.53	4.155	80.14	4.160	80.37	4.207	82.40	4.207	82.4
12	4.113	4.301	4.56	4.506	9.54	4.437	12.72	3.953	20.42	5.110	24.23	5.205	26.54	5.253	27.71	5.324	29.42	5.333	29.66	5.414	31.9
13	2.082	2.550	22.50	2.865	37.60	3.067	47.30	3.492	67.71	3.750	80.13	3.866	85.67	3.903	87.46	3.922	88.36	3.986	91.44	3.916	88.0
14	3.040	3.423	12.59	3.867	27.19	4.033	32.65	4.373	43.84	4.456	46.58	4.622	52.03	4.643	52.70	4.702	54.64	4.752	56.30	4.752	56.3
15	2.914	3.320	13.93	3.452	18.44	3.797	30.29	3.993	37.01	4.256	46.03	4.355	49.44	4.395	50.82	4.468	53.29	4.616	58.39	4.560	57.6
16	3.388	3.805	12.30	3.812	12.51	4.478	32.16	4.696	38.60	4.765	40.64	4.914	45.03	4.941	45.85	4.948	46.02	5.022	48.21	5.115	51.0

GRECO - LATIN SQUARE SPECIMENS

* all E values to be multiplied by 10^6

TABLE XI

8 Months Tensile Strength of Greco-Latin Briquettes (kg/cm²)

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Tensile Strength	35.2	58.6	47.2	56.2	39.2	32.9	31.5	47.4	35.4	21.5	25.8	29.9	41.1	42.5	44.7	38.9

TABLE XII

Variance Analysis on Tensile Str. basis

Type of Add.	Percent Add.	Sulfate Concent.	w/c Ratio
3.524	.323	.175	.745

TABLE XVII

1.1.2 Tabulated Data of Bartin and Darica Cements

Characteristics of Samples	Test	Bartin	Darica	t	s
D=5.1cm, H=10,4cm cylinders w/c = 0.50, 1:2 Mortars Water cured	7days Compressive Strength (kg/cm²)	121.78	175.50	5.02	18.64
	28days Compressive Strength (kg/cm²)	216.25	207.33	0.55	28.40
Tension briquettes (standard) w/c = 0.50, 1:2 Mortars stored in 5 % MgSO₄	8 Months Tensile Strength (kg/cm²)	40.82	47.93	1.90	6.50
Concrete prisms, 2x2x11.2 inch w/c = 0.50, 1:2 Mortar Storage in 5 % MgSO₄	8 Months Young's Modulus (psi)	4.42×10^6	5.42×10^6	11.28	.08
	1 week - 8 Months Change in E	51 %	40 %		
	1 week - 8 Months Percent Expansion	0.0473	0.0321	2.27	11.67

TABLE XIII

$$t = \frac{\text{Mean sqR}}{\text{Error mean}}$$

s = probability Level

1.2 Tabulated Results of Greco - Latin Square

VARIANCE ANALYSIS RESULTS OF GRECO-LATIN SQUARE ON EXPANSION BASIS

Factor	2 Weeks	3 Weeks	1 Months	2 Months	3 Months	4 Months	5 Months	6 Months		7 Months		8 Months	
	F	F	F	F	F	F	F	F	S	F	S	F	S
Percent Additive	1.189	.398	.443	1.837	2.362	2.034	2.196	2.335	~20%	2.189	20%	1.45	–
Type of Add	.657	.800	2.239	2.583	4.916	4.438	5.027	6.572	10%	8.480	5%	5.02	10%
Sulfate Concent	1.114	.699	.802	.837	1.532	.960	1.665	1.798	–	1.919	–	1.14	–
W/C Ratio	1.132	.619	.707	.768	1.262	.922	.990	1.439	–	1.505	–	.79	–

TABLE XIV

$$F = \frac{\text{MEAN SQR}}{\text{ERROR MSQR}}$$

S = Probability level

VARIANCE ANALYSIS RESULTS OF GRECO-LATIN SQUARE ON E BASIS

Factor	2 Weeks	3 Weeks	1 Months	2 Months	3 Months	4 Months	5 Months	6 Months		7 Months		8 Months	
	F	F	F	F	F	F	F	F	S	F	S	F	S
Percent Additive	3.123	1.984	10.598	3.095	4.302	3.802	3.358	4.127	20%	2.739	~20%	5.47	10%
Type of Add.	1.911	1663	1.039	0.974	1.532	1.689	1.636	2.673	~20%	1.399	–	2.40	20%
Sulfate Concent	1.748	1.484	3.731	2.650	4.276	3.555	2.995	3.597	20%	2.999	20%	6.48	10%
W/C Ratio	10.279	10.342	28.415	10.272	13.458	11.290	9.402	10.656	5%	6.862	10%	16.69	5%

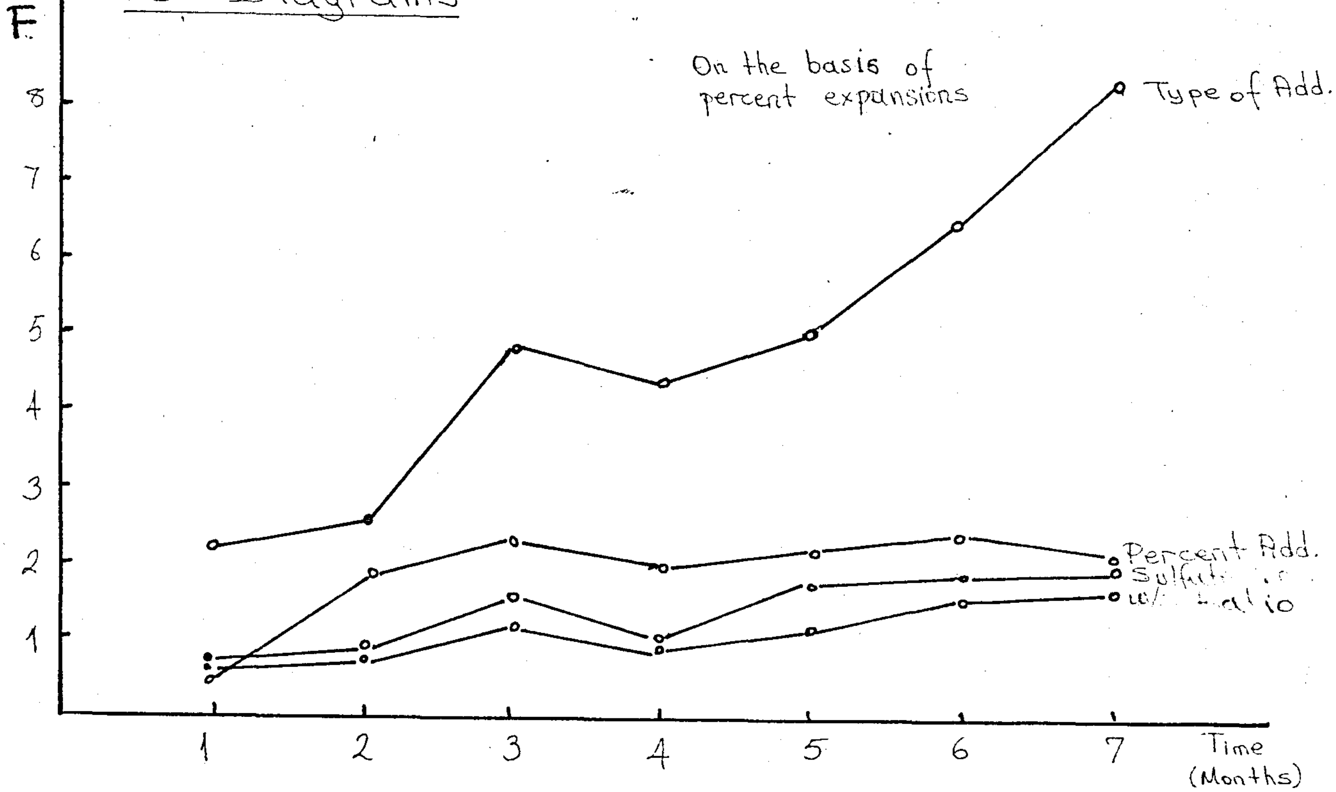
TABLE XV

Percent Expansions

	2 Weeks	3 Weeks	1 Month	2 Months	3 Months	4 Months	5 Months	6 Months	7 Month	8 Months
Bartin	0.0068	0.0104	0.0138	0.0283	0.0299	0.0370	0.0405	0.0414	0.0416	0.0473
Darica	0.0098	0.0145	0.0200	0.0243	0.0260	0.0308	0.0324	0.0336	0.0351	0.0321
Neat cement Paste	0.0080	—	0.0100	0.0120	0.0150	0.0170	0.0290	0.0230	—	0.0240

TABLE XVI

1.3 Diagrams



$F = \frac{\text{Mean Sqr}}{\text{Error Mean}}$ (significance)

CHART I

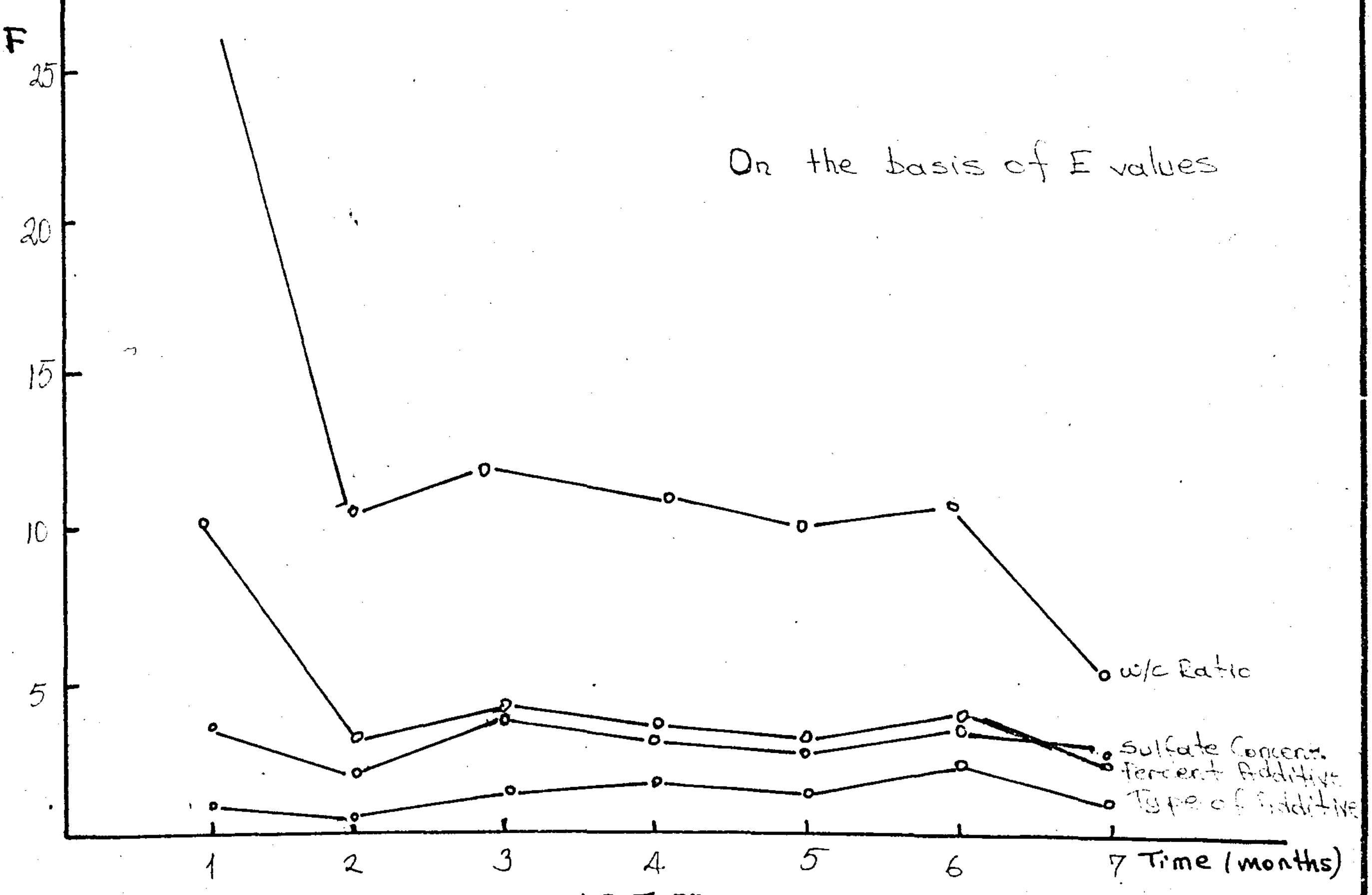


CHART II

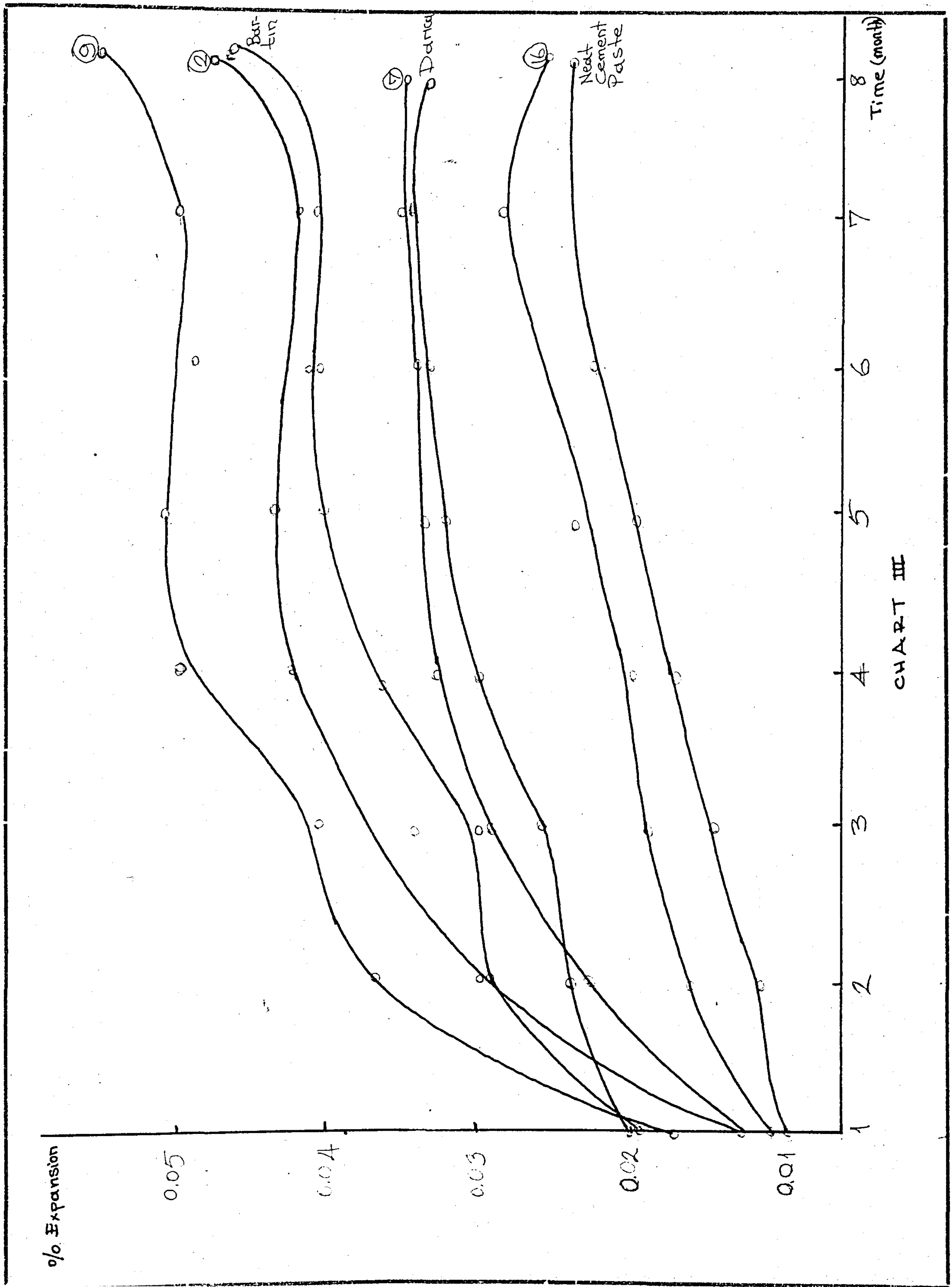

% Expansion
0.05
0.04
0.03
0.02
0.01
1
2
3
4
5
6
7
8
Time (month)
9
2
Bar-tin
7
Darıca
16
Neat Cement Paste

CHART III

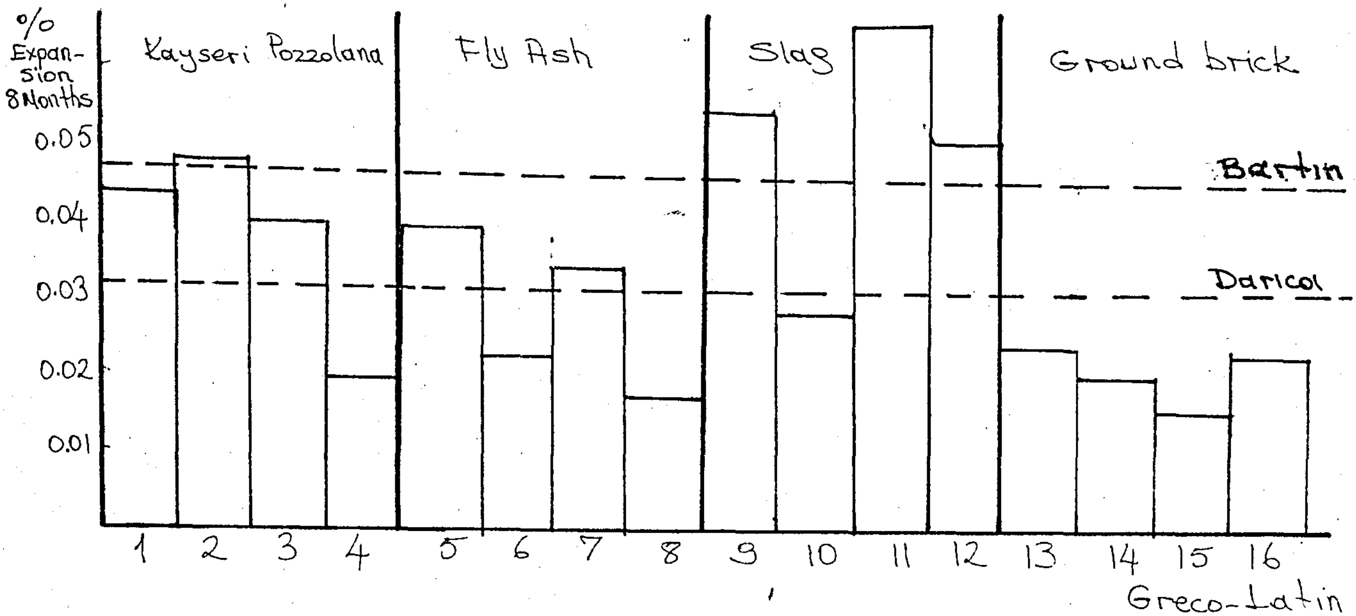


CHART IV

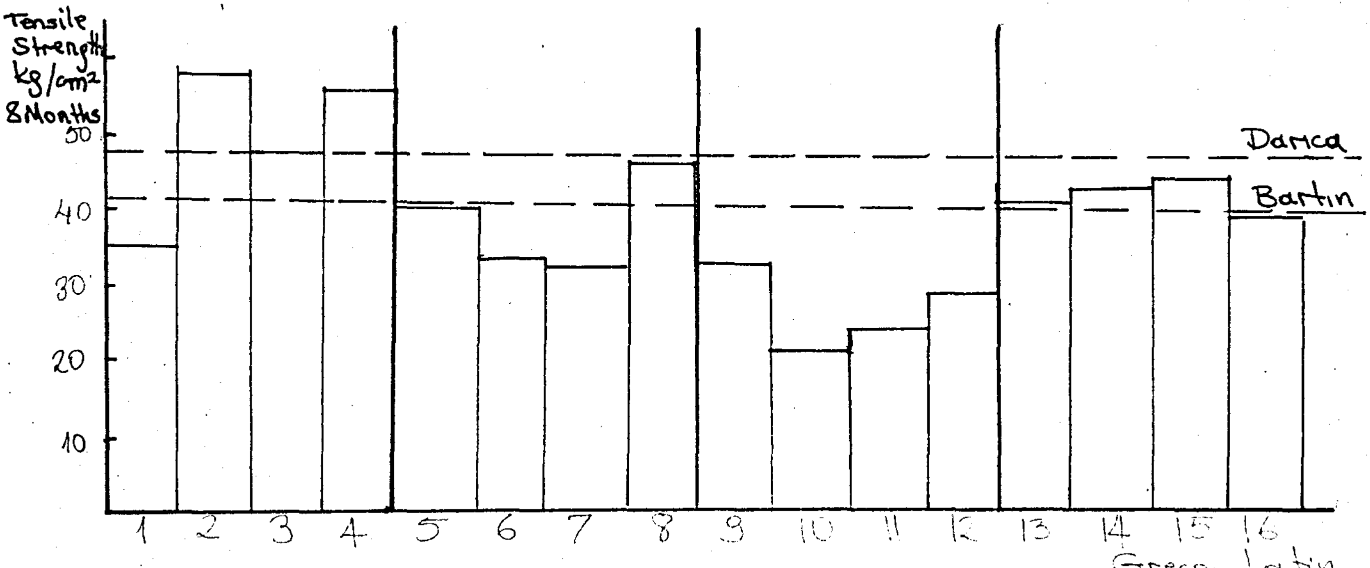


CHART V

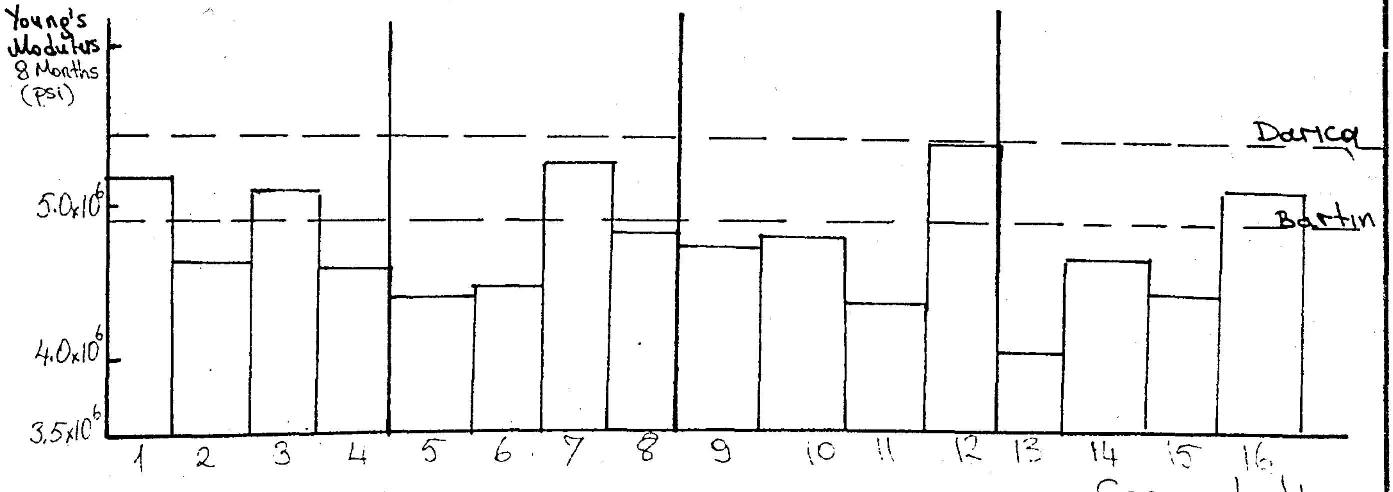


CHART VI

APPENDIX 2

2.1 Background to the Theory of Statistical Methods Used(59)

2.1.1.1 Analysis of variance

The variance is defined as the mean squared deviation from the mean..

$$\sigma^2 = \frac{\sum (x-\mu)^2}{n}$$

In practice μ, the true mean, is usually not known, but is only estimated from the sample mean $\bar{x}=\sum x/n$. To counteract the bias that tends to minimize the sum of squares of deviations when they are calculated from $\bar{x}$ instead of from μ, the variance is estimated by dividing by n-1 instead of by n. The estimated variance $s^2(x)$ is calculated as follows:

$$s^2(x) = \frac{\sum (x-\bar{x})^2}{n-1}$$

2.1.1.2 The F Test for Variances

The F test provides a method for determining whether the ratio of two variances is larger than might be expected by chance if they had been drawn from the same population.

$$F = \frac{s^2(x_2)}{s^2(x_1)}$$

$s^2(x_1)$ and $s^2(x_2)$ are the estimated variances of the variables x_1 and x_2. If $s^2(x_1)$ and $s^2(x_2)$ are in fact measures of the same thing, i.e., samples drawn from the same population, or from populations with identical variances, the two estimated variances will not necessarily be the same, no more than the means of the two sets of measurements would be exactly identical. F measures the difference, in the form of a ratio, of two estimates of the same variance that can be expected to occur, depending on the number of degrees of freedom available for the calculation of each estimate- The F value at the 2α level indicates that there is only a 2α probability of observing a ratio this large if the two variance estimates were obtained from the same population or from two populations with the same variance.

The F values have been tabulated to test specifically whether one variance estimate is larger than another, not just whether two variances are significantly different. This corresponds to one side of the F distribution and the probabilities are half the 2α probabilities. If the tables are to be used for a two-sided test, i.e., to see if there is significant difference between two variance estimates, then the indicated probability levels must be doubled.

2.1.1.3 Multiple Balanced Blocks

An extension of the simple two-factor arrangement of data is one in which the number of rows and columns is the same. This is the balanced block design or arrangement of data. Each set of runs at one level of first factor would contain one made at each level of second factor, so that in comparing the means at different levels of first factor the effect of second factor would be canceled.

With the balanced block it is possible to superimpose on the existing unique combinations of the two factors another variable in such a manner that the runs at each level of each variable include one run at each level of the other two variables. In this way the comparison of totals or means for each variable is not affected by the levels of the other variables. In some cases it is possible to include additional variables with the same number of levels and not duplicate any combination of two levels of two variables. The balanced block with three variables is called a Latin square; with four variables it is called Greco-Latin square.

With a 4x4 Greco-Latin square, there are four factors at four levels each and 16 data points. The sum of squares for each factor is calculated from the totals for the four levels of that factor, and therefore with 3 degrees of freedom. The four factors utilize 12 degrees of freedom leaving 3 for an estimate of error. Therefore, with 16 data points properly taken, it is possible to find the effect of four levels of four factors and still have 3 degrees of freedom for estimating error without any replecation of measurements. The calculation of mean squares are demonstrated with an example in the Sample Calculations section.

2.1.2.1 The t-test

t can be defined as the difference between the mean of a sample and the true mean of the population from which the sample was drawn, divided by the estimated standard deviation of the mean. Thus, if μ designates the true mean, t may be written

$$t = \frac{|\bar{x} - \mu|}{s(\bar{x})}$$

The t test deals with the estimation of a true value from a sample and the establishing of confidence ranges within which the true value can be said to lie. The values of t for different degrees of freedom are tabulated with the probability levels for observing larger absolute values than those tabulated.

The execution of the t-test involves setting up a hypothesis and calculating t on the basis that the hypothesis is true. The tabulated values of t are the maximum that can be expected at the indicated probability levels if the null hypothesis is true. If the calculated t exceeds the tabulated value at a certain probability level we reject the the null hypothesis, accepting the risk of being in error with the chance indicated by the probability level. This error, of falsely rejecting the null hypothesis, is called an error of type I. If the data do not satisfy the null hypothesis but give a t value less than the critical value for the test, then the hypothesis will be incorrectly accepted as being true. This false acceptance of the null hypothesis is an error of type II. A decrease in the probability of error of type I causes an increase in the probability of error of type II, and vice versa. For practical purposes, with the ordinary size of samples encountered, the 0.05 to 0.01 probabilities for errors of type I usually give the optimum, i.e., the minimum, probability of both types of errors.

2.1.2.2 The Confidence Range.

$\bar{x}$ is an estimate of the true mean μ. The t function gives the distribution of deviations of $\bar{x}$ from μ in terms of relative probabilities. We can express the true mean as:

$$\mu = \bar{x} \pm t\, s(\bar{x})$$

to be within the range of the calculated mean included in the limits of plus and minus t times the estimated standard deviation of the mean.

Difference between the Mean and Zero. Measurements are often made in pairs to compare two processes or two different materials. The purpose of the test is to determine whether there is a significant difference between the two items under test or whether the mean difference is significantly different from zero. The null hypothesis therefore is

$$H_o \, ; \, \mu = 0$$

The t test for this hypothesis is as

$$t = \frac{|\bar{y} - 0|}{s(\bar{y})}$$

where y is the difference between pairs of measurements.

2.1.2.3 Difference between Two Means

The hypothesis is

$$H_o \, ; \, \mu_1 = \mu_2$$

The prupose of the test is to determine whether the means of two different samples could have come from the same population or from populations with the same means. The t expression is as follows:

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{\bar{s}(x)\sqrt{1/n_1 + 1/n_2}}$$

where $\bar{s}(x)$, pooled estimate of standard deviation from both sets of data, is calculated from the following equation

$$\bar{s}(x) = \sqrt{\frac{\Sigma' x_1^2 + \Sigma' x_2^2}{n_1 + n_2 - 2}}$$

t is calculated from the equation and is compared with the tabulated values at the degrees of freedom equal to n_1+n_2-2.

2.2 Sample Calculations

Percent changes in Young's Moduli are also calculated in the computer by the Program Two given in the Appendix 4.

2.2.1 Program Three does the variance analysis calculations. A sample calculation done on the 1-4 weeks percent Young's Modulus values is given below:

	Kayseri Pozz.	Fly-Ash	Slag	Ground Brick	Persent Addtion Tot
40 %	21.0 Aα	28.3 Bβ	19.4 Cγ	47.2 Dδ	115.9
30 %	31.5 Cδ	24.2 Dγ	23.8 Aβ	32.6 Bα	112.1
20 %	28.1 Dβ	18.2 Cα	42.0 Bδ	30.2 Aγ	118.5
10 %	28.4 Bγ	21.8 Aδ	12.7 Dα	32.1 Cβ	95.0
Time Tot.	109.0	92.5	97.9	42.1	441.5

$MgSO_4$ Concentration Tot.		W/C Ratio Tot.		
A	96.8	α	84.5	n=4
B	131.3	β	112.3	n=16
C	101.2	γ	102.2	
D	112.2	δ	142.5	

$\sum x = 441.5$

$\sum x^2 = (21.0)^2 + (31.5)^2 \ldots\ldots\ldots\ldots (32.1)^2 + (142.1)^2 = 13320$

$\frac{(\sum x)^2}{N} = \frac{(441.5)}{16} = 12182$

$\sum(\text{Type . Tot})^2/4 = \frac{(1090)^2 + (142.1)^2}{4} \pm 12555$

$\sum(\text{Percent. Add. Tot})^2/4 = \frac{(115.9)^2 + \ldots\ldots + (95.0)^2}{4} = 12262.5$

$\sum(MgSO_4 \text{ concent. Tot})^2/4 = \frac{(96.8)^2 + \ldots\ldots + (112.2)^2}{4} = 12355$

$\sum(\text{w/c Ratio Tot})^2/4 = \frac{(84.5)^2 + \ldots\ldots + (142.5)^2}{4} = 12620$

Source	Sum of Squares	D.F.	Mean Square
Type of Add.	12555-12182=373.0	3	124.3
Percent Add.	12262.5-12182=80.5	3	26.8
SO_4 Concent.	12355-12182=173.0	3	57.6
w/c Ratio	12620-12182=438.0	3	146.0
Error	Diff: 1064.5-1138=73.5	3	24.5
Total	13320-12182=1138		

Type of Additive: $F = \frac{124.3}{24.5} = 5.075$

Percent of Addition : $F = \frac{26.8}{24.5} = 1.095$

SO_4 Concentration: $F = \frac{57.6}{24.5} = 2.35$

w/c Ratio: $F = \frac{146.0}{24.5} = 5.96$

2.2.2 The 6 specimens of Darica cement are compared with the 6 specimens of Bartin cement by means of Computer Program Four.

Sample Calculation: % L values, 1-6 Months

Sample	Bartin Cement	Darica Cement
1	28.5	4.5
2	31.5	18.0
3	20.5	18.5
4	25.5	12.5
5	23.0	13.0
6	22.0	8.0
Total	151.0	75.5

Bartin Mean $= \frac{151.0}{6} = 25.2$

Darica Mean $= \frac{75.5}{6} = 12.6$

$\sum x^2_{Bartin} = (28.5)^2 + \ldots + (22.0)^2$

$\sum x^2_{Darica} = (4.5)^2 + \ldots + (8.0)^2$

$n=6 \quad f=5$

$$\text{Variance}_{Bartin} = \frac{\sum x^2 - \bar{x}\sum x}{f} = 17.56$$

$$\text{Variance}_{Darica} = 30.14$$

$$\text{Pooled Estimate Standard Dev.} = \sqrt{\frac{S_{Bartin} + S_{Darica}}{n_2 - n_1 - 2}} = \sqrt{\frac{17.56+30.14}{10}}$$

$$= 4.88$$

$$t = \frac{\bar{x}_{Darica} - \bar{x}_{Bartin}}{\text{Pooled estimate of Std. Dev.} \sqrt{1/n_1 + 1/n_2}} = 4.54$$

In all these calculations data is coded and this doesn't affect the results.

2.2.3 Confidence ranges of measurements with the Electro-Sonometer and the Length Comparator:

Torsional Frequencies (12 measurements of the same sample)

1	2550
2	2555
3	2550
4	2540
5	2545
6	2550
7	2550
8	2540
9	2545
10	2560
11	2540
12	2550

$n=12$

$\Sigma x=30575$

$\bar{x}=\frac{\Sigma x}{n}=2547.9$

$\Sigma x^2= 77,902,975$

$\Sigma x'^2=\Sigma x^2 - \bar{x}\Sigma x$

$= 77.902.975 - 77.902.042 = 933$

$s^2(x)=\frac{\Sigma x'^2}{n-1} = \frac{933}{11} = 84.818$

$s^2(\bar{x})=\frac{s^2(x)}{n} = \frac{84.818}{12} = 7.068$

$s(\bar{x}) = \sqrt{7.068} = 2.66$

$\mu = \bar{x} \pm ts(\bar{x})$ $t_{0.05,11} = 2.201$

(Table 6,1, Volk)

$\mu = 2547.9 \pm 5.86$

with 0.05 probability of error, the true mean, is within the above range. Or this is the 95 % confidence range of the mean.

Length Measurements (19 measurements of the same sample)

1	51
2	52
3	51
4	51
5	51
6	50
7	49
8	52
9	51
10	50
11	49
12	51
13	52
14	49
15	51
16	48
17	51
18	53
19	51

$n = 19$

$\Sigma x = 963$

$\bar{x} = \frac{x}{n} = 50.68$

$\Sigma x^2 = 48.837$

$\Sigma x'^2 = \Sigma x^2 - \bar{x}\Sigma x = 48837-48804 = 33$

$s^2(x) = \frac{x^2}{n-1} = \frac{33}{18} = 1.833$

$s^2(\bar{x}) = \frac{s^2(x)}{n} = \frac{1.833}{19} = 0.096$

$s(\bar{x}) = 0.31$

$\mu = \bar{x} \pm ts(x)$ $t_{0.05,18} = 2.101$

$\mu = 50.68 \pm 0.652$ 95 % Confidence Range

2.2.4 Comparison of Random Duplicates of Greco-Latin

ΔL 10 - 10'

x_1	x_2	Δx	Δx^2
-3.0	4	-7	49
- .5	7	-7.5	56.25
10.5	8.5	2	4
16.0	13	3	9
21.5	16	5.5	30.25
26.0	21.5	4.5	20.25
27.0	18	9	81
27.0	21.5	5.5	30.25
33.5	19	14.5	210.00
		29.5	490.00

$\bar{x} = \frac{29.5}{9} = 3.27$

$\sum' x = 393.5$

$\frac{\sum' x}{8} = \frac{393.5}{8} = 49.2$

$\frac{49.2}{9} = 5.4$

$s(\bar{x}) = 2.3$

$t = \frac{|3.27-0|}{2.3} = 1.421$

$t_{8,0.05} = 2.306$

$\alpha = 0.05 \quad 0.01 < \beta < 0.05$

No significant diffirence

ΔL 16 - 16'

x_1	x_2	Δx	Δx^2
5	2	3	9
8	4.5	3.5	12.25
11	6	5	25
16.5	12	4.5	20.25
19	14	5	25
20	18	2	4
24	18	6	36
23	22.5	0.5	0.25
29		12	144.00
		31.5	275.75

$\bar{x} = \frac{31.5}{9} = 3.5$

$\sum' = 165.50$

$s^2(x) = \frac{165.50}{8} = 20.7$

$s^2(\bar{x}) = \frac{20.7}{9} = 2.3$

$s(\bar{x}) = 1.52$

$t = \frac{3.5}{1.52} = 2.3$

$t_{0.05,8} = 2.306$

$\alpha = 0.05 \quad \beta < 0.01$

ΔL 3 - 31

x_1	x_2	Δx	Δx^2
1	0.5	0.5	0.25
9.5	3.5	6	36
17	11.5	5.5	30.25
26.5	26.5	0	0
33	32.5	0.5	.25
37.5	39.5	-2	4
39.5	40.0	-0.5	0.25
41	37.0	4	16
46.5	39.0	7.5	56.25
40.0	34.5	5.5	30.25
		27.0	173.50

$\bar{x} = \frac{\Sigma x}{10} = \frac{27}{10} = 2.7$

$\sum x' = 100.5$

$s^2(x) = \frac{100.5}{9} = 11.65$

$s^2(\bar{x}) = 1.165$

$s(\bar{x}) = 1.08$

$t = \frac{2.7}{1.08} = 2.5$

$t_{0.02,9} = 2.821$

$\alpha = 0.02 \quad \beta < 0.01$

or $\alpha = 0.01 \quad \beta < 0.01$

$t_{0.01,9} = 3.250$

APPENDIX 3

Sample Procedure of Analysis

The calculation of the Young's Moduli from the measured resonance frequencies was done in IBM 1620 according to the Computer Program One given in the appendix.

It is mainly the evaluation of formula

$$E = CWN^2$$

Where W = weight

N = natural frequency

$$C = \frac{4\pi^2 L^3}{gIm^4}$$

Here L = length

I = moment of inertia

g = gravitational constant

m = a constant equal to 4.730.

Only C is corrected as $C = C'T$

$$\text{where } T = 1 + 81.79(r/l)^2 - \frac{1314(r/l)^4}{1+81.09(r/l)^2} - 125(r/l)^4$$

$$\text{for } \mu = 1/6 \text{ and } C' = \frac{4\pi^2 L^3}{8Im^4}$$

In put data to the computer consists of width, length, weight, vibrational frequency and damping frequencies. And Young's Modulus and internal damping are calculated out.

APPENDIX 4

Computer Programs One, Two, Three, Four

```
      PROGRAM  ONE
C     CALCULATION OF YOUNGS MODULUS OF CONCRETE BAR
C     B=WIDTH,U=LENGTH,W=WEIGTH
      DIMENSION NR(31),B(31),U(31),W(31),F(31),WW(31)
      READ 10,(NR(I),B(I),U(I),W(I),F(I),I=1,31)
   10 FORMAT(I5,4F10.4)
      CM=4.730
      PUNCH 500
      PUNCH 600
  500 FORMAT(45H   NR  YOUNGS MODULUS.                       )
  600 FORMAT(45H            PSI.                             ,//)
      DO 222 I=1,31
      A=B(I)*B(I)
      R=B(I)**4/12.
      S=B(I)**4/12.
      V=4.732*U(I)/(386.4*A)
      C=(39.438*U(I)**3)/(386.4*S*CM**4)
      AA=R/U(I)
      T=1.+81.79*(AA)**2-1314.*(AA**4)/(1.+81.09*(AA**2))-125.*AA**4
      CC=C*T
      WW(I)=W(I)/454.
      EE=CC*WW(I)*F(I)**2
      PUNCH 700,NR(I),EE
  700 FORMAT(I5,E20.8)
  222 CONTINUE
      STOP
      END
```

```
      PROGRAM  TWO
      CHANGE OF E
      GIVE INITIAL RESULTS FIRST
      DIMENSION NR(62),EE(62)
      READ 10,(NR(I),EE(I),I=1,62)
   10 FORMAT(I5,E20.8)
      PUNCH 500
  500 FORMAT(45H   NR            DELTA E                     )
      PUNCH 600
  600 FORMAT(45H                 PERCENT                     ,//)
      DO 222 I=1,31
      DEL=100.*(EE(I+31)-EE(I))/EE(I)
      PUNCH 700,NR(I),DEL
  700 FORMAT(I5,E20.8)
  222 CONTINUE
      STOP
      END
```

```
      PROGRAM THREE
      4X4 GRECO LATIN SQUARE VARIANCE ANALYSIS
      DIMENSION A(16)
      READ 100,(A(I),I=1,16)
  100 FORMAT (4F15.4)
      T1=A(1)+A(5)+A(9)+A(13)
      T2=A(2)+A(6)+A(10)+A(14)
      T3=A(3)+A(7)+A(11)+A(15)
      T4=A(4)+A(8)+A(12)+A(16)
      TTOT=T1+T2+T3+T4
      PRINT 200,TTOT
  200 FORMAT (F15.4)
      TTOTSQ=(T1)**2+(T2)**2+(T3)**2+(T4)**2
      STSQR=TTOTSQ/4.
      PRINT 200,STSQR
      P1=A(1)+A(2)+A(3)+A(4)
      P2=A(5)+A(6)+A(7)+A(8)
      P3=A(9)+A(10)+A(11)+A(12)
      P4=A(13)+A(14)+A(15)+A(16)
      PTOTSQ=(P1)**2+(P2)**2+(P3)**2+(P4)**2
      SPSQR=PTOTSQ/4.
      PRINT 200,SPSQR
      C1=A(1)+A(8)+A(10)+A(15)
      C2=A(4)+A(5)+A(11)+A(14)
      C3=A(2)+A(7)+A(9)+A(16)
      C4=A(3)+A(6)+A(12)+A(13)
      CTOTSQ=(C1)**2+(C2)**2+(C3)**2+(C4)**2
      SCSQR=CTOTSQ/4.
      PRINT200,SCSQR
      W1=A(1)+A(7)+A(12)+A(14)
      W2=A(3)+A(5)+A(10)+A(16)
      W3=A(4)+A(6)+A(9)+A(15)
      W4=A(2)+A(8)+A(11)+A(13)
      WTOTSQ=(W1)**2+(W2)**2+(W3)**2+(W4)**2
      SWSQR=WTOTSQ/4.
      PRINT 200,SWSQR
      CORR=((TTOT)**2)/16.
      SSQR=0.
      DO 10 I=1,16
   10 SSQR=SSQR+(A(I))**2
      T=STSQR-CORR
      P=SPSQR-CORR
      C=SCSQR-CORR
      W=SWSQR-CORR
      STPCW=T+P+C+W
      TOT=SSQR-CORR
      DIF=STPCW-TOT
      PRINT 100,CORR,SSQR,STPCW,DIF
      TMSQR=T/3.
      PMSQR=P/3.
      CMSQR=C/3.
      WMSQR=W/3.
      ERMSQR=DIF/3.
      PRINT200, TMSQR,PMSQR,CMSQR,WMSQR,ERMSQR
      FT=TMSQR/ERMSQR
      FP=PMSQR/ERMSQR
      FC=CMSQR/ERMSQR
      FW=WMSQR/ERMSQR
      PRINT400,FT,FP,FC,FW
  400 FORMAT (4F10.4)
      END
      STOP
```

```
      PROGRAM    FOUR
      T TEST FOR THE COMPARISON OF TWO MEANS
      DIMENSION A(6),B(6)
      READ 100,A,B
  100 FORMAT (6F13.4)
      ATOT=0.
      BTOT=0.
      PRINT 100,A,B
      DO 10 I=1,6
      ATOT=ATOT+A(I)
   10 BTOT=BTOT+B(I)
      AMEAN=ATOT/6.
      BMEAN=BTOT/6.
      PRINT 200, AMEAN,BMEAN
  200 FORMAT (2F15.4)
      ATS=0.
      BTS=0.
      DO 11 I=1,6
      ATS=ATS+A(I)**2
   11 BTS=BTS+B(I)**2
      ATDS=ATS-AMEAN*ATOT
      BTDS=BTS-BMEAN*BTOT
      AVR=ATDS/5.
      BVR=BTDS/5.
      PRINT 200,AVR,BVR
      PESD=SQRT((ATDS+BTDS)/10.)
      T=(AMEAN-BMEAN)/(PESD*0.5745)
      PRINT 300,PESD,T
  300 FORMAT (F15.4)
      STOP
      END
```

APPENDIX 5

X - ray Diffractions of the Four Additives

They are given in the envelope attached to inside of the back hard cover.

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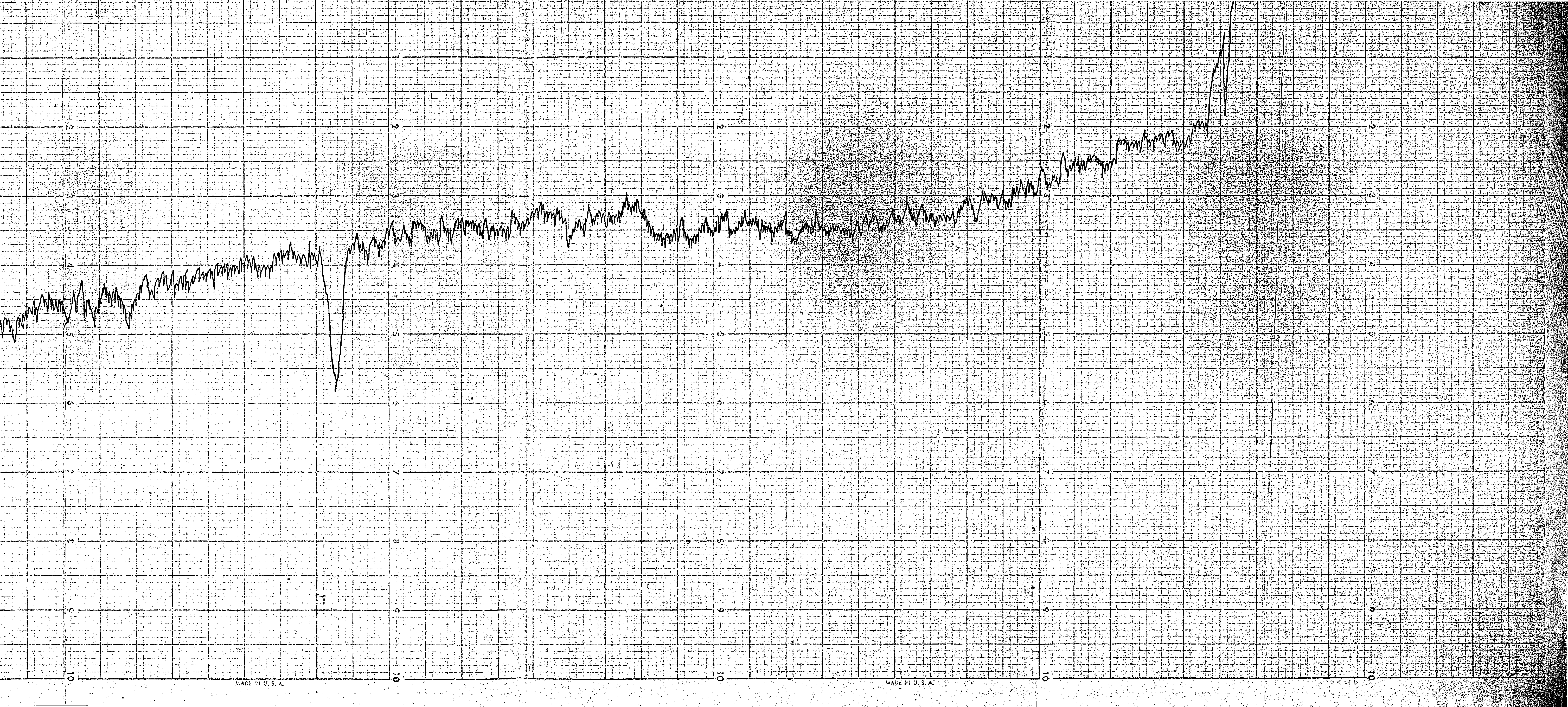
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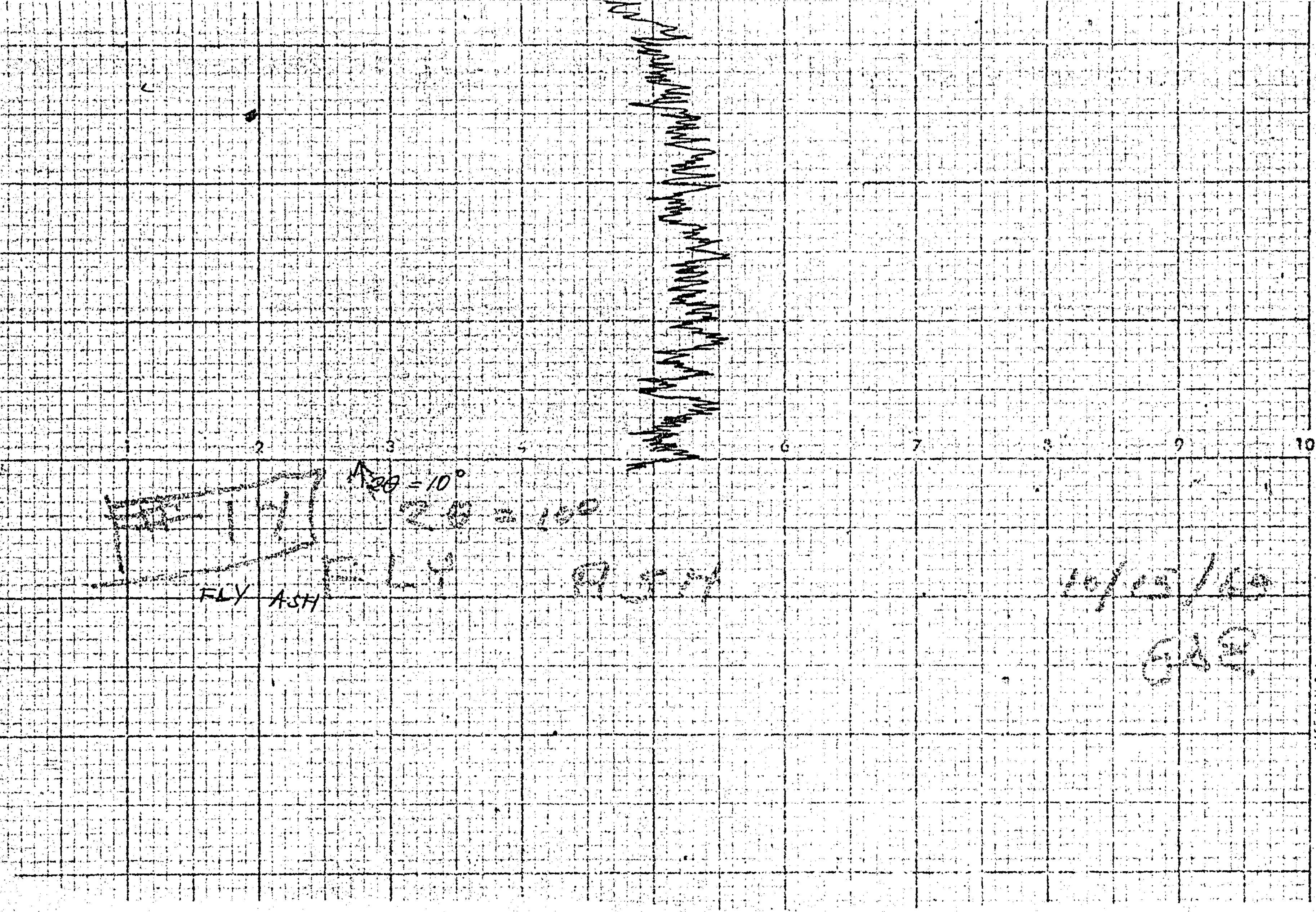2
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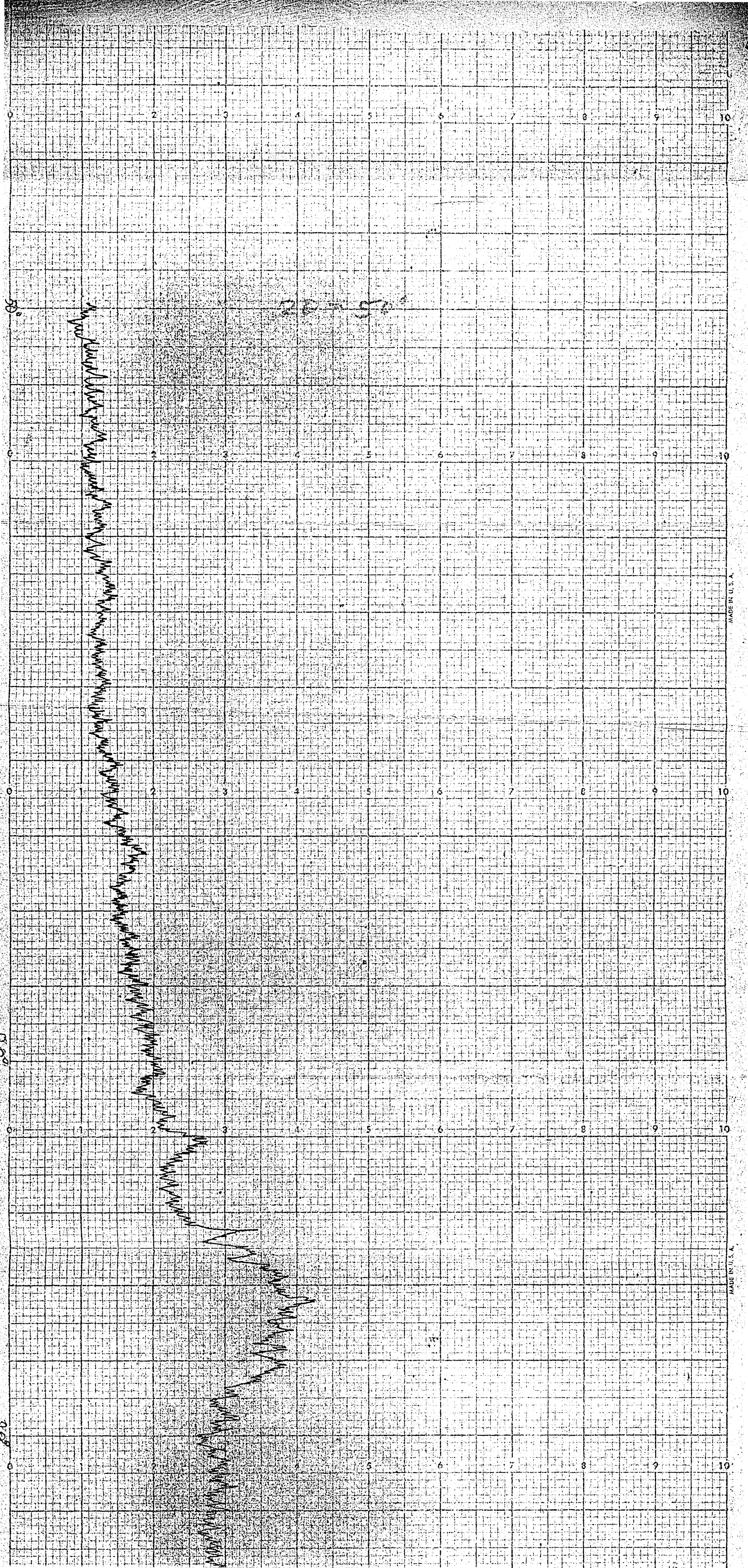
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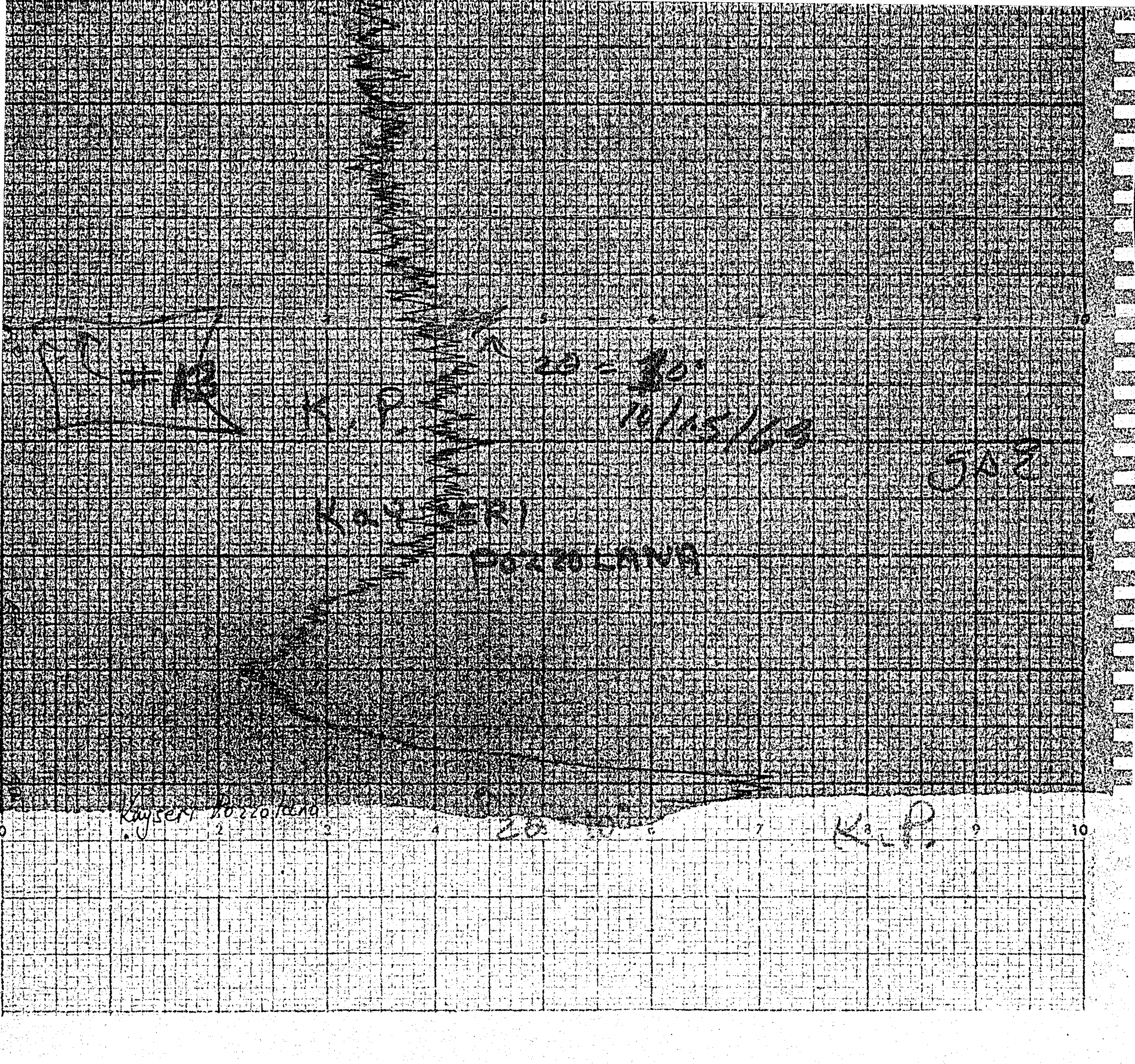
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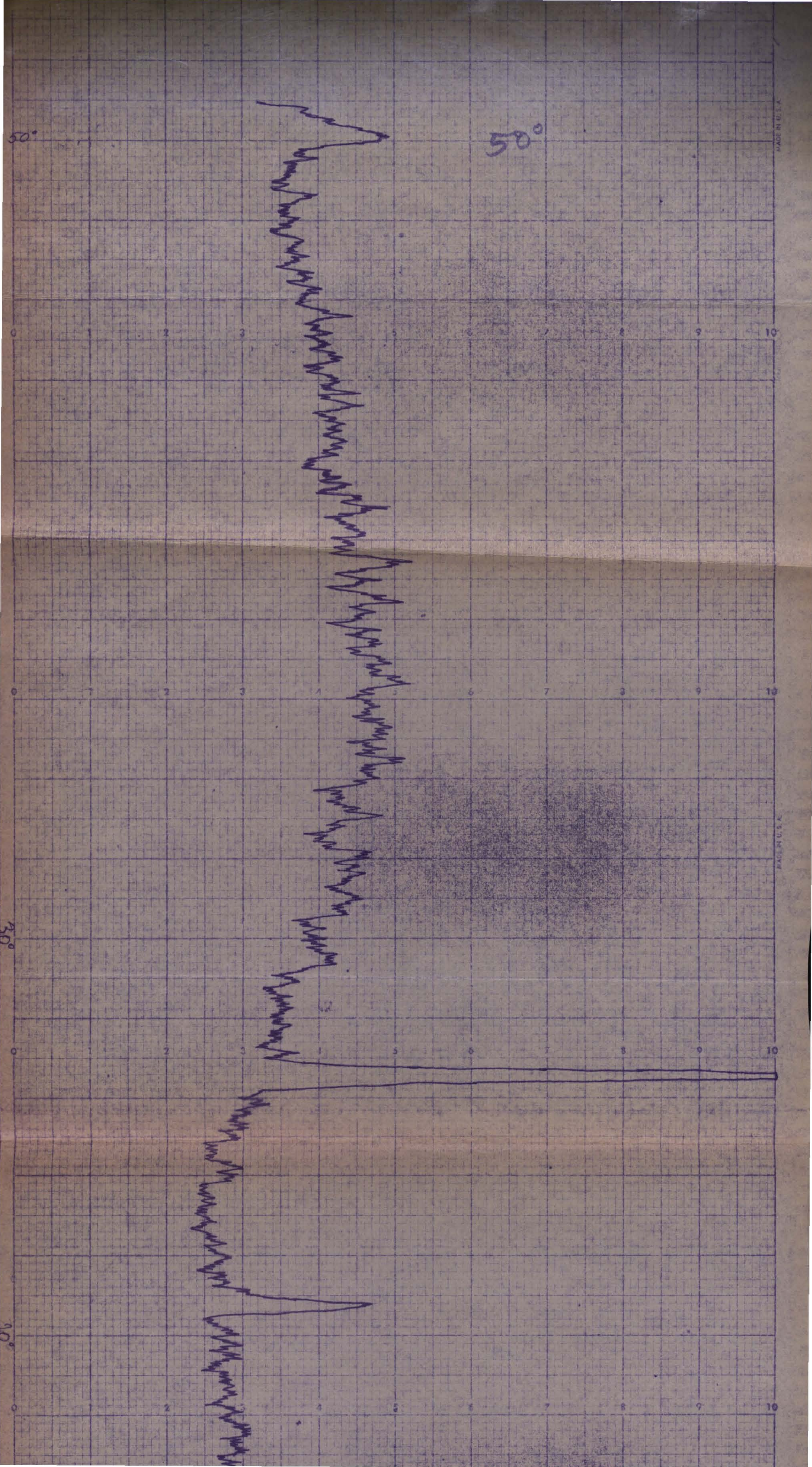
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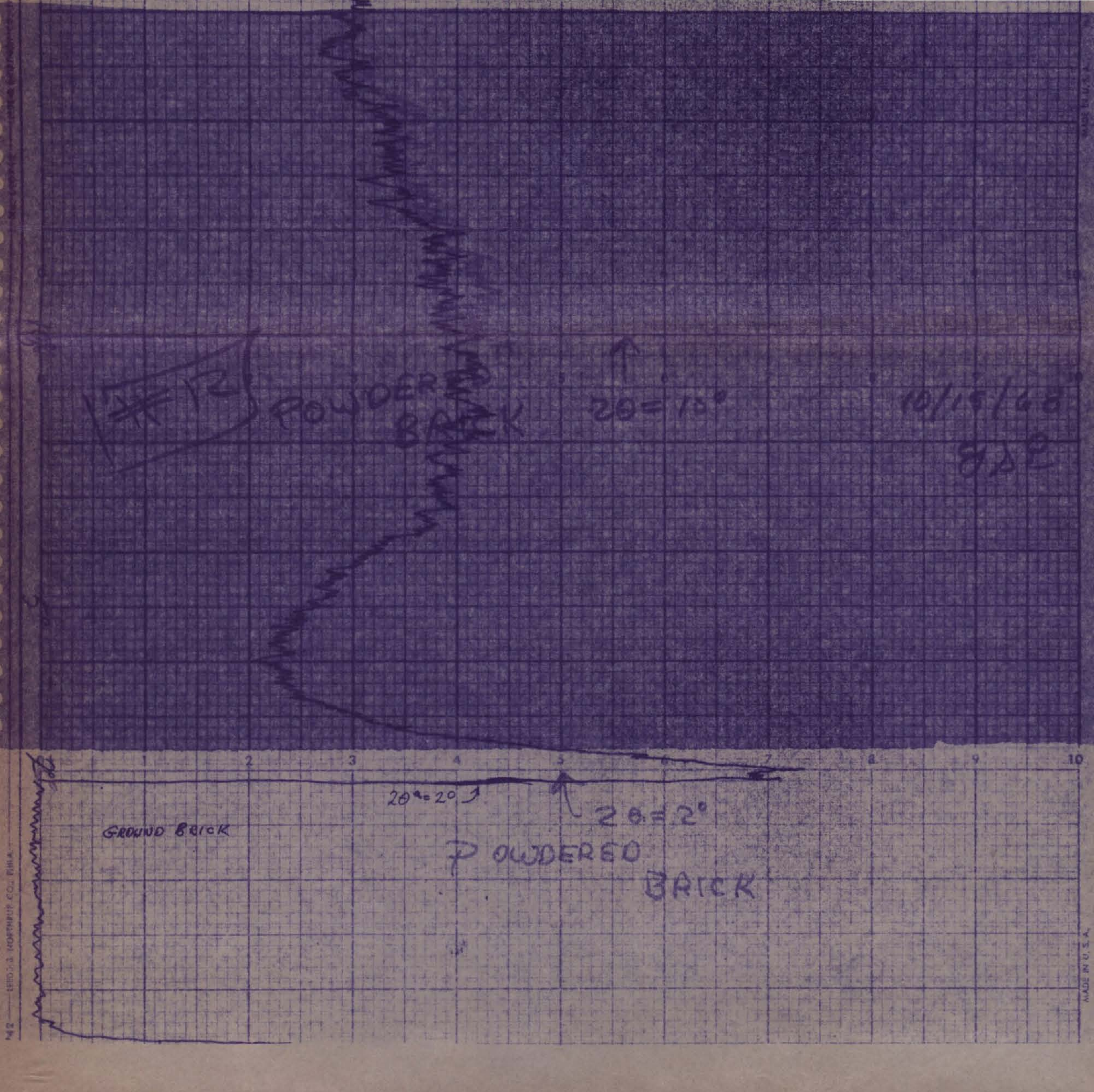
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POWDERED BRICK
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MADE IN U.S.A.
LEEDS & NORTHRUP CO. PHILA.

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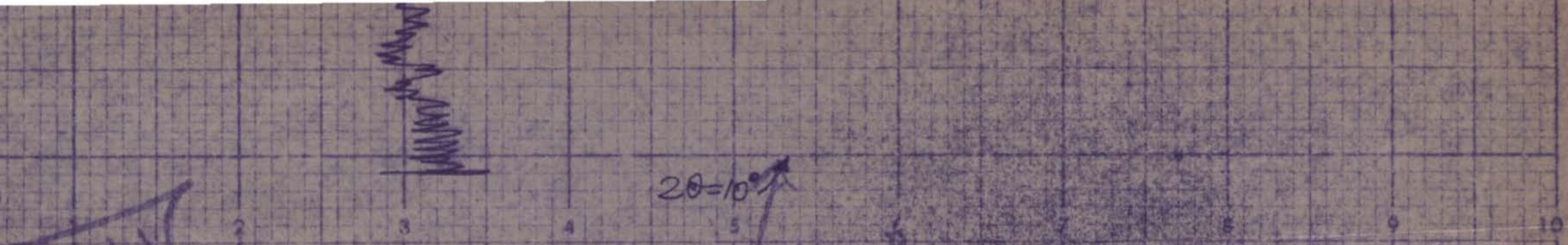

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2θ=10

BLAST FURNACE SLAG

BLAST FURNACE SLAG

10/15/68