

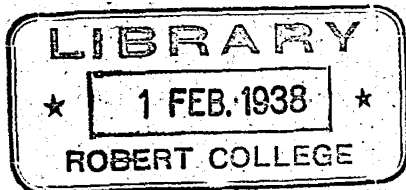
T H E S I S

on

The Corrosion in Sulphate Solutions
of Cements Used and Manufactured in
Turkey

by

Alexander M. Touritzin

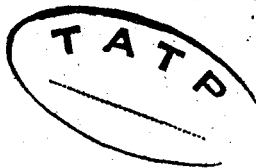


Submitted in partial fulfillment
of the requirements for the degree
of Bachelor of Science in
Civil Engineering (B.S. in C.E.)
from Robert College Engineering
School, Istanbul, Turkey.

1937



Special acknowledgement is due to Professor Edward S. Sheiry (S.M. in C.E.), Head of the Civil Engineering Department, for his valuable advice, and to Doctor Robert L. Fox (Ph.D.), Head of the Chemistry Department, for his guidance in cement analysis.



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PART I

INTRODUCTION

CHAPTER I

HISTORICAL

This paper contains the results of experiments, performed in the Material Testing and Chemistry Laboratories of Robert College Engineering School, concerning the effect of ammonium, magnesium and sodium sulphates on neat cement, and mortar specimens made of cements used and manufactured in Turkey.

Cementing properties of materials composed of calcareous and argillaceous substances were known so long ago that it is difficult to attribute to any people their discovery and first use.

Throughout centuries many engineering constructions built by Romans, Egyptians, Greeks, and Assyrians are still standing. The Pyramids of Ghiseh, for which a special mortar called "corrasan" was used, and about which we shall speak later, endured more than forty centuries. The exterior mortar finishing is not in good condition, undoubtedly because of the mechanical action of rain and sand abrasion. But the interior, in some parts, is still in good form.

Mortar used for the first Roman aqueduct, called Aqua Appia built about 312 B.C., and for the construction of the Anio Novas aqueduct completed about A.D. 52, exhibit in a high degree the skill of the ancient Romans in selecting the raw materials for their cements, without the resources of modern analytical chemistry.

However, ancient masonries with mortar joints were not all successful, and although many of the structures built in the days of Imperial Rome on earth and in sea water are still standing, the writings of Vitruvius (Roman architect who lived in the

first century B.C.) show that many failures occurred.

It is interesting to mention that in the middle of the eighteenth century, an Englishman called John Smeaton (1729-1792), the first man who called himself Civil Engineer, ("Civil Engineer" April 1937, Vol.7 No.4), after many experiments, followed Roman principles and used similar materials for the cement in the Eddystone Lighthouse, which stood for over one hundred years. But neither in the case of Roman cement nor in that used by Smeaton was the chemistry of the compound known.

In 1818, in France, Vicat proved that it is possible to manufacture artificial hydraulic lime. The first French Portland cement mill was built in 1850. Vicat was the first who studied cements for use in sea water. He discovered the fundamental principle of anticorrosive cements on which all the modern anticorrosive cement industry is built.

"A cement which would resist the chemical attack of sea water must be^{so} constituted, that when it sets, the lime released in the process of setting would all be combined with silica and alumina."

Many investigators followed Vicat, among them Le Châtelier, Candlot and Feret in France; Michaelis Burkhartz and Kuhl in Germany; Baykoff, Shoulashenko Droujinin in Russia; Van Kufflen in Holland; Paulsen in Denmark; Jeannenet in Switzerland; Luigi in Italy; De Castro in Spain; Day, Wright, Rankin in the United States; and many others. But we have to confess that in spite of extensive chemical investigations, there are still many questions concerning the nature of chemical substances produced by the ad-

dition of water to cement and that the changes that take place during the process of setting remain to be solved.

Each year, more and more papers are written and investigations are performed, data are constantly being accumulated. At the present time important researches are carried on with microscopic examinations and X-ray photography. By these means of investigation, together with chemical and mechanical analysis, we may expect in the near future the solution of the problem of resistance of cement to chemical corrosion. Only then will it be possible to design the composition of raw materials for cement which will resist certain undesirable solutions and definitely predict its life.

The rapid growth of industry in Turkey increased the use of concrete. More and more concrete is used for constructions in sea water (wharves, lighthouses, jetties, piers, piles, abutments, sea-walls), and in different branches of industry for pipes, storage tanks, decanters, etc. Engineers, who realized the effect of disintegration of materials made of cement and other aggregates (sand, crushed stones), started to advise the use of anticorrosive or special cements. Many new cements were imported from abroad, but their price, the present clearing system for foreign products, and the delay in their arrival limited their use. These facts favored the improvement of a process of manufacture of common Portland cement and the production of anticorrosive cements in natural conditions of construction as in sea water and alkali soils.

The author devoted the larger part of his time to investigations on cement mortars, and made only a few observations on the behavior of neat cement specimens in corrosive sulphate solutions. The results obtained in testing mortar and cement specimens may be applied to concrete, since its resistive capacity to chemical corrosion chiefly depends upon the quality of cement used, and, to a much smaller extent, upon coarse and fine ingredients which are inert and which work contrary to cement paste, which is usually the only element subjected to chemical changes.

Reinforced concrete is also subjected to attacks by cement corrosive agencies, but in addition, it may be destroyed by the corrosion of the reinforcement and the disruption of concrete from the bursting pressure of expanding reinforcement.

It seems certain that the rate of deterioration of concrete, all other factors being the same, is in proportion to permeability and porosity, but it was observed that concrete made of good cement seldom deteriorates seriously. In the report of the Committee on Marine Piling Investigations of the Division of Engineering and Industrial Research of the National U. S. A. Research Council, William G. Atwood and A. A. Johnson stated: "Some structures built with lean mixtures and the consequently comparatively porous concrete were reported to have been satisfactory. Such concrete is subject to disintegration by ice in the colder latitudes, but the cases where it has a

good service record in warmer waters seem to indicate that some binding media resist chemical attack, even though the water have easy access to the interior of the mass". ("Marine Structures", p.155, published by the National Research Council, Washington D.C.

To show the importance which must be attached to investigations on the resistive qualities of cements to chemical aggression, it is worth while to mention some failures caused by chemical agents. In Santa Monica, California, piles of the municipal pleasure pier have been succumbing to sea water attack since erection ten years ago. "Disintegration of concrete was so severe that concrete could easily be cut away with a knife. Steps are being taken to rebuild another, since the failure of piles means the failure of the pier". (Eng.News p.121-123, Vol.86 No.3 January 20, 1921). In another magazine, we find the description of the disintegration of several miles of the Gleen County concrete highway due to alkali-bearing waters mostly sodium and magnesium sulphates (Eng.News Vol.92 P.65-67, July 13). In the same article, Irving Furlong makes interesting observations on the effect of sodium sulphate on the crumbling of mortar between bricks of the Norman Warehouse in Gleen County. In "Marine Structures", the author gives many examples of concrete disintegration, which clearly show the necessity of the use of special anticorrosive cement for sea-water constructions, at least for considerations of economy. A concrete sea-wall about 450 feet long at Fort Lyon on the Maine Coast was built in

1905, and in 1922 75 feet of this wall were so deteriorated that it required immediate repair. A wharf at Fort Williams was built in 1908; in 1910 cavities began to appear, in 1912 some of the cavities had a maximum depth of about 6 inches; in 1918 repairs were made by removing disintegrated concrete, which required about 100 cubic yards of concrete. A concrete pier in Boston Harbor built in 1903, by 1919 was so eroded that a contract made with Dewey Cement Gun Company, who wished to repair it, was abrogated because, in the work of cutting away poor portions of concrete, the deterioration was found much deeper than originally expected, requiring large masses of new concrete to replace the old; granite facing was used for replacement of the deeply eroded section.

In European technical literature, the author also found many cases of concrete disintegration. Engineer A. G. Feodorovsky in the Russian magazine "Building Industry" No.6-7, 1931, gives an interesting example of the action of sea-water on concrete made of different cement. One part of Port-Arthur Harbor at Vladivostok was built in 1896-1898 and for that part cement from Novorossiysk Mill was used and in 1930 was in excellent condition. Another part of the harbor was built in 1915 with Japanese cement, which has completely disintegrated and has required many repairs.

According to Prof. Paulsen, who made several investigations in European Harbors, the life of concrete made of ordinary Portland cement is about 20-30 years, depending on the local climatic conditions.

Solutions used for testing cements are, as we have

said, ammonium, magnesium and sodium sulphates. They are very abundant in nature, in ground waters and surface waters and, therefore, may often be found in contact with concrete constructions.

Ammonium sulphate may derive its nature from:

- a) Decomposition of vegetable and animal organic matter
- b) Sewage effluent
- c) Fertilizer
- d) Coke and gas plants

Magnesium sulphate

- In ground water:
- a) from dolomitic limestone
 - b) nearly all silicate rocks of earth's crust contain magnesium

In sea water: By weathering, the silicate rocks yield up their soluble constituents. 1.7 gr. per liter.

Sodium sulphate

All igneous rocks, which contain a certain amount of sodium salts, are easily leached from the surface by the water.

Salts used for the experiment were chemically pure, being the product of E. Merck, Chemical Factory, Darmstadt.

In spite of the greatest accuracy and the care employed, using the apparatus in the Testing Material Laboratory, it is not claimed that numerical results of the experiments are of absolute value. They are only comparative, which is due chiefly to the extreme difficulty in taking absolute data on materials under disintegration.

CHAPTER II

CHEMISTRY OF PORTLAND CEMENT

The term of "Portland cement" is applied to the finely pulverized product resulting from the calcination to incipient fusion of an ultimate artificial mixture of argillaceous and calcareous materials.

Raw materials most commonly used are:

Argillaceous materials

1. Clay
2. Shale
3. Slate rock
4. Blast furnace slag

Calcareous materials

1. Limestone
2. Chalk
3. Marl

"Chemically speaking", cement is chiefly composed of:

Lime (CaO)	63-66%
Alumina (Al_2O_3)	22-23%
Silica (SiO_2)	5-6 %

To that, 2 to 3 percent of gypsum (CaSO_4) is added, which has the effect of lengthening the time required for cement to set.

The chief natural impurities of raw materials are:

Na_2O)	0.6%	MnO - 1%
K_2O)		
Fe_2O_3	4%	MgO - 1%

Sodium, potassium and magnesium oxides do not produce any effect whatever when they are in small quantities (less than 1%). A larger amount, however, gives a cement of inferior strength because of the too rapid fusion. Iron oxide exists in cement either as an impurity of the raw material, or added in the form of iron ore to regulate the fusion of clinker. The greenish-gray color of cement is principally due to iron oxide and manga-

nese oxide. A cement devoid of these two oxides would be pure white, but would offer no other advantage. Manganese oxide occurs in Portland cement not because it was added directly, but because it is found in iron ore.

We see that only lime, alumina and silica are the essential constituents of cement, and the destruction of one of these elements causes complete disintegration of the material, as we shall see later.

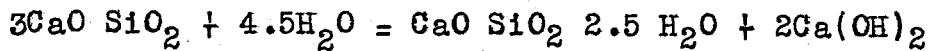
When cement is mixed with water alone or with water plus sand and gravel, cement takes an initial set within a few hours and thereafter hardens slowly through a period of months or years. What chemical actions take place during setting and hardening? The process is so complicated that many divergencies exist even among authorities on the matter. The many theories and opinions concerning chemical combinations among lime, silica, and alumina on the addition of water, may be divided into three groups:

I. Theory of Henri Le Chatelier (1887)

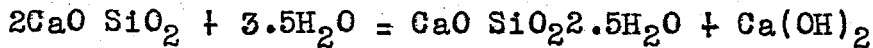
According to the eminent French investigator, Henri Le Chatelier, the setting and hardening of cements is due to the formation of crystals whose intermixture gives resistance to cement.

Under the action of heat in the rotary kiln, lime combines or fuses with silica and alumina giving calcium silicates and aluminates (clinker). Under the addition of water, the process of formation of crystals is as follows:

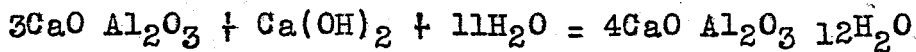
- a) Tricalcium silicate, reacting with water, produces monocalcium silicate and calcium hydroxide (hydrated lime).



- b) Bicalcium silicate on the action of water gives the same products.



- c) Tricalcium aluminate reacting with water and with calcium partly formed by the two previous reactions, gives:



Setting and hardening of cement is explained by Le Chatelier by the fact that the results of reaction $\text{CaO SiO}_2 \cdot 2.5\text{H}_2\text{O}$ and $4\text{CaO Al}_2\text{O}_3 \cdot 12\text{H}_2\text{O}$ are less soluble in water than the original products and therefore it crystallises.

II. Theory of Wilhelm Michaëlis (1892)

Michaëlis, the well known German investigator, explains the setting and hardening of Portland cement as a result of colloidal processes which take place during the setting. According to his theory, calcium silicates reacting with water produce an amorphous colloidal matter called "gel". The hardening of that amorphous gel, according to Michaëlis, results from the fact that the gel which is formed later absorbs the water from the gel which was formed previously, the latter gel losing its water solidifies.

III. Modern Theory of Setting and Hardening

Today, most scientists agree on the fact that during the setting of cement we have to consider two different formations: colloidal (Theory of Michaëlis), and crystalline (Theory of Le

Chatelier). That consideration may be explained as follows: Under the addition of water, cement grains react with it, giving calcium hydrosilicates, calcium hydroaluminate and calcium hydroxide, which are in colloidal state, but calcium hydroxide, being more soluble than the two other components, crystallises, while calcium hydrosilicate and calcium hydroaluminate remain in their original colloidal state. The result of this is a crystallo-colloidal system, a special reinforced concrete, where the role of skeleton is taken by the crystals.

Causes of Corrosion:

Irrespective of the theory of the setting and hardening of Portland cement, we see that all authorities agree on the fact that calcium hydroxide forms after the Portland cement has set. On the other hand, due to the lack of exact formula of chemical reaction, it is difficult to proportion raw materials to obtain a balanced reaction where all materials would react with each other, without leaving uncombined particles. According to Russian and German investigators, lime, which does not combine with silica and alumina to form silicates and aluminates, represents from 33 percent to 50 percent of the total lime in cement. According to American investigators, common Portland cement made in the U.S.A. after setting, leaves a residue of from 15% to 30% of free lime. Calcium hydroxide is the most objectionable constituent of cement:

- 1) because of the ease with which it combines with sulphate and chloride ions, which are very abundant in sea and under-ground waters, the result of that combination is the formation of crystals whose volume is greater than that of the volume of original

substances. These crystals occupy a larger volume and produce cracks. 2) Calcium oxide is easily dissolved by pure water giving lime water. At normal temperature one liter of water dissolves 2 grams of calcium oxide.

The presence of free lime in cement was observed by the author himself during an experiment made in the Robert College Testing Laboratory by A. Simuhine on the percolation of water under pressure throughout concrete specimens. On the face of concrete specimens which was exposed to the air opposite to that under water pressure, and from which water was outflowing, many white crystals were formed. These crystals were calcium carbonate resulting from the combination of calcium hydroxide and carbon dioxide from air. This example is a good illustration of the effect of ordinary water on chemically uncombined lime.

The presence of free lime in cement may also be easily shown by the following simple experiment. Into a glass beaker with pure water, add a few drops of phenolphthalein. The color of the water will not change, then drop a few grams of cement and immediately the water becomes pink (neutral and acid solutions remain colorless on addition of phenolphthalein solution).

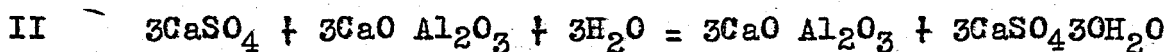
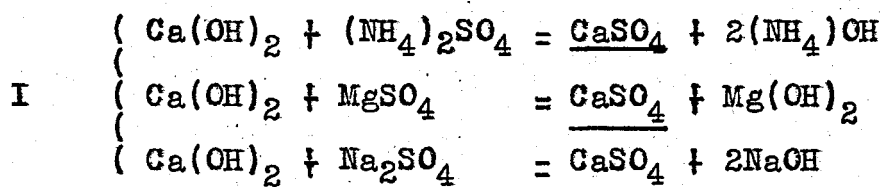
Removal of free lime from cement produces voids, thereby reducing the crushing strength of concrete, but what is worse is that tricalcium silicate, in the presence of a great amount of water, decomposes. This process, once commenced, continues until the concrete is reduced to a disintegrated mass of sand and other aggregates.

CHAPTER III

SPECIAL CEMENTS

The term of "special cements", is given by the author to those cements which were improved to counteract the effect of chemical corrosion.

On the previous pages we have seen that sulphate ions occurring in most natural waters react with free calcium oxide, producing crystals whose increase in volume produces cracks. The process of the formation of these crystals may be shown in two steps:



The first step shows that in the presence of sulphate-ions calcium oxide is changed to calcium sulphate (gypsum). Calcium sulphate is by itself a destructive agent, since calcium sulphate crystals occupy roughly 1.4 times the volume occupied by lime, resulting in the explosive effect of cement, mortars, concretes.

But very often the process is not limited by the formation of calcium sulphate crystals. Calcium aluminate resulting from the setting of cement reacts with the formed calcium sulphate producing a salt called calcium sulfoaluminate $3\text{Ca Al}_2\text{O}_3 + 3\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$, often called salt of Deval in European literature

and even sometimes "cement bacteria". This salt has a volume 2.5 times larger than that occupied by the free lime in cement specimens.

Therefore, in order to avoid its formation, we have first to reduce the amount of free calcium oxide, and second, avoid the formation of calcium aluminate. One method of reducing free calcium oxide is by adding to the cement powder, finely ground active silica, having the necessary qualities, and in proper quantities that, on setting, silica will combine with free lime and form insoluble compounds in sulphate solution.

The addition of silica to Portland cement or to lime, not only results in the formation of compounds, slightly affected by the attack of sulphates, but is also of considerable value in making the concrete more impervious. This action is supposed to be caused by the colloidal properties of silica which closes the pores of the concrete. More impervious concrete obtained by the use of silica admixture resists disintegration much better, by the formation of ice crystals within the concrete, than does the concrete in which silica is not used.

Siliceous materials, which are used for this purpose, are different in nature. The activity may be measured by the amount of lime which combines with a definite amount of silica in a certain period of time. Below we shall consider different admixtures used throughout the world for the purpose of increasing cement life in corrosive solutions. All special cements used for civil engineering constructions may be classified as:

I. Blended cements

1. Natural admixtures

- a) Pozzuolana
- b) Trass
- c) Diatomaceous earth
- d) Trepel

2. Artificial admixtures

- a) Argillaceous materials
- b) Sissof
- c) Ashes

II. Alumina cements

III. Slag cements

IV. Slag-Portland cements

V. Iron-Ore cements

VI. Super-Portland cements.

I. Blended Cements

Blended cements are called cements to which silica has been added.

1. Natural admixtures

a) Pozzuolana

During the process of volcanic eruption, beside masses of lava, which outflow from the crater directly on the earth, fine dust-like particles of lava under the explosive forces are tossed to the air. These particles, after travelling some distance, fall to the surface and form volcanic ash deposits. They may cover extensive areas and accumulate to considerable depths. In that way in 79 B.C. Pompei was covered by ashes from Vesuvius. If the secondary process under the earth does not affect the hydraulic properties of ash, it is called "pozzuolana", but all volcanic ashes

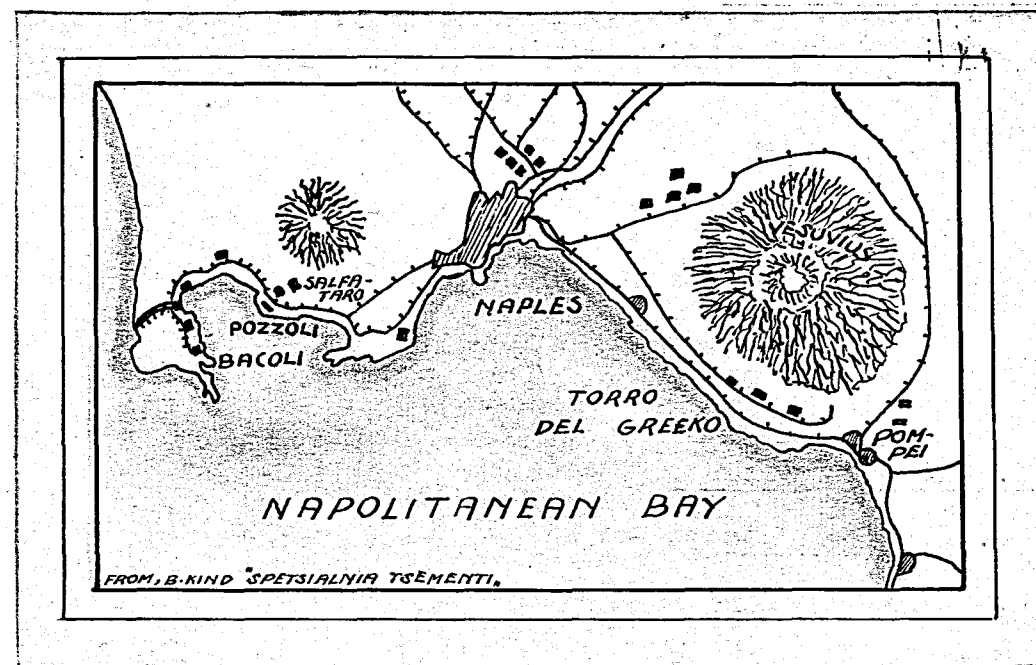


Fig.1 Neapolitan Bay
Places of puzzuolana quarriers are shown on the map in black rectangles.

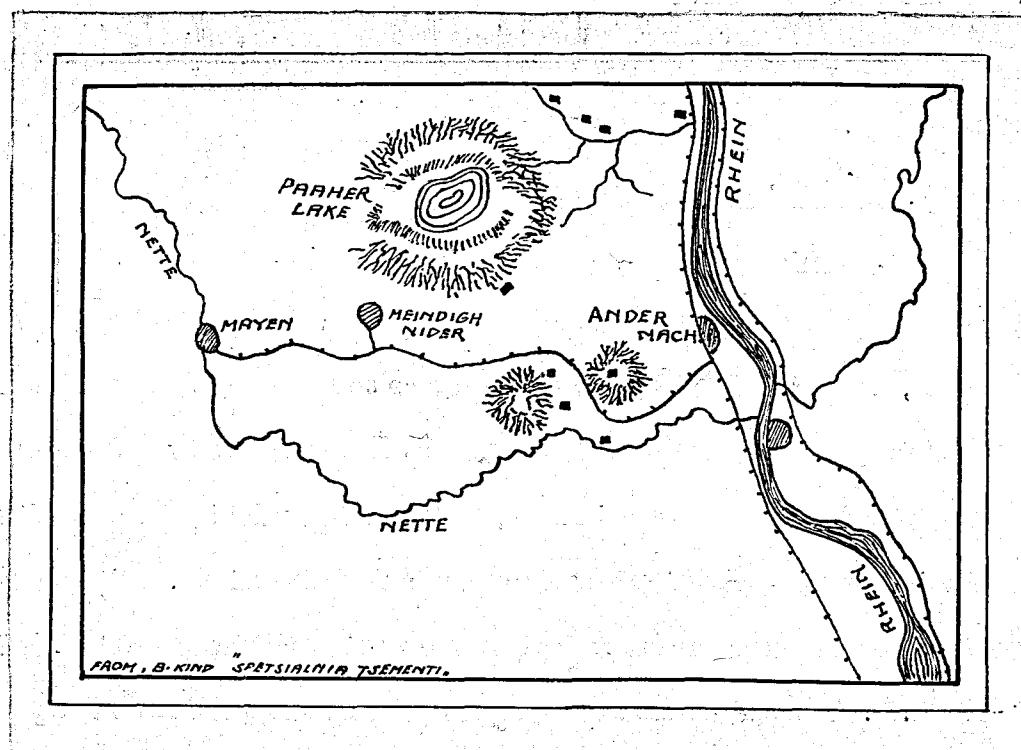


Fig.2 Region near Andernach Town.
Places of trass quarriers are shown on the map in black rectangles.

do not have puzzuolanic properties because they were subjected to certain transformations, which changed their properties.

Italian Puzzuolana:

Puzzuolana derives its name from a seaport Pozzuoli, in the province of Naples. At the present time puzzuolana is quarried near Pozzuoli and Boccioni (Fig.1). The strata of puzzuolana is also quarried near Rome some distance from the Laciala volcanoes, and also near the base of Vesuvius at Torro del Greeko (Fig.1).

Greek Puzzuolana or Santorin Earth

Santorin is a volcanic island in the Egean Sea, in the Southernmost part of the Sporades. Its ground is covered with tufaceous ashen agglomerates, its cliffs are made in horizontal bands by black lava, white porous tufa and other volcanic rocks. Before the World War (1914-1918), large amounts of Santorin earth were exported to Turkey. Today large quantities are sold to different countries, especially to those around the Mediterranean Sea.

French Puzzuolana

It is found in Auvergne.

Japanese Puzzuolana

In Japan, puzzuolana is quarried in Goto Island, and has the name of "Kasambay". Its color is brown red because of a large percentage of iron oxide. It is often used in that country for different underwater constructions.

North-American Puzzuolana

In the U.S.A. large amounts of puzzuolana are found in Nebraska. This puzzuolana was used successfully as silica admixture for cement in the construction of Niobrara Dam. For the

Los Angeles Aqueduct, puzzuolana from California was used. In "Marine Constructions" G. Atwood and A. Johnson state that for that Aqueduct silica was used as an economy, and not because of its ability to resist attack by sulphates. This work is in excellent condition, while concrete in the Elephant Butte Dam and Arrowrock Dam is not as good. In these two latter structures, ground granite was used as a substitute for siliceous materials, while in the former, volcanic tuff. For Bonnevill Spillway Dam Portland cement with puzzuolana admixture was used. Puzzuolana was dredged from San Francisco Bay but, before blended with the clinker and gypsum, was calcined at about 1650°F ("Engineering News Record", February 11, 1937; Vol.118 No.6).

Russian Puzzuolana

In Russia, puzzuolana occurs in two places: one in the Crimea near Kara Dag Mountain, 18 km. from Feodosia, and the other, recently found, at Nalchik near the base of Elbrous Mountain. Puzzuolana occurs also near Nouhi in Azarbaydjan. In 1913 Crimean puzzuolana was used for the construction of Tuapse Harbor on the Black Sea.

b) Trass

The origin of trass is also volcanic, but it differs from puzzuolana because of its older origin. Its structure is more compact than that of puzzuolana, which is rather granular. Puzzuolana found near Vesuvius is so granular that 60% of its particles are larger than 2 mm. in diameter.

German Trass

Deepest stratas of trass occur near Andernach in Germany

(Fig.2). In European technical literature, it is commonly called "Trass from Rhein". In spite of the fact that it was used by the Romans for the construction of an aqueduct from Trir to Keln, and for the Mosel Bridge construction, its hydraulic properties started to be appreciated only in the XVII century and only a few years before the World War did German engineers make a complete study of it. Now it is extensively employed in Germany for hydraulic works: the Gestemunde and Bremenghawan canals and Schwartzbach Dam are built with concrete of Portland cement mixed with Rhein trass.

Hollanden Trass

In Holland, trass is recognized as the most efficient means of preventing concrete disintegration in sea water. Several harbors are built with Portland cement with trass as silica admixture.

Russian Trass

In Russia, trass occurs in the Crimea; it has been used since 1914 for the manufacture of Novorossiysk puzzuolanic cement.

Armenian Trass

It occurs near Tadjiraback; its activity is much lower than that of Crimean trass.

c) Diatomaceous Earth

Diatoms are minute unicellular plants belonging to the Algae group and living in fresh and salt water. Their soft vegetative parts are covered by a siliceous core which is secreted by the plant itself. They are so small that they are undiscernible to the naked eye. Some notion may be formed of the extreme

minuteness of these plants from the fact that the length of 1/200th of an inch may be considered as beyond the medium size (Fig.3). Diatoms are most abundant in cold latitudes, having a general preference for cold water. They are very abundant in the Arctic and Antarctic Oceans. Not only are these minute plants assisting at the present time in the accumulation of oceanic and lake deposits, but in former ages they gave rise to considerable deposits of diatomaceous earth. When the plant has fulfilled its natural course, the siliceous covering sinks to the bottom of the water in which it has lived, forming sediments, which harden into solid rocks. This earth is generally of a white or gray color. Much of this sediment is of economic importance, being used as polishing powders, absorbents for nitroglycerin in the manufacture of dynamite, and dentifrice powders. They are also used to a large extent in the manufacture of non-conducting and sound-proof materials. In geological classifications, they are usually associated with rocks of tertiary formation.

In the U.S.A.

Vast deposits of Diatomaceous Earth are found in Richmond (Virginia) and are widely used for underwater constructions.

In Denmark

In Denmark diatomaceous earth is considered as an excellent binding material for free lime. "Aalborg Company" manufacture a Portland cement using diatomaceous earth as silica admixture.

In Russia

It occurs in vast quantities near Novgorod, Kamishlov and in Georgy.

Diatomaceous earth is also quarried in France, Scotland, Germany, Algiers, Japan, etc.

d) Trepel

Trepel or Tripoli differs from diatoms by the fact that under the microscope, the fossil of living organisms is not seen. Trepel is formed of amorphous siliceous material with grains from 0.0025 to 0.0050 millimeter.

The origin of Trepel is yet unknown. According to the American scientist, Trepel is a result of the purely natural disintegration of calcium silicates. Russian investigators derive its origin from diatoms whose siliceous material under the geological processes melted and solidified into an amorphous state (calcareous period). In any case, trepels are considered more active than diatomaceous earths. Beside its use as a binding material for free lime in cements, it is largely used for the same purposes as diatomaceous earths. In the U.S.A. it is found in Missouri, and in Russia near the Ural Mountains and Georgy. Two Russian cement mills manufacture Portland cement with trepel as admixture. Before its use, diatomaceous earth must be subject to calcination because of the organic materials that it contains, while trepel does not require such treatment and, therefore, is much preferred to the former.

2. Artificial admixtures

a) Argillaceous materials

Clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) by itself cannot be called a siliceous admixture due to the fact that silica, being chemically com-

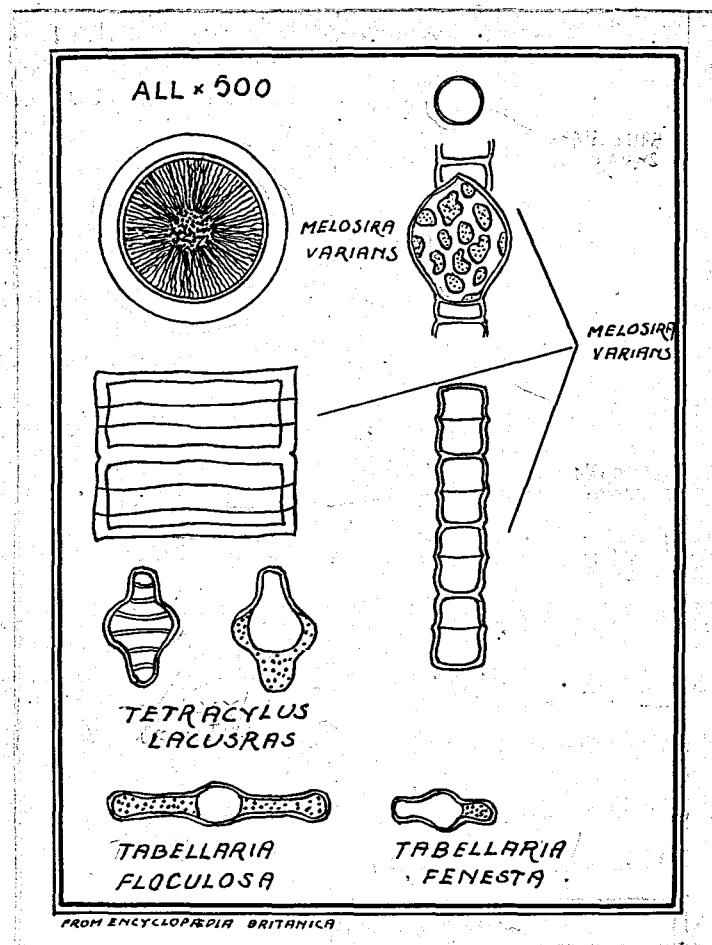


Fig.3 - Some features of diatoms under the microscope

bined with alumina, is not in as free a state as the natural siliceous admixture. But clay burnt between 600°C and 800°C gains its hydraulic properties, because between these temperatures clay is dissociated into alumina and silica. Silica being in a free state, easily combines with free calcium with the addition of water. If clay is burnt at a temperature higher than 800°C , the hydraulic properties of clay are largely decreased, because at a high temperature, dissociated alumina and silica have a tendency to combine again by melting.

In Turkey and the Orient

Before the World War in Asia Minor a special admixture was used together with sand and lime for concrete making, this admixture being called "Corrossan". With the addition of water, it had cement-like hydraulic properties. Corrossan is the name given to an artificial puzzuolana which is made by grinding burnt clay tiles and bricks. Cement made with the resulting powder is called in France "Ciment de Tuileaux"; the Greeks call it "Korassani"; the Arabs "Homra", and the Turks "Corrossan". According to A. M. Raymond ("L'art du constructeur en Turquie", Alexandrie 1908), mortar made with corrossan, sand and lime, because of its plasticity, is much more appreciated for the construction of brick arches and minarets in the Orient, than the mortar made with cement. In addition, for a long time corrossan was a substitute for Portland cement in Turkey. It was largely used by the famous Turkish architect Sinan in buildings, fountains, reservoirs, baths, etc. The author of the above mentioned book states that corrossan was used for the construction of the Ghizeh pyramids. Archeological ex-

cavations proved that it was commonly used by the Assyrians in building their towns. Many traces of its use before the Christian era are left in Greece, Palestine and Mesopotamia. In some parts of these countries it is still used. In the construction of Sennar Dam on the Nile River, Egyptian Sudan (39.9 m. high and 302.5 m. long), in 1922-1926 "red cement" was used. This cement was composed of 70% Portland cement and 30% burnt and ground clay. But special care must be taken in selecting and burning clays because, as we mentioned above, such an admixture, if not properly prepared, may produce a very slight protective effect against corrosion.

b) Sistoff

Sistoff is a German compound name and is derived from si-(silicium) and stoff(matter) This name is given to silica which remains from clay after the alumina is extracted for the purpose of manufacturing aluminium. Sistoff is a very active product for free lime binding. In Russia it is commonly used by cement mills built near centers where aluminium is extracted from clayey ores containing a high amount of it.

c) Ashes

Ash obtained by burning brown coals and certain slates may be used as silica admixture for Portland cement in making blended cements. In Germany such a cement is called "Cement Urament". Some cement mills around Moscow commonly use it for the same purpose. In the U.S.A. ashes are not used to such a large extent as in Russia and Germany. At the present time, Prof. R.E. Davis of the University of California is doing extensive investigations on the use of fly ash from powder coal plants as silica

admixture (See Report of American Concrete Institute Meeting "Engineering News-Record", March 4, 1937, p.340-341).

Strength and durability of blended cements

In general blended cements show a higher strength at the end of 28 days than the ordinary Portland cement, but its chief advantage is its highly relative resistance to sulphate attack. This property is of more importance for certain constructions than high strength. However, blended cements are slowly setting and hardening cements; that unfavorable property is caused by silica added to bind free lime. It was found by European investigators that the more active a silica admixture is, the quicker the cement sets and hardens. In spite of its lower price, many contractors prefer ordinary Portland cement because of its relatively ^{fast} setting and hardening qualities.

II. Alumina Cements

"Alumina cement", "Alca cement", "Ciment Fondu", or "Ciment Electrique" are the names given to a cement manufactured from aluminium ore, called "bauxite".

Alumina cement was invented by Colonel Henry Spackman in 1908 and before the World War was used to some extent in the United States. In Europe, and especially in Germany, engineers were sceptical about its special qualities. But in France independently of H. Spackman, Jules Bied (inspired by the famous French investigator Vicat), searching for a cement which would not liberate free lime, made the discovery of alumina cement. Vicat in 1857 had found a ratio of elements which combined together gave a cement which would not be disintegrated in sea water. Some years later,

in 1913, the "Teil" cement mill was reorganized and J. Bied started its manufacture under military control. So, before the Great War, alumina cement in France was only known by military forces which kept the process and the manufacture as a military secret. Its first practical use (according to the Lafarge cement company, which manufacture it at the present time in France) was in 1916 on the French front during the World War. It was used by the French army for rapid work on gun emplacement, roads and bridge repairs, while it was totally unknown by the German military forces. Germans wondered how French engineers in Verdun could repair in one night fortifications which had been destroyed by their artillery during the previous day.

It is only in 1918 that alumina cement appeared on the market. The famous Vicat ratio later called hydraulic and chemical resistance modulus is:

$$\frac{\text{SiO}_2 + \text{Al}_2\text{O}_3}{\text{CaO}} > 1$$

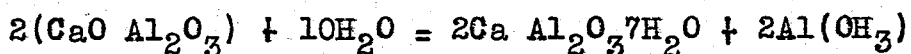
That is, in order to obtain a cement which will not be readily affected by destructive agents, it is necessary to increase silica and alumina and on the other hand decrease calcium oxide to such relative proportions as to obtain a ratio larger than one.

In our discussion on blended cements, we saw that we could increase silica by using special admixtures, but at the same time the time of set decreased proportionally. Jules Bied had the idea of increasing alumina, using clay with high alumina content (40-75%). Cement obtained as the base of that admixture showed quick setting and hardening properties, with three days

strength equal and even superior to that of the best Portland cement tested after 28 days. In 24 hours alumina cement acquires a strength of 75% of its ultimate 28-day strength. Tests made after a period of eight years, showed even a greater increase in strength.

The process of the manufacture of alumina cement is different from that of Portland cement. Aluminium ore and lime stones are fused in a blast furnace or in an electric furnace instead of being clinkered in a kiln. The manufacturing process and raw materials, especially aluminum ore (bauxite), are more expensive than those for the common Portland cement. The cost at the present time (1937) is about three times as much in France as that of Portland cement; in Turkey it is four times as much.

The process of setting under water addition is not yet well understood, but many investigators state that the chief reaction is as follows:



Alumina cement does not liberate calcium oxide as Portland cement does, but liberates gelatinous alumina $\text{Al}(\text{OH})_3$, which is not easily corroded by sulphates.

III. Slag Cements

Slag cement is the product obtained by grinding together powdered slaked lime and granulated blast-furnace^{slag}/without previous calcination. The slag cement should not be confused with Portland cement, for which blast-furnace slag is used as an ingredient. Blast-furnace slags, suitable for the use of slag cements, are fusible lime silicates derived as waste products from the operation of blast-furnace in smelting iron from its ore.

Slag is formed for the most part by the combination in the furnace of earthy parts of the ore, e.g. the "gangue" with lime from limestone, which is charged into the furnace as a flux.

This cement is likely to contain so much sulphur in the form of sulphides as to make it unfit for use in the air, since, on exposure, sulphides change to sulphates and, in so doing, expand; and hence such cements are liable to destroy the structure. But slag cement is an excellent cement under water and in other places where it is constantly exposed to moisture.

Slag cement was first made in 1866 in Europe and appeared on the market in 1878. Slag cements are slow hardening cements and, therefore, are not very much appreciated by contractors. In any case, it was used in the United States in several important works and is still commonly used there and in Europe for sea water constructions.

IV. Slag-Portland Cement

Slag-Portland cement is the product of calcination of Portland cement clinker and metallurgical iron slag. In Germany slag-Portland cement, which contains up to 30% of slag, is called "iron-Portland cement" and that which contains 30-85% of slag is called "blast-furnace cement".

Slag-Portland cement has the same anticorrosive properties as slag-cement. These properties are due to the high content of silica and alumina in slag which bind a large amount of free lime. In Germany slag-Portland cement was used for the construction of Gesterkunde Harbor, for military fortifications on Vangeroug Island and for several other underwater constructions. Its

chief disadvantage is that it is a slow setting and hardening cement.

V. Iron-Ore Cement

Iron-ore cement is made by fusing in a rotary kiln limestone and iron-ores. Laboratory investigations showed that it has high resistive properties to chemical aggression. It was first manufactured in 1901 in Germany. Iron-ore cement was used on a large scale for constructions of harbors in the North and Baltic Seas. It is also manufactured to some extent in the United States.

VI. Super Cement

Super cement is the ordinary Portland cement with improved hydraulic properties. It sets and hardens much more quickly than the ordinary Portland cement. That improvement is due to an extra addition of lime and a very fine grinding of the clinker. The addition of extra lime, however, may decrease its resistance to chemical attacks.

PART II

. ANALYSIS OF MATERIALS USED IN THE THESIS

CHAPTER I

CEMENTS

Cements and their chemical analysis

At the time of the investigations, described in the subsequent chapters, ^{and} which had been started in October 1936, seven different Portland cements were in use in Turkey for civil engineering constructions:

<u>Quality</u>	<u>Place of Manufacture</u>	<u>Trade Name</u>
1. Common Portland	Kartal, Vilayet of Izmit	"Yunus"
2. Common Portland	Daridja-Eskihisar, Izmit	"Aslan"
3. Common Portland	Zeytin Burnu, Istanbul	"Aslan"
4. Super Portland	Kartal, Izmit	Super "Yunus"
5. Super Portland	Daridja-Eskihisar, Izmit	Super "Aslan"
6. Blended Portland	Daridja-Eskihisar, Izmit	"Aslan" with tras
7. Alumina Cement	Le Teil, Ardèche, France	"Lafarge"

All these cements, except the two super cements and one blended cement, may be easily found on the market in Istanbul (center of cement manufacture). The other three have a limited use because of their special properties and higher price (10% more expensive than ordinary Portland cement). To obtain them, one must send an order to the company in advance.

Chemical analysis of cements were carried out in the Robert College Chemistry Laboratory, with the help of Doctor R.L. Fox, Head of the Chemistry Department. Chemical analysis renders valuable service in the detection of adulteration of cement with considerable amounts of inert material, and also the presence of

magnesium oxide and sulphur anhydride which may be in inadmissible proportions.

The method of analysis was taken partly from "Quantitative Analysis" by Mahin, especially for the determination of silica, alumina, and iron oxides, partly from Russian standard specifications of cement testing, for calcium and magnesium oxides determination. This combination was made to obtain a method which would give a quick and efficient procedure of cement analysis. Because of its special character, it is given in the Appendix.

The results of the analysis of cements are given in the table of Results. They represent the average of the two analyses.

According to the Turkish specifications of Portland cement, good Portland cement must satisfy the following conditions:

a) The hydraulic modulus must be more than or at least equal to 2:

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \geq 2$$

b) Sulphur anhydride be equal or less than 2.5% by weight

c) Magnesium oxide less than 4.00% by weight

Normal consistency of cements and mortars

The determination of normal consistency of cements was performed with the Vicat apparatus according to the standard specifications of A.S.T.M. The normal consistency is defined as the percentage of water by weight, which must be added to a cement to give a penetration of 10 mm. below the original surface of the paste with the Vicat rod in 30 sec. after being released.

The normal consistency of mortars (1:3 by weight) was determined from the normal consistency of cements by use of table

made by means of Feret formula.

$$W = \frac{2P}{3(S+1)} + K, \text{ where}$$

- W - percentage of water to obtain a mortar of normal consistency.
P - percentage of water to obtain a normal consistency of neat cement.
S - number of parts of sand in mortar.
K - Constant, depending on the character of the sand (taken as 6.5 in usual tables for standard mortars).

Table of percentage of water for standard mortars

For neat cement paste

For 113 mortars of standard Ottawa sand

18	9.5
19	9.7
20	9.8
21	10.0
22	10.2
23	10.3
24	10.5
25	10.7
26	10.8
27	11.0
28	11.2
29	11.3

The results of the determination of normal consistencies of Turkish cements and mortars with Florya sand are given in the Table of Results.

Fineness of grinding of cements

The determination of the fineness of grinding of cements was performed according to the standard specifications of A.S.T.M.

The fineness is expressed in terms of percentage of a 50-gr. sample which is retained on a No.200 sieve.

Cement	WT in gr. of cement retained on # 100 sieve	WT in gr. of cement retained on # 200 sieve	WT in gr. of cement passed thru # 200 sieve	Check weight gr.	Fineness
Kartal "Yunus" Common	0.183	7.199	42.603	49.985	14.39
Daridja Eskihisar "Aslan" common	0.431	9.528	40.031	49.990	19.02
Zeytin Burnu "Aslan" common	0.131	18.627	31.211	49.979	37.12
Kartal "Yunus" Super	0.097	5.660	44.240	49.997	11.32
Daridja Eskihisar "Aslan" super	0.102	5.271	44.615	49.988	10.54
Daridja Eskihisar "Aslan" blended	0.118	7.710	42.168	49.996	15.42
Alumina cement "Lafarge"	0.098	5.291	54.607	44.995	10.58

The residue on a standard No.200 sieve shall not exceed 22% by wt., if a cement is to meet the A.S.T.M. specifications.

Tensile Strength of Mortars

The tensile strength test, was performed according to the standard specifications of A.S.T.M.

Briquettes of one square inch cross section were prepared with 3 parts of Florya Beach sand, one part of cement by weight, with the percentage of water that would give normal consistency.

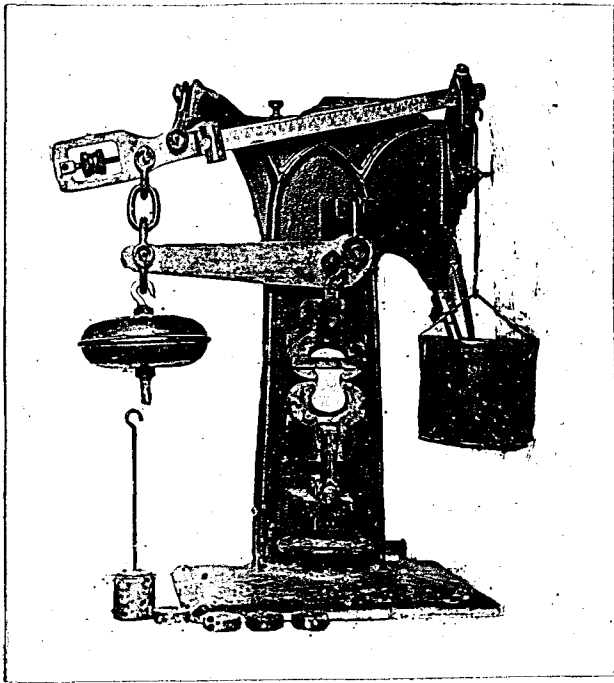


Fig.4 - Fairbanks Testing Machine

Briquettes were tested by a Fairbanks Tension briquettes testing machine at one day in moist air and one day in water; one day in moist air and six days in water; one day in moist air and 27 days in water.

Tensile Strength of Mortar Specimens

		<u>2 days specimen</u>		<u>7 days specimen</u>		<u>28 days specimen</u>	
Mortar (1:3) :		Tensile :		Tensile :		Tensile :	
with Florya :		strength in:		strength in:		strength in:	
Beach sand :		lbs.per	Aver-	lbs.per	Aver-	lbs.per	Aver-
and cement. :		sq. in.	age	sq. in.	age	sq. in.	age
Kartal	) :	111	:	232	:	273	:
"Yunus"	) :	117	:	241	:	254	:
common	) ::	114	:	224	:	260	:
cement	) :	113	114	219	229	285	268
Daridja-	) :	109	:	245	:	296	:
Eskihisar	) :	112	:	240	:	287	:
"Aslan"	) :	116	:	243	:	292	:
common	) :	107	111	236	240	301	294
cement	) :						
Zeytin Burnu)	:	57	:	140	:	196	:
"Aslan"	) :	59	:	143	:	210	:
common	) :	53	:	144	:	195	:
cement	) :	61	57	137	141	189	197
Kartal	) :	137	:	302	:	342	:
"Yunus"	) :	145	:	334	:	317	:
super	) :	139	:	285	:	353	:
cement	) :	146	142	291	303	350	340
Daridja-	) :	138	:	239	:	368	:
Eskihisar	) :	129	:	322	:	341	:
"Aslan"	) :	135	:	304	:	374	:
super	) :	136	135	313	319	367	360
cement	) :						
Daridja-	) :	48	:	372	:	421	:
Eskihisar	) :	46	:	361	:	397	:
"Aslan"	) :	49	:	365	:	381	:
Blended	) :	44	47	357	364	416	404
Alumina	) :	283	:	321	:	357	:
cement	) :	275	:	316	:	343	:
Lafarge	) :	268	:	318	:	354	:
	:	273	260	325	320	350	351

Compressive Strength of Mortar Specimens

Compressive strength test was performed according to the standard specifications of A.S.T.M.

Cubes of $2\frac{3}{4} \times 2\frac{3}{4} \times 2\frac{3}{4}$ inches were prepared with 3 parts of Florya Beach sand, 1 part of cement by weight, with the percentage of water that would give normal consistency.

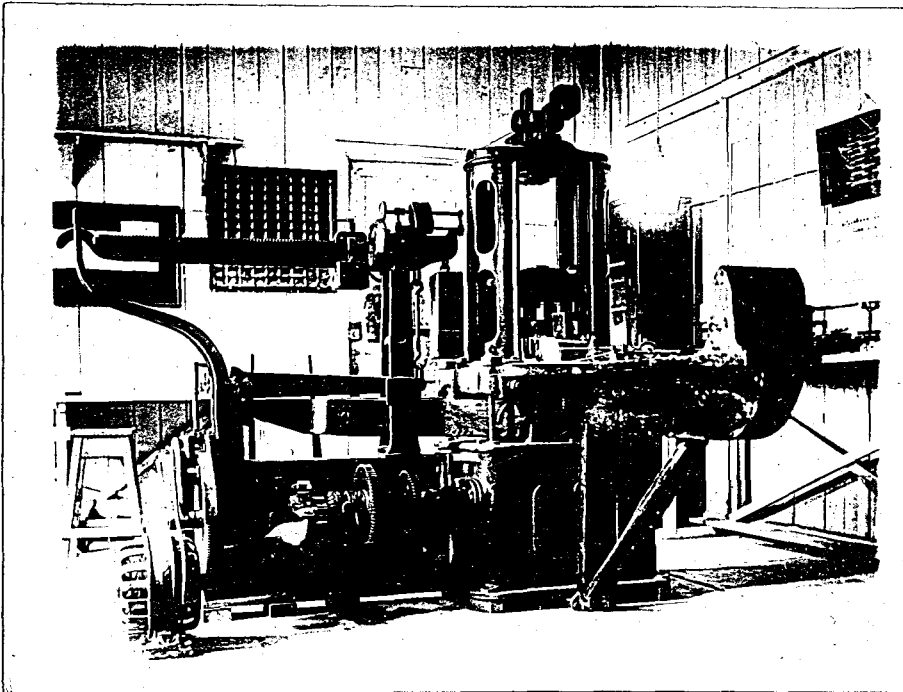


Fig. 5 - Riehle Universal Testing Machine

Cubes were tested by a Riehle Universal Testing Machine (1 day in moist air and 27 days in water).

Compression Strength of 28 days Mortar Specimens

Dimension of specimens: $2\frac{3}{4} \times 2\frac{3}{4} \times 2\frac{3}{4} \text{ in}^3$

Area of specimens: 7.56 in^2

Mortar (1:3) with Florya Beach sand &	Total loads in lbs.	Unit stresses in lbs. per sq. in.	Average value in lbs./in ²
Kartal "Yunus" common cement	22,100 21,600 21,750	2930 2860 2880	2890
Daridja-Eskihisar "Aslan" common	25,800 24,500 27,600	3420 3240 3640	3430
Zeytin Burnu "Aslan" common	19,210 18,500 18,700	2550 2450 2480	2490
Kartal "Yunus" super cement	29,350 29,800 31,700	3890 3950 4200	4010
Daridja-Eskihisar "Aslan" super	32,050 31,100 32,200	4250 4125 4270	4200
Daridja-Eskihisar "Aslan" blended	37,600 36,550 37,000	4980 4850 4920	4920
Alumina cement Lafarge	3,800 3,900 3,880	5050 5180 5160	5130

TABLE OF RESULTS OF TESTS ON CEMENTS AND MORTARS

CEMENT	The number of linear inch.	MECHANICAL ANALYSIS						CHEMICAL ANALYSIS					
		NORMAL CONSISTENCY % OF WATER BY WEIGHT		FINE- NESS % BY WEIGHT	TENSILE STRENGTH OF MORTAR IN LBS PER SQ. IN.		COMPRESSIVE STRENGTH OF MORTAR LBS PER SQ. IN.	Sample SiO ₂ %	Al ₂ O ₃ + Fe ₂ O ₃ % of total oxide	CaO %	MgO %	SO ₃ + IMPURITIES	
		CEMENT	MORTAR		2 DAYS	7 d.							28 d.
KARTAL "YUNUS" COMMON	1	24.5	10.65	14.39	114	229	268	2890	20.07	10.02	66.10	1.50	2.21
DARIDJA-ESKIHISAR "ASLAN" COMMON	2	22.0	10.20	19.02	111	240	294	3430	21.65	9.62	65.30	1.55	1.88
ZEYTIN-BURNU "ASLAN" COMMON	3	26.5	10.90	37.12	57	141	197	2490	21.00	10.3	65.10	1.62	1.98
KARTAL "YUNUS" SUPER	4	25.5	10.75	11.32	142	303	340	4010	19.75	10.17	66.90	1.52	1.76
DARIDJA-ESKIHISAR "ASLAN" SUPER	5	24.0	10.50	10.54	135	319	360	4200	19.84	10.21	66.40	1.45	2.10
DARIDJA-ESKIHISAR "ASLAN" BLENDED	6	28.5	11.25	15.42	47	364	404	4920	29.40	12.22	54.30	1.20	2.80
ALUMINA CEMENT "LAFARGE"	7	24.5	10.65	10.58	275	320	351	5130	10.16	46.53	42.74	0.20	0.47

CHAPTER II

SAND

Mechanical Analysis of Florya Beach Sand

The object of the mechanical analysis of sand is to determine by sieving the percentages of various sized particles in the sample of aggregate.

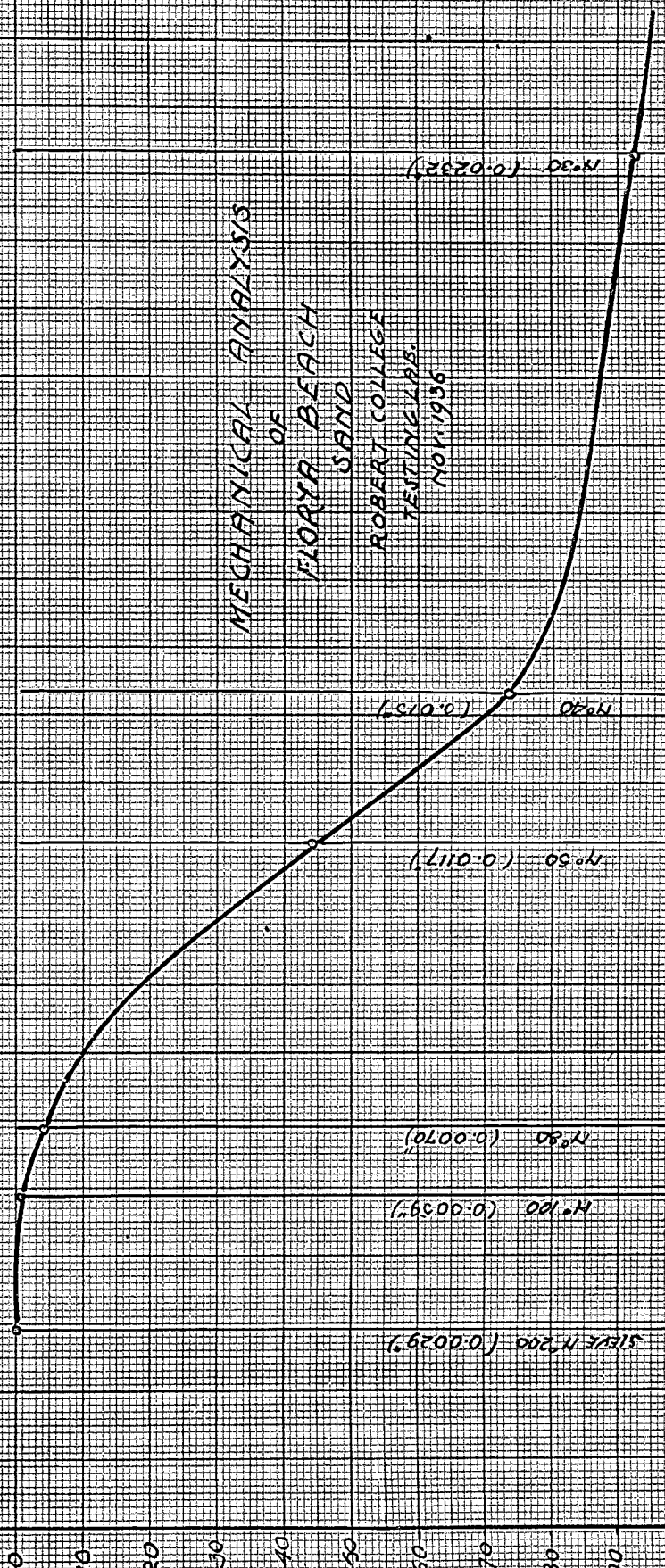
The analysis of all Florya beach sand was performed according to the A.S.T.M. specifications: a sample weighing about 2500 grams was taken and moistened according to standard prescriptions. The material was spread out in a thin layer, and a representative sample weighing about 500 grams was selected by taking a small portion from various parts of the layer. The representative sample was dried in the oven at 110°C . The weight of the sample was found to the nearest gram and then placed in the nest of sieves, having previously arranged them with the largest mesh at the top.

After thoroughly sieving, each part retained in the successive sieves was weighed carefully.

The A.S.T.M. series of sieves for fine aggregate is:
No.200, 100, 80, 50, 40, 30, 20, 10

The number of sieve represents the number of holes in a linear inch.

PERCENT BY WEIGHT OF SAND SMALLER THAN THE GIVEN SIZE



MECHANICAL ANALYSIS
OF
FLORIDA BEACH
SAND

ROBERT COLLEGE
TESTING LABS.
NOV. 1936

DIAMETER OF SAND IN INCHES

Mechanical Analysis of Florya Beach Sand

Sieve Number	First Method Finer than		Second Method Coarser than		Third Method			
	Weight gr.	%	Weight gr.	%	Sieve Size Finer than	Coarser than	Weight gr.	%
10	491.85	97.96	7.96	1.59	10	20	6.53	1.30
20	485.32	97.00	14.60	2.92	20	30	23.35	4.67
30	461.97	92.38	37.91	7.58	30	40	95.24	19.48
40	366.73	73.34	133.20	26.64	40	50	144.28	28.95
50	221.95	44.39	277.96	55.49	50	80	201.02	40.24
80	20.93	4.18	478.89	95.77	80	100	17.59	3.51
100	3.34	.67	496.23	99.24	100	200	2.49	.49
200	.85	.17	499.10	99.82	200		.85	.17

Calorimetric Test for Organic Impurities in Florya Beach Sand

The calorimetric or sodium hydroxide test is performed to determine the presence of organic impurities in sand. A too great amount may considerably reduce the strength of mortar. The relative amount of impurities is determined by comparison with a standard solution.

The standard solution is obtained by adding 2.5 cc. of alcohol to 22.5 cc. of 3% solution of sodium hydroxide, and placing it in a 350 cc. bottle, with stopper, and allowing it to stand for 24 hours with 25 cc. of water.

For testing the sand, a bottle with stopper is filled to the 135 cc. mark with the sand, and a sodium hydroxide solution is added until the volume is 210 cc. Shaking thoroughly, sufficient solution is added to restore the reading to 210 cc. Then the stopper is inserted and the bottle is shaken again.

Allowing the mixture to stand 24 hours, the color of the liquid is compared with the standard solution.

The color of the liquid obtained by treating the Florya Beach sand was very light. That indicates practically the absence of organic impurities.

CHAPTER III

WATER

Terkos water was used for the preparation of mortar, neat cement specimens and sulphate solutions.

CHEMICAL ANALYSIS OF TERKOS WATER

Examen Physique:

Limpidité Hafif bulanik
Réaction PH.7
Koku Yok

Analyse Chimique:

Degré hydrotimétrique total (Anglais) 7,70
Degré hydrotimétrique permanent 2,80

	<u>Par litre</u>
Résidu à 110	0,gr.210
Résidu après calcination	0,gr.165
Alcalinité, en CaO	0,gr.055
Chlorure de Sodium, en NaCl	0,gr.044
Chlore Correspondant, en Cl	0,gr.028
Fer	Néant
Sels ammoniacaux, azoteorganique	Néant
Nitrites	Néant
Nitrates, en azote nitrique	Néant
Matières organiques, en O	0,gr.0015
dosage en solution alcaline	

(By courtesy of A. N. Loukianovsky, M.E.)

PART III

EFFECT OF SULPHATE SOLUTIONS ON MORTAR AND NEAT CEMENT SPECIMENS

INTRODUCTION

Conditions of Testing and Preparation of Mortar Specimens

For the preparation of mortar briquettes for testing purposes different cements and the same Florya Beach sand was used in the proportion of 1 to 3 by weight, with the percentage of water that would give normal consistency. Specimens were prepared at practically constant temperature (20°C). However, the record of temperatures shows a total variation of 13°C from the average temperature. Before being put in corrosive solutions, all specimens were kept 1 day in moist air and 1 day in water. That short seasoning time was chosen to secure as similar conditions as possible for the preparation of mortar specimens and for their presence in corrosive solutions, since the activity of these latter changes with temperature changes. The fact that specimens were seasoned for only two days does not decrease their resistive properties to chemical corrosion. It was shown by Doctor K. Dorsh (Tverdenie i Koroziya Tsementov p.118 - Harkov 1936) that the longer a mortar specimen is seasoned the lower is its resistance to chemical corrosion.

Mortar specimens were kept in 640 cubic cm. receptacles filled with 500 cubic cm. of corrosive solution under a normal atmospheric pressure and gage pressure of 15.7 lbs. per ft.² (for 15% solution of ammonium sulphate).

The tops of the receptacles were covered with thin paper and sealed in an appropriate way to keep dust away from the solution as shown in figure 6.



Fig.6 - Specimens in receptacles filled with corrosive solutions.

The receptacles themselves were kept in a place where the heat from the sun's rays would not affect any of them and speed up chemical reactions.

Every month the evaporated water was replaced by the same amount. In spite of these precautions, we cannot claim that our results are absolute because of the extreme difficulty of taking exact data on materials subjected to corrosion. They are only relative and represent the mean of several tests.

CHAPTER I

TENSION TEST OF MORTAR SPECIMENS IN 20% AMMONIUM SULPHATE SOLUTION

Four General Groups of Mortars

According to the type of corrosion and the behaviour of mortar specimens in ammonium sulphate solution, it is possible to divide them into four general groups and name them according to the cements with which they are made.

I Group

1. Daridja-Eskihisar "Aslan" common cement
2. Kartal "Yunus" common cement

II Group

1. Daridja-Eskihisar "Aslan" super cement
2. Kartal "Yunus" super cement

III Group

1. Daridja-Eskihisar "Aslan" blended cement
2. Zeytin Burnu "Aslan" common cement

IV Group

1. Teil (France) "Lafarge" alumina cement

Daridja-Eskihisar "Aslan" blended cement is called in Turkey "Deniz için Çimento" or cement for sea water, that is a common Daridja cement but with an admixture of German Trass. Alumina cement Lafarge, or, as it is called in French "Ciment Fondu Lafarge", in Turkish "Siyah Çimento", is manufactured in France but commonly used in Turkey because of its high qualities. Jetties of Zonguldak Harbor on the Black Sea are made by using "Lafarge" cement.

Group I

1. Daridja-Eskihisar "Aslan" common cement
2. Kartal "Yunus" common cement

The first sign of corrosion appeared six days in the first, and 8 days in the second cement, after the specimens were put in the solution of ammonium sulphate (Fig.7). Corrosion started on the edges and progressed so rapidly that after 14 days, it was possible to determine its character. All around the edges the cement had become so loose that it completely lost its binding properties and could be easily separated from sand. Cracks with loose edges were easily seen all around the specimens following the contour of their edges (Fig.8). These cracks were the result of irregular edge expansion, more intensive at extremities and less toward the centers of specimens, which were hard and in good condition. This irregular expansion was due to the relative porosity of specimens, increased by the disintegration of binding medium; indeed, the depth to which the corrosive solution penetrated was increased in volume. Progressive penetration is well seen on "Lafarge" specimens (Fig.11). In later days, the number of cracks increased toward the center, thus marking limits to the progressive infiltration of solution as may be seen on Fig.9, especially on the inclined specimen on the right side of the picture. On that picture specimens are shown in their latest stage of corrosion beyond which it was impossible to take any readings on the testing machine. Specimens were in such a loose state that they fell in pieces during their removal from

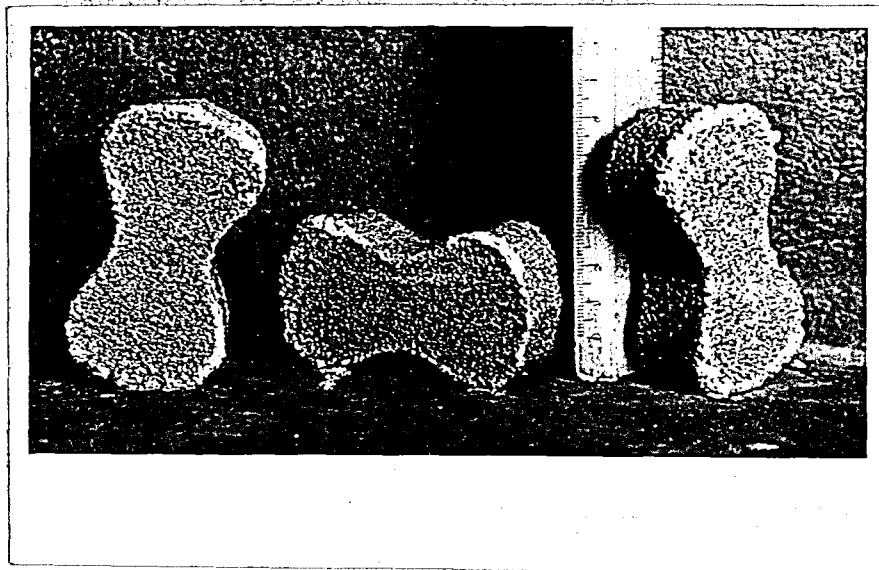


Fig.7 - Kartal "Yunus" common cement mortar after staying immersed for one week in 20% ammonium sulphate solution.

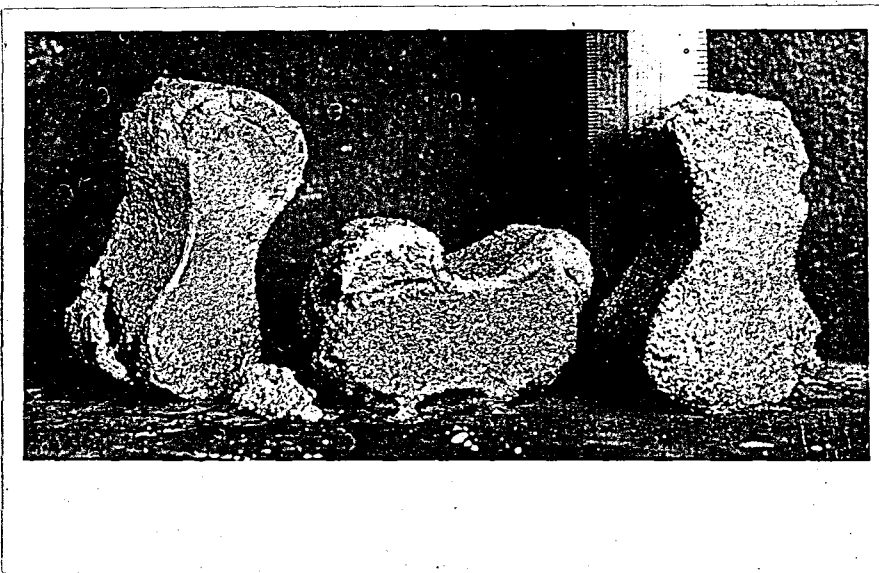
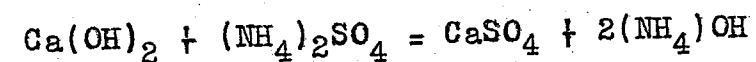


Fig.8 - Kartal "Yunus" common cement mortar after staying immersed for two weeks in 20% ammonium sulphate solution.

the receptacles. Such a specimen may be seen on the left side of the picture (Fig.9). The right side specimen was taken out of the receptacle with great precaution to show the transverse crack which is produced by the corrosive solution and was not caused during the process of mechanical testing.

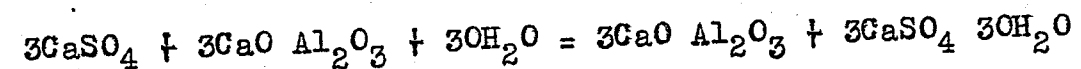
At the time when one set of specimens was put in corrosive solution, another set was put in water to test their strength after a certain time and to find out mortars which would shrink. After 7 months in water, no single crack was detected on the specimens. Therefore, we may conclude that all cracks produced in corrosive solution are due to the expansion caused by chemical changes within the specimens.

Corrosion of specimens in ammonium sulphate solution is due primarily to the formation of calcium sulphate from free lime which reacted with the corrosive solution.



This reaction liberates ammonium hydroxide, whose presence was distinctly noticed by its characteristic odor.

The result of the secondary reaction is the formation of calcium sulphoaluminate.



By means of these two reactions, the author will try to explain later the physicochemical phenomenon of corrosion in its original way.

The tension test performed on the specimen has the object of showing not especially the absolute value of one or other kind of mortars, but their comparative results which



Fig.9 - Kartal "Yunus" common cement mortar after staying immersed for three weeks in 20% ammonium sulphate solution.

would show the degree to which binding material is destroyed. It is evident that the greater the disintegration of cement, the smaller the resistance to mechanical forces, since corroded cement loses completely its binding power.

Group I

Tensile strength of Mortar Specimens (1:3)

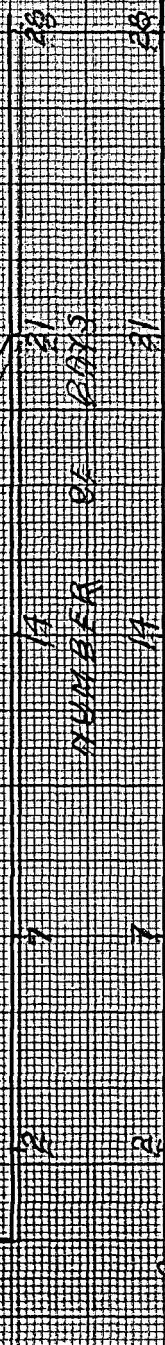
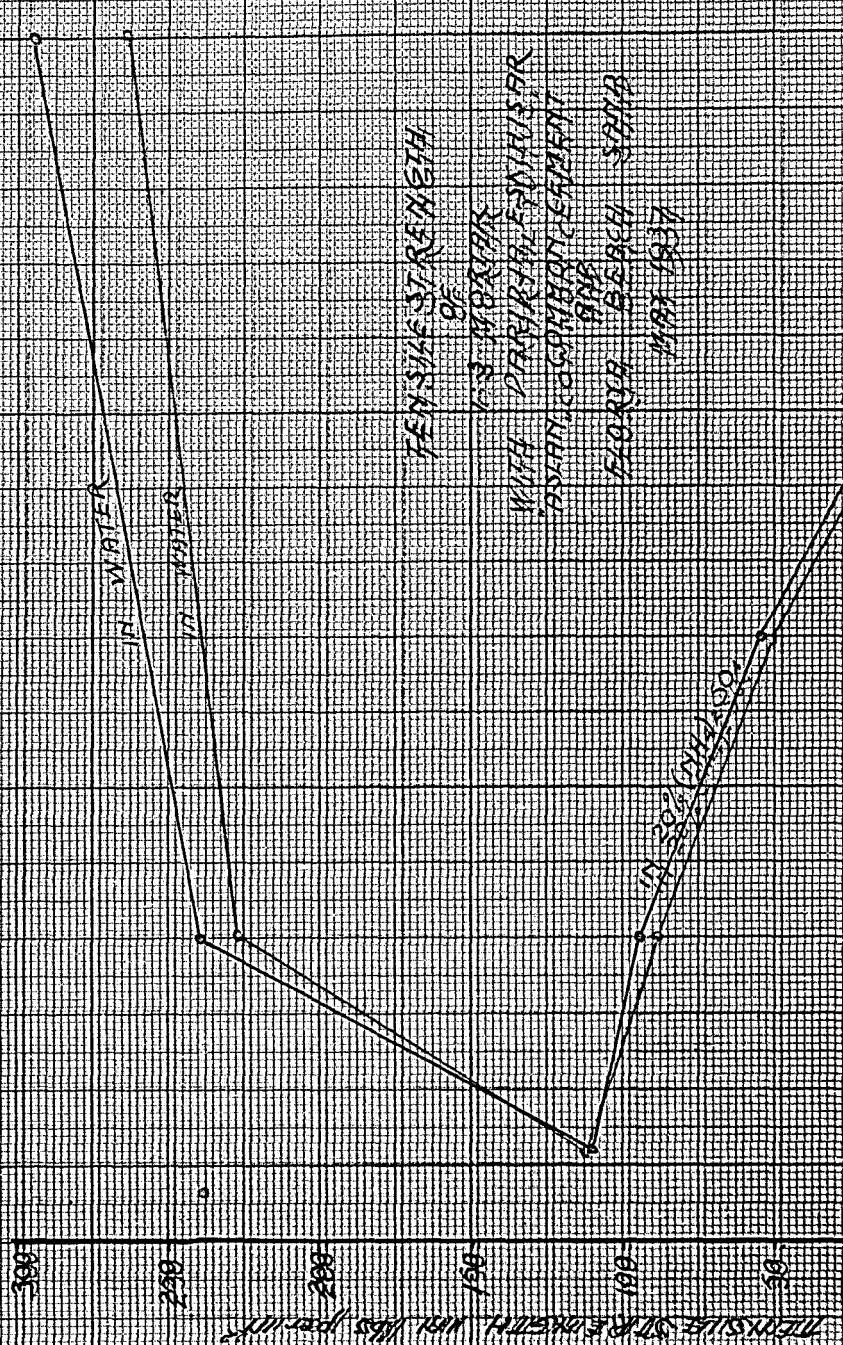
1. With common cement Daridja-Eskihisar "Aslan".

<u>No. of days in Solution</u>	<u>Strength in pounds per sq. inch</u>			<u>In water (Average)</u>	<u>Total Decrease in strength</u>	<u>%age of relative Decrease</u>
	<u>in 20%</u> <u>(NH₄)₂SO₄</u>	<u>Average</u>				
7	1	89				
	2	103	95	240	145	60.5
	3	92				
14	1	62				
	2	49	55	255	200	74
	3	—*				
21	1	0				
	2	0	0	275	275	100
	3	0				

2. With common cement Kartal "Yunus".

7	1	98				
	2	85	93	229	136	59
	3	95				
14	1	62				
	2	49	55	240	185	77
	3	53				
21	1	0	0	255	255	100
	2	0				
	3	0				

* Neglected because comparatively low.



Group II

1. Daridja-Eskihisar "Aslan" super cement
2. Kartal "Yunus" super cement

As we saw in the chapter of special cements, super portland cement differs from common Portland cement by its greater amount of lime and by its finely ground clinker. It would be reasonable to think that an extra addition of lime, reducing the time of setting would, on the other hand, reduce its resistance to sulphate solution attack because of the larger amount of free lime present in cement. But laboratory experiments showed, contrary to expectation, higher resistance than for common cement. This fact may be explained by the higher density or compactness of mortar specimens made with smaller grains and, therefore, of lower absorptive quality.

In general, the type and process of corrosion is similar to that of mortars of the first group with one special characteristic, which was only observed on super cements: that is, greater internal distortion resulting in bending of specimens. Corrosion started at the end of 8 days was much slower for that group than for the first one.

Group II

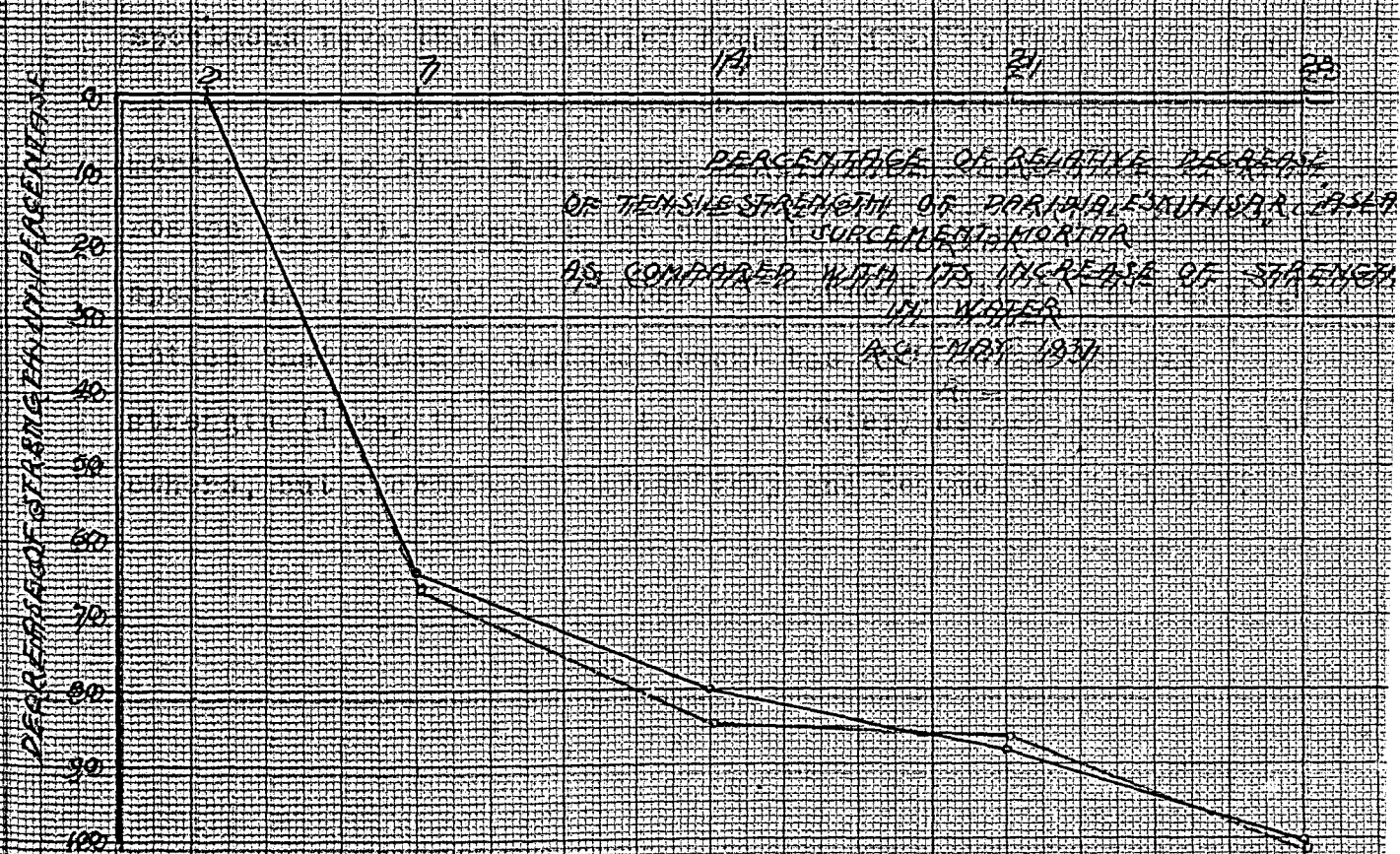
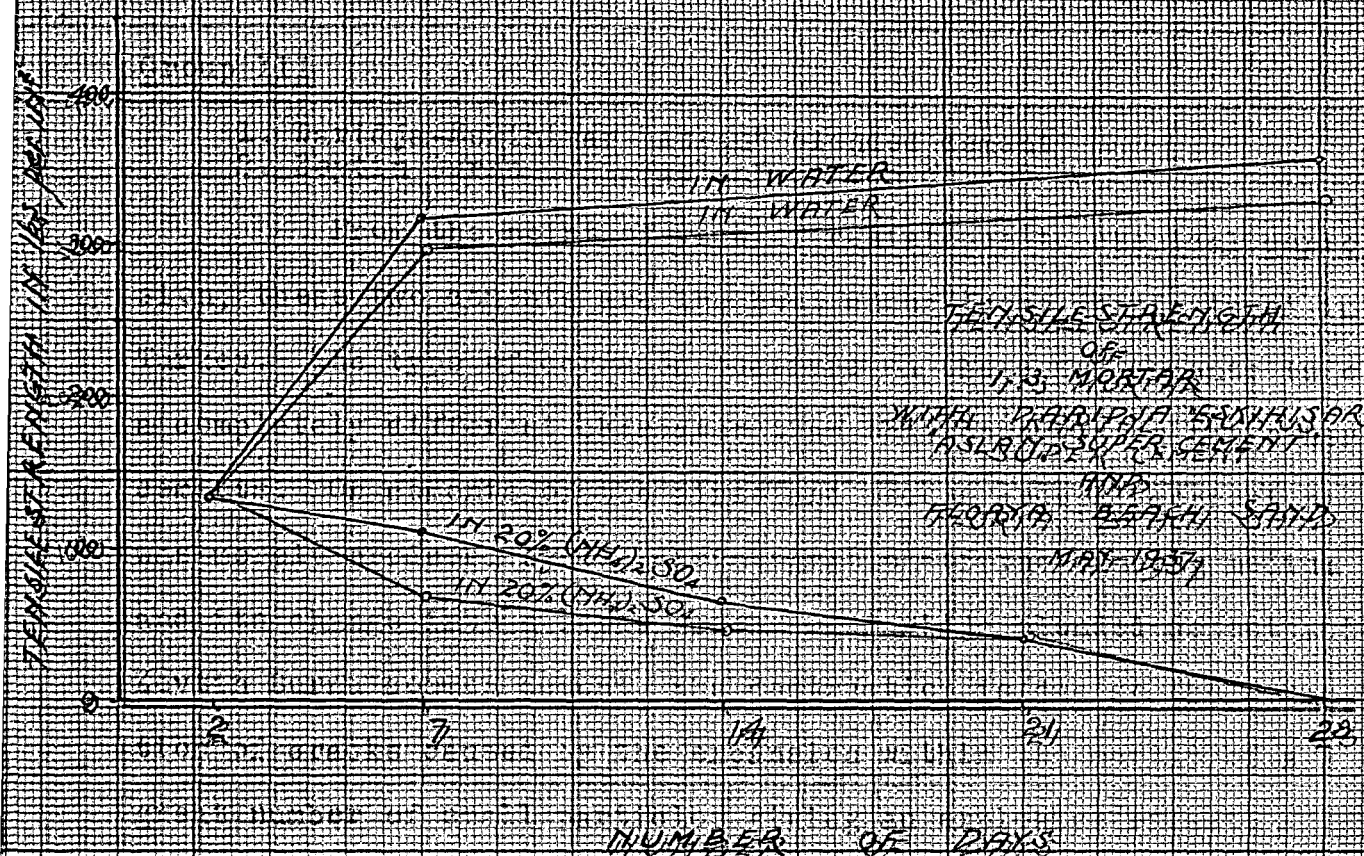
Tensile Strength of Mortar Specimens (1:3)

1. With super cement - Daridja-Eskihisar "Aslan".

No. of days in Solution	Strength in Pounds per sq. inch				% age of relative Decrease	
	in 20% (NH ₄) ₂ SO ₄	Average	In water (Average)	Total Decrease in Strength		
7	1	124	114	319	205	64
	2	108				
	3	110				
14	1	62	68	332	264	79.5
	2	74				
	3	67				
21	1	37	42	345	303	88
	2	41				
	3	48				
28	1	0	0	360	360	100
	2	0				
	3	0				

2. With super cement - Kartal "Yunus".

7	1	68	74	303	229	75
	2	-				
	3	79				
14	1	38	51	315	264	83.5
	2	60				
	3	46				
21	1	40	48	325	277	85
	2	38				
	3	46				
28	1	0	0	340	340	100
	2	0				
	3	0				



Group III

1. Daridja-Eskihisar "Aslan" blended cement
2. Zeytin Burnu "Aslan" common cement

From the point of view of resistance to chemical corrosion, these two cements are the best among those manufactured in Turkey. The type of corrosion observed on these two cements is of a completely different character than that observed on the other cements. On cements of the first and second groups, corrosion was merely produced by the disintegration of the binding medium and its change into a loose mass. On Daridja blended cement and Zeytin Burnu common cement, the destruction is due to the formation of cracks caused by the expansion within the mortar of a great number of small particles giving an explosive effect.

As may be seen in Fig.10, in spite of large cracks, the specimens have their exterior forms similar to that which they had before being put in solution. This cannot be said for the mortar of the first and second groups at the same stage of corrosion (Fig.9). Compare the sharpness of edges and cracks of the specimens in Fig.10 with those of Figure 9. It is interesting to notice that Daridja blended cement has the lowest original strength (1 day in air and 1 day in water) as compared with the others, but increases progressively and becomes even higher.

Group III

Tensile Strength of Mortar Specimens (1:3)

1. With blended cement (Turkish cement with German trass as silica admixture) Daridja-Eskihisar "Aslan".

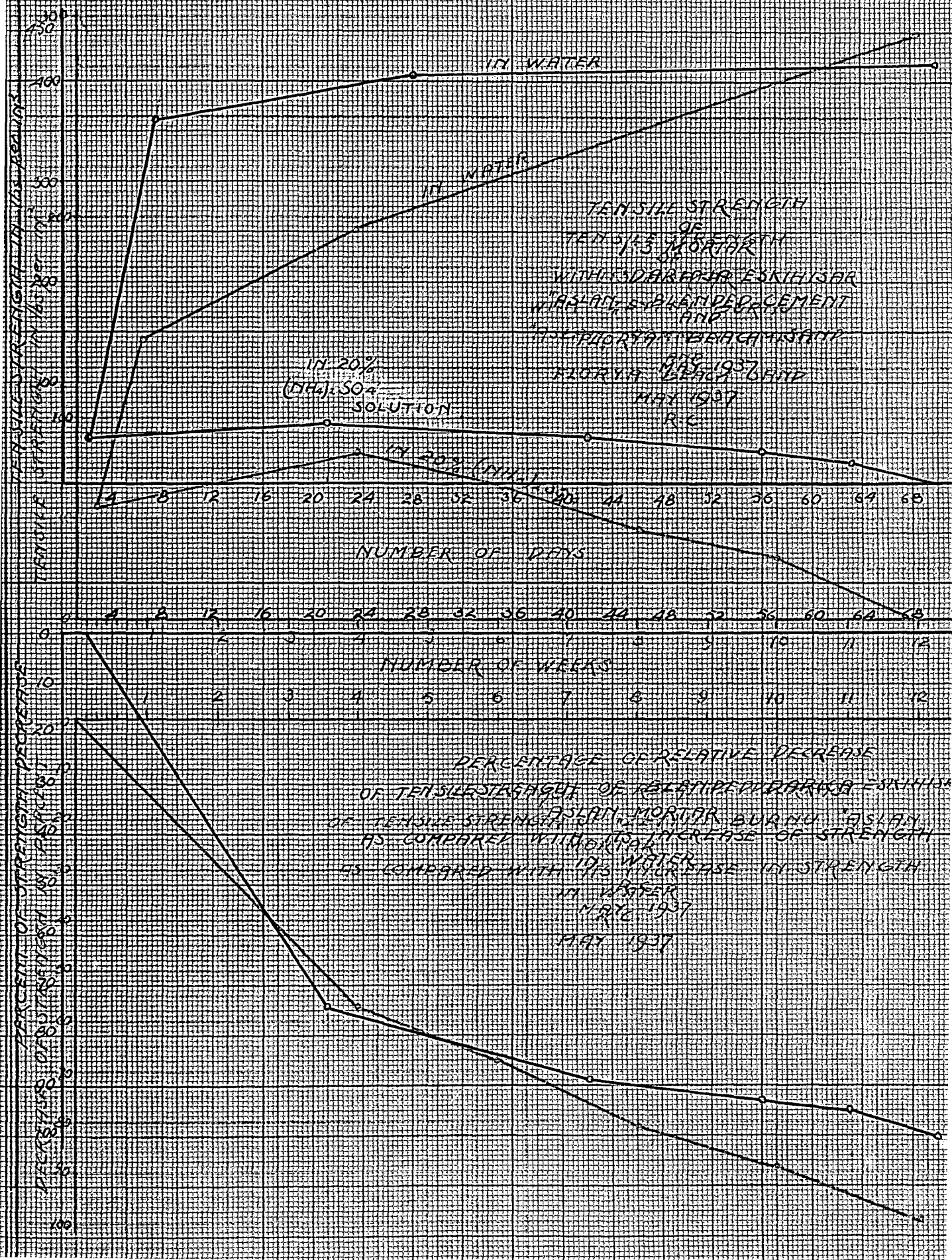
No. of days in Solution	Strength in Pounds per sq. inch			Total Decrease in Strength	% age of relative Decrease	
	in 20% (NH ₄) ₂ SO ₄	Average	In water (Average)			
21	1	53	60	390	330	84.6
	2	68				
	3	59				
42	1	52	47	410	363	88.6
	2	43				
	3	45				
56	1	-	31	414	383	92.5
	2	30				
	3	31				
63	1	24	21	415	394	95
	2	26				
	3	22				
70	1	0	0	419	419	100
	2	0				
	3	0				

2. With ordinary cement - Zeytin Burnu "Aslan".

28	1 88	84	197	113	57.3
	2 78				
	3 85				
42	1 -	71	223	152	68
	2 73				
	3 69				
56	1 49	48	246	198	80.5
	2 53				
	3 43				
70	1 27	29	264	235	89
	2 -				
	3 32				
84	1 0	0	292	292	100
	2 0				
	3 0				



Fig.10 Daridja-Eskihisar "Aslan" blended cement mortar after staying immersed for 10 weeks in 20% ammonium sulphate solution.



Group IV

1. Alumina cement "Lafarge".

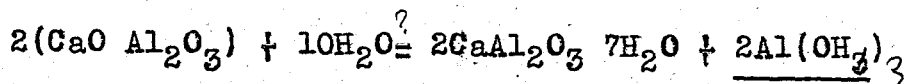
Alumina cement tested in our experiment was manufactured in France. Because of its known high resistive capacity to chemical corrosion in sea water, it was tested with Turkish cements for the sake of comparison.

Alumina cement "Lafarge" showed the highest resistance to corrosion in ammonium sulphate, which cannot be said for its behavior in sodium sulphate solution, as we shall see later. In common, blended and super cements, corrosion was due to the formation of free lime which combining with sulphate ions of the solution produced a corrosive effect.



Fig.11 - Mortar specimens with alumina cement "Lafarge".

In alumina cement the process of setting liberates gelatinous alumina. This material in the presence of sulphate ions is comparatively much more stable than lime.



Alumina cement is chiefly composed of alumina monocalcite. On the addition of water during the process of its setting, it is changed to alumina dicalcite and gelatinous alumina.

The progressive formation of gelatinous alumina in mortar specimens is shown in Fig. 11. Alumina hydroxide having a white color is clearly seen on the black body of the mortar.

The first specimen on the left side of the picture is the "Lafarge" specimen kept during 216 days in tap water. The second specimen was kept during the same time in 20% ammonium sulphate solution.

Group IV

Tensile Strength of Mortar Specimens (1:3)

1. With alumina cement "Lafarge".

No. of days in Solution	Strength in Pounds per sq. inch				% age of relative Decrease
	in 20% (NH ₄) ₂ SO ₄	Average	In water (Average)	Total Decrease in Strength	
28	1 282	280	347	67	19.3
	2 284				
	3 275				
56	1 272	259	354	95	26.8
	2 251				
	3 256				
84	1 253	250	355	105	29.6
	2 254				
	3 255				
140	1 235	227	357	130	36.9
	2 224				
	3 221				

TENSILE STRENGTH IN LBS PER IN²

TENSILE STRENGTH
OF
MORTAR WITH ALUMINA CEMENT
AND FLOPPY SAND

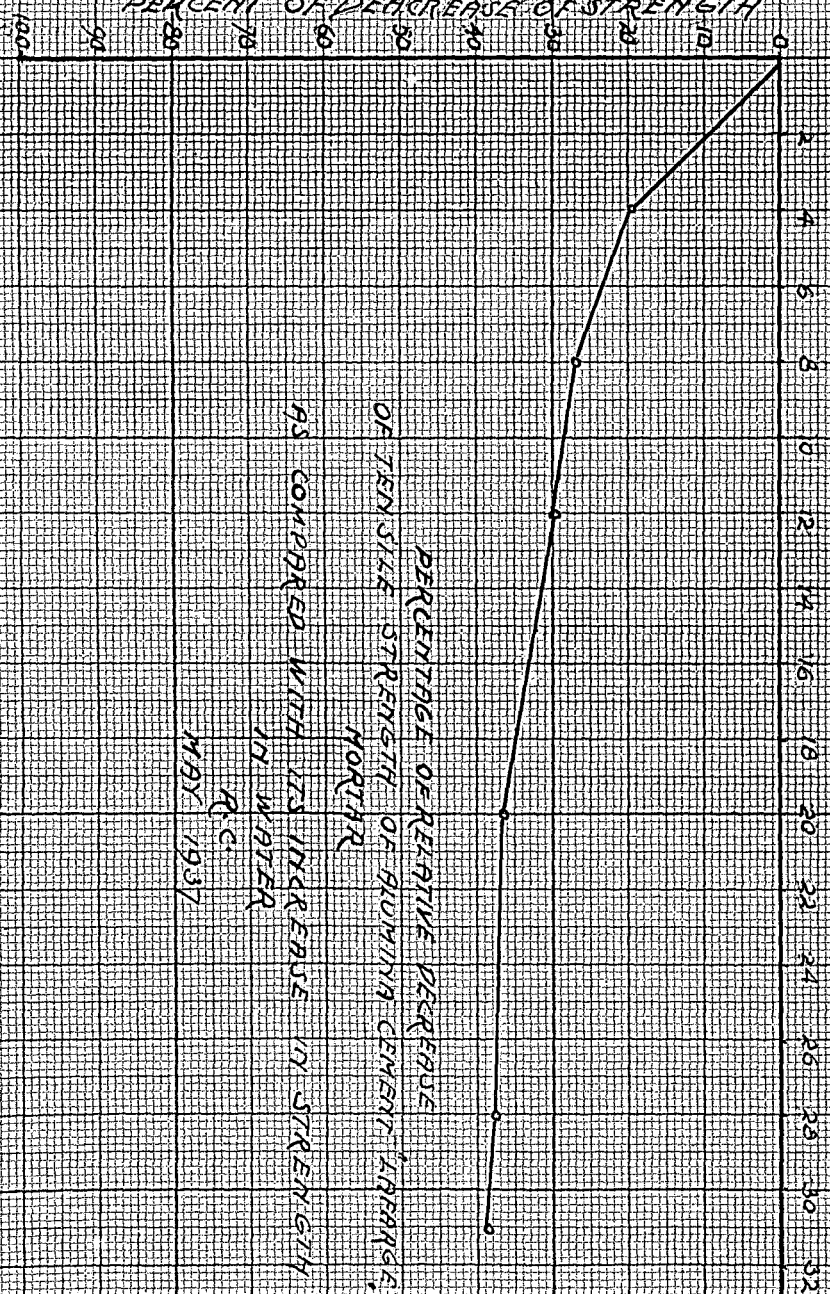
IN WATER

IN 20% (NH₄)₂SO₄

NUMBER OF WEEKS

PERCENT OF DECREASE OF STRENGTH

PERCENTAGE OF RELATIVE DECREASE
OF TENSILE STRENGTH OF ALUMINA CEMENT MORTAR,
AS COMPARED WITH ITS INCREASE IN STRENGTH
IN WATER
A.C.
MAY 1937



196	1	230	223	358	135	37.8
	2	219				
	3	221				
216	1	220	220	358	138	38.6
	2	215				
	3	225				

Results

From the tension test of mortar specimens at different stages of corrosion, we see that the most resistive specimens to chemical corrosion are those with alumina cement "Lafarge", and the least resistive are those with common cements Daridja-Eskihisar "Aslan" and Kartal "Yunus". These cements are so similar in their properties that it is difficult to tell definitely which of them is the most resistive. The same applies to super cements. Cements according to their increasing resistive capacity may be arranged in the following way:

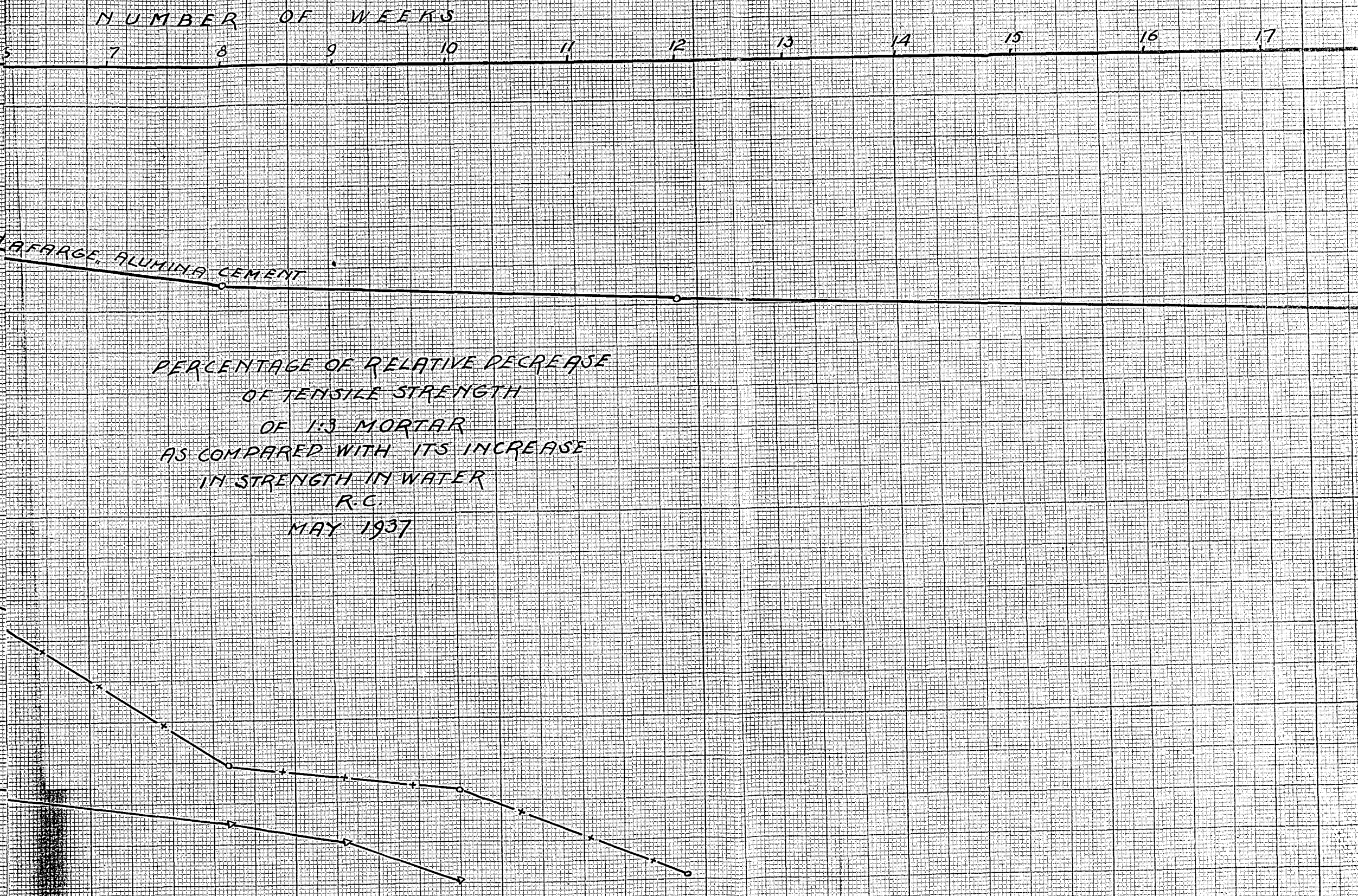
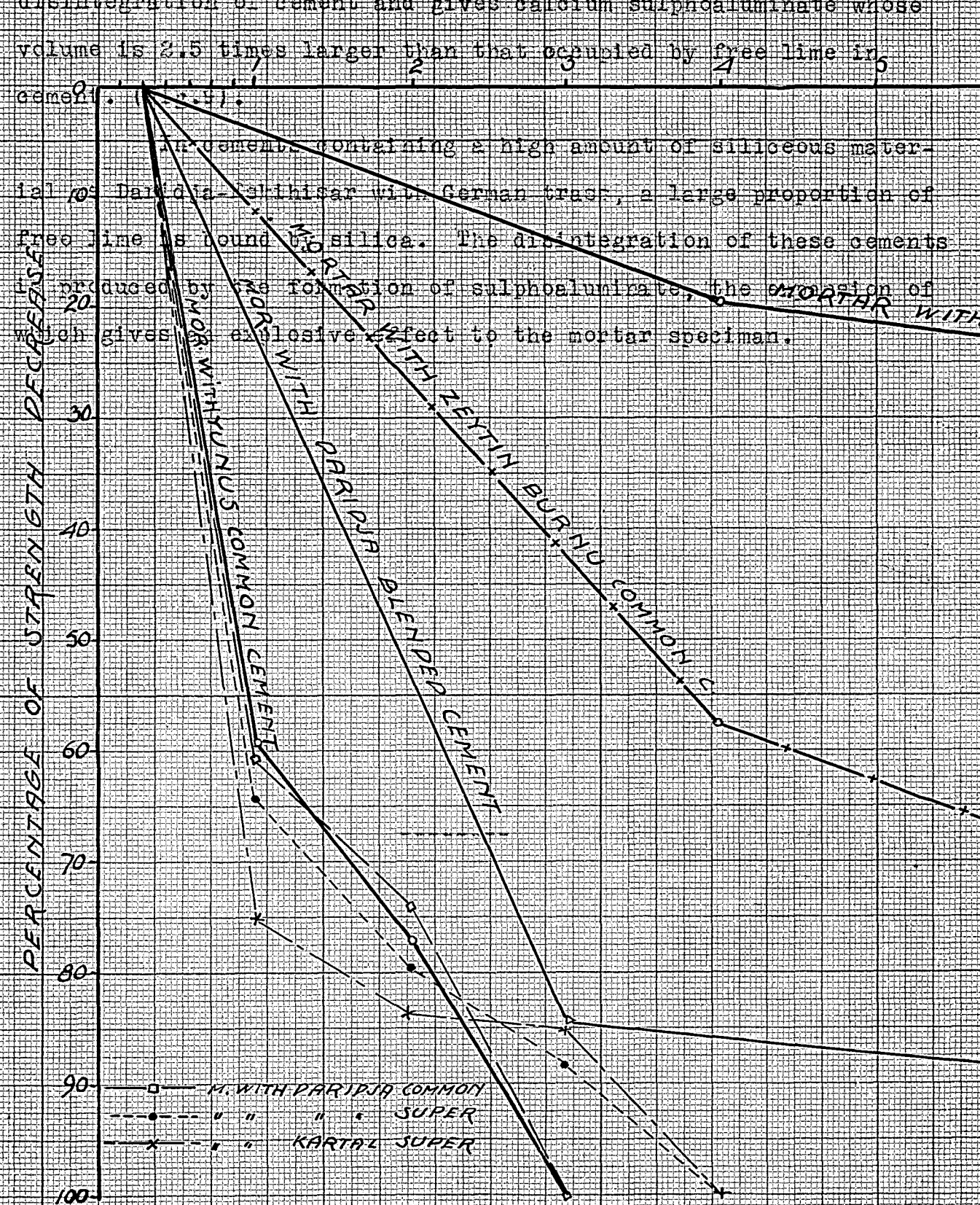
1. Common cements "Aslan" and "Yunus"
2. Super cements "Aslan" and "Yunus"
3. Daridja-Eskihisar "Aslan" blended cement
4. Zeytin Burnu "Aslan" common cement
5. Alumina cement "Lafarge".

From several observations made on mortar specimens in the corrosive solution, we have to distinguish two kinds of disintegration: one is caused by the internal expansion and the other by the direct disintegration of binding material in contact with the corrosive solution.

In common and super cements lime produced by cement setting is in a free state. Therefore, it reacts directly with sulphate ions and the material is changed into a slimy semi-fluid substance; furthermore, calcium aluminate, a result of the process of setting, combines with calcium sulphate produced by the

disintegration of cement and gives calcium sulphoaluminate whose volume is 2.5 times larger than that occupied by free lime in cement.

In cements containing a high amount of siliceous material (as Daridja, Karihisar with German trust, a large proportion of free lime is bound by silica. The disintegration of these cements produced by the formation of sulphoaluminate, the mortars of which gives explosive effect to the mortar specimen.



disintegration of cement and gives calcium sulphoaluminate whose volume is 2.5 times larger than that occupied by free lime in cement. (Fig.9).

In cements containing a high amount of siliceous material as Daridja-Eskihisar with German trass, a large proportion of free lime is bound by silica. The disintegration of these cements is produced by the formation of sulphoaluminate, the expansion of which gives an explosive effect to the mortar specimen.

CHAPTER II

TENSION TEST OF MORTAR SPECIMENS IN

A. 15% sodium sulphate solution

B. 20% magnesium sulphate solution

Mortars in 15% sodium sulphate solution and 20% magnesium sulphate solution

Specimens prepared in the previously described conditions were placed in 20% MgSO_4 and 15% Na_2SO_4 solutions. A 20% sodium sulphate solution could not be prepared at room temperature because of the low solubility of sodium sulphate crystals. At 20°C. it is possible to dissolve only 18.5 gr. of salt in 100 gr. of water (Deming "General Chemistry" second ed. p.101). Even when the room temperature decreased during the winter, a 15% sodium sulphate solution became supersaturated. That resulted in the formation of crystals entirely coating mortar specimens, and therefore, producing a different condition from that in which other specimens were tested.

Beside that, a sodium sulphate solution under the normal room temperature exhibited a high efflorescence leaving deposits of amorphous salt on the top of the receptacles under the process of evaporation, and, therefore, decreasing the concentration of the solution.

No trace of corrosion was observed on mortar specimens in a 15% sodium sulphate solution except for mortar specimens made with alumina cement Lafarge, which were slightly disintegrated especially on faces.

All mortar specimens in MgSO_4 solution were in perfect condition. Tension tests performed on these specimens showed even an increase in strength. This is the sign of their resistive capacity in these salts for a testing period of 7 months.

CHAPTER III

VOLUMETRIC TEST OF MORTAR SPECIMENS IN -----

- A. 15% ammonium sulphate solution
- B. 15% sodium sulphate solution
- C. 15% magnesium sulphate solution

Volumetric Test of Mortar Specimens

The volumetric test of specimen was used to check the results obtained in testing mortar specimens on the Fairbanks testing machine.

Usually concrete structures in harbors do not need high strength, in such structures resistance to sulphate attack is of more importance than great strength. The same principle applies to storage tanks, sewers, decanters in chemical industry.

Observations made in previous experiments show that we have to consider two types of corrosion: first, the disintegration of mortar by the explosive effect, that is, by an interior expansion which produces cracks only; and second, the direct disintegration of binding medium and its change into loose fluid mass. Mortars having the first type of corrosion are made on Blended Daridja-Eskihisar "Aslan" cement and common Zeytin Burnu "Aslan" cement.

Mortars made with these cements cannot be tested by the volumetric method since their complete disintegration is produced by cracks without leaving loose material, the amount of which, may serve as a measure of corrosion.

Alumina cement "Lafarge", very resistive in ammonium and magnesium sulphates, was not in sodium sulphate.

Cements subjected to volumetric test were:

1. Common Portland cement - Kartal "Yunus"
2. Common Portland cement - Daridja-Eskihisar "Aslan"
3. Super Portland cement - Kartal "Yunus"
4. Super Portland cement - Daridja-Eskihisar "Aslan"
5. Alumina Portland cement- Teil, "Lafarge".

Procedure and condition of testing

For the previous tensile strength experiment, a 20% ammonium sulphate solution was used. The concentration of solution was taken arbitrarily. The results of the experiment show that for chemically weak cements a 20% solution was too concentrated, since some of the specimens at the end of three weeks were completely destroyed.

Willing to compare on a common base results obtained from specimens in ammonium sulphate with those in sodium sulphate, it was decided to use 15% solutions and put specimens in the Robert College Boiler Room where the temperature for 70% of the time was at about 35°C, and the rest of the time at about 25°C. That was governed by the fact that for a sodium sulphate solution, a concentration of 15% by weight at ordinary room temperature was very near to saturation point, which resulted in the formation of sodium sulphate crystals completely coating mortar specimens.

The test for corrosion consisted of weighing seasoned specimens, choosing those of approximately the same weight and putting one part of them in corrosive solution and the other part in tap water for a definite length of time.

At the end of that time, the specimens were taken out from the receptacles and weighed again; after that all loose material was gently swept out with a piece of cotton. The difference between these two weights minus the solution absorbed gives the weight of corroded substance, from which the volume may be computed.

Specimens were kept in similar receptacles, and prepared under A.S.T.M. prescriptions as specimens used for a tensile strength experiment.

Let W_1 : original weight of specimen (mortar + water of seasoning)

W_2 : weight of specimen after being a certain length of time in the water

$W_2 - W_1 = W_a$: water absorbed in a certain length of time

d : density of 15% of solution

$W_a \times d = S_a$: weight of the absorbed solution

M_1 : weight of mortar specimen after being a certain time in solution (original weight and solution absorbed).

$M_1 - S_a = M_2$: original weight of specimen

$W_1 = M_2$: if corrosion did not take place

$W_1 - M_2 = L$: loss in weight of specimen due to corrosion

From "International Critical Tables", Vol.3, p.60

Density of 15% by weight of $(NH_4)_2SO_4$ solution at 30-35°C is 1.081

Density of 15% by weight of Na_2SO_4 solution at 30-35°C is 1.1286

Results

Results obtained from the experiment showed a fact which was not foreseen by the author and which gives to the volumetric method for measuring cement corrosion a questionable value.

Theoretically a mortar specimen absorbing W_a grams of water will absorb $W_a \times d$ grams of solution, "d" being the density of the solution. The absorption is due to the porosity or the presence of voids in the mortar specimen. However, specimens put in the corrosive solution expand. Therefore, mortar under the process of corrosion absorbs much more water than the same specimen put in water, where it tends to shrink. That unequal absorptive capacity of specimen in water and in corrosive solution, resulted

in the fact that it was impossible to determine the loss of material by subtracting from M_1 (weight of mortar specimen after being a certain time in solution). The weight of solution determined by theoretical assumption $S_a = W_a \times d$. In all cases the weight of corroded specimens after the subtraction of the computed absorbed solution was much larger than the original weight of specimens.

But nevertheless the author tried to interpret the results in a different manner and obtained values which determine the comparative cement resistive properties.

In Table II the weight of water absorbed by different mortars is given. Table III shows the changes of weight of specimens after staying immersed in sulphate solution. Taking the weight of the seasoned mortar specimens and subtracting from it the weight of the specimen after staying immersed in solution, we find positive or negative values which represent the deviation, that is, gain or loss in weight of the weight of the original specimen.

Mortar specimens increase considerably in weight during the first 30 days when the weight of the corroded material is smaller than the weight of the absorbed water. At the end of a period of 30 days. The condition is totally different: that is, specimens are more or less in a saturated condition and the weight of them rapidly decreases because of the corrosion of material which drops away. At the end of 90 days, the degree of corrosion is such that it is impossible to determine the relative resistance of cement. Cements according to their increasing resistive capacity may be arranged in the following way:

1. Daridja-Eskihisar "Aslan" common cement
2. Kartal "Yunus" common cement
3. Daridja-Eskihisar super cement
4. Kartal "Yunus" super cement

Alumina Lafarge cement mortars, which were very slightly corroded in 20% ammonium sulphate, were much more corroded in a 15% sodium sulphate solution. The corrosion was very superficially of laminar character, not on the edges as in other mortar specimens, but only on the top surface (Fig.11, third specimen from the left side). The lack of time did not allow the taking of further observations.

Specimens in magnesium sulphate did not show any trace of corrosion even after 110 days in the solution.

TABLE II

-58-12-

WATER ABSORBED BY MORTAR SPECIMENS

MORTAR WITH CEMENT	30 DAYS				60 DAYS			90 DAYS		
	ORIGINAL WEIGHT OF SPECIMEN IN GR. W_1	WEIGHT OF SPEC. AFTER BEING IN WATER W_2	WT. OF ABSORBED WATER $W_2 - W_1 =$ W_a	AVERAGE W_a IN GR.	W_2 GR.	$W_2 - W_1 =$ W_a GR.	AVER. W_a GR.	W_2 GR.	W_a GR.	AVER. W_a GR.
KARTAL-YUNUS, COMMON	143 147 145	146 151 149	3 4 4	4	151 157 152	8 10 7	8	153 157 153	10 10 8	10
PARIDJA-ESKIHISAR "ASLAN" COMMON	134 133 133	146 144 145	12 10 12	12	151 147 148	17 13 15	15	152 149 149	18 15 16	16
KARTAL-YUNUS, SUPER	138 139 137	141 142 141	3 3 4	3	145 145 142	7 6 5	6	148 147 143	10 8 6	9
PARIDJA-ESKIHISAR "ASLAN" SUPER	134 135 132	139 141 138	5 6 6	6	143 146 143	9 11 11	11	144 149 144	10 14 12	12
ALUMINA CEMENT "LAFARGE"	139 138 140	140 140 142	1 2 2	2	141 141 144	2 3 4	3	141 142 144	2 4 4	4

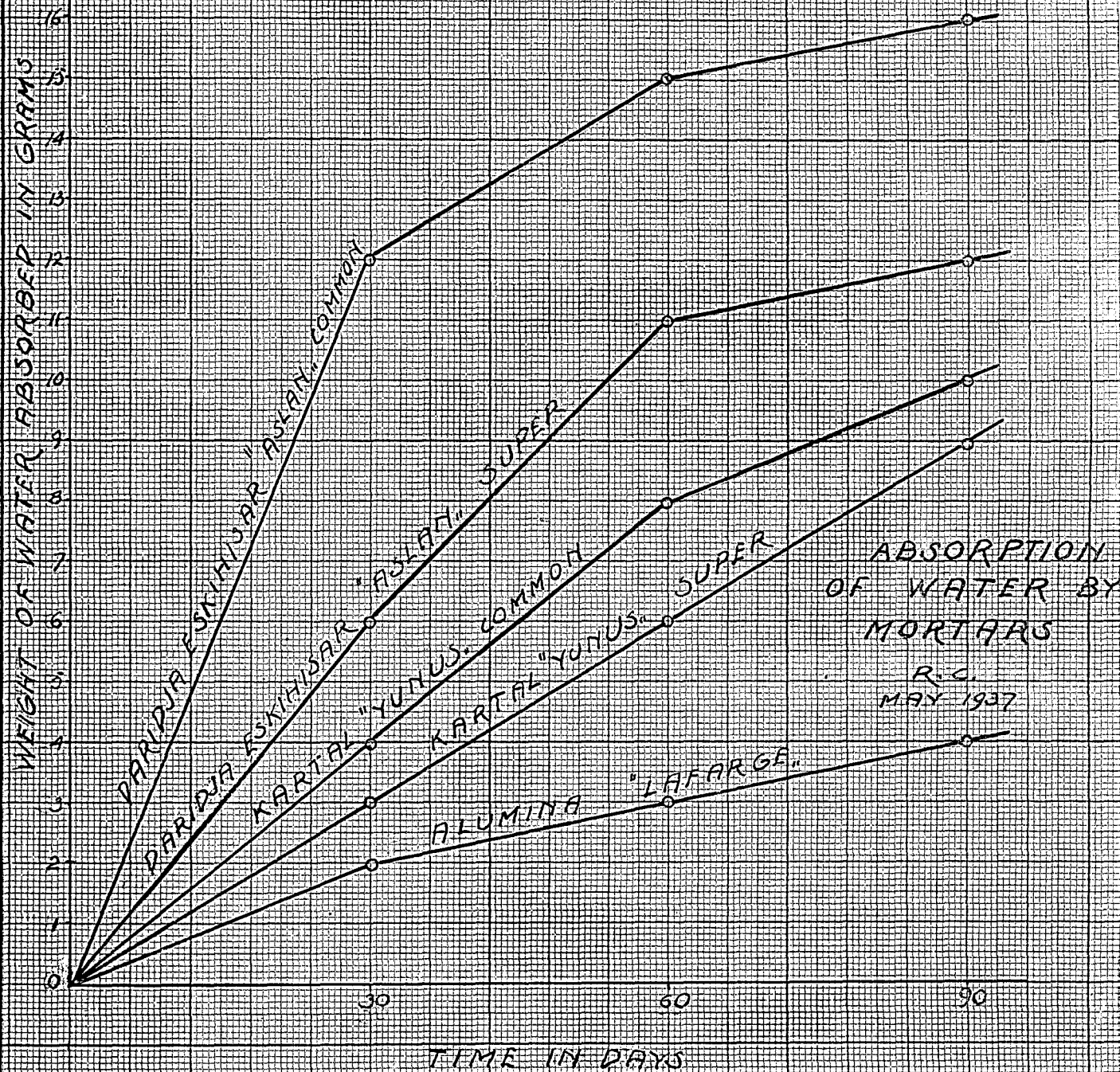


TABLE III - WEIGHT OF MORTAR SPECIMENS AFTER BEING IMMERSED
IN 15% SOLUT. OF AMMONIUM SULPHATE

MORTAR WITH CEMENT	ORIGIN. WEIGHT GR.	AVER. WEIGHT GR.	WEIGHT OF SPECIMEN AFTER BEIGN IMMERSED IN SOLUT.								
			30 DAYS			60 DAYS			90 DAYS		
			M, lbs	AVERAGE	DEVIATION FROM ORIG.	M,	AVER	DEVIAT.	M,	AVER.	DEVIAT.
KARTAL "YUNUS, COMMON	144	144	158	156	+2	145	145	-1	105	114	-30
	144		155			134			118		
	145		156			156			131		
PARIDJA "ASLAN, COMMON	130	130	150	147	+17	112	116	-19	80	88	-42
	131		146			121			85		
	130		146			116			98		
KARTAL "YUNUS, SUPER	139	140	154	156	+16	142	145	+5	136	129	-11
	140		152			145			124		
	141		150			147			127		
PARIDJA "ASLAN, SUPER	134	135	146	147	+12	148	144	+9	120	116	-19
	135		146			145			118		
	135		148			143			109		

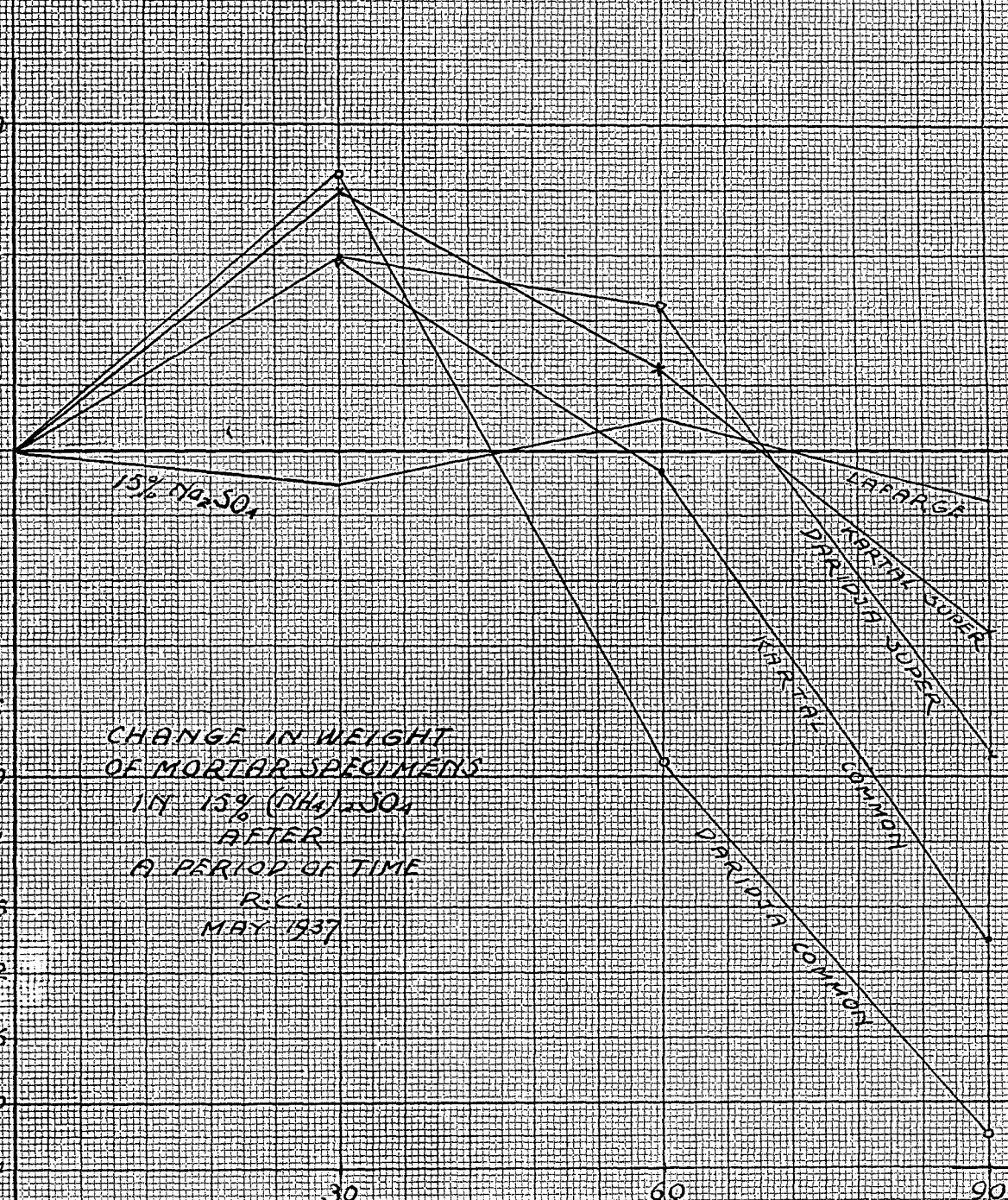
WEIGHT OF MORTAR SPECIMENS AFTER BEING IMMERSED
IN 15% SOLUT. OF SODIUM SULPHATE

ALUMINA LAFARGE	139	139	137	137	-2	142	141	+2	135	136	-3
	138		138			141			137		
	140		137			140			134		

CHANGE IN WEIGHT FROM THE ORIGINAL WT. OF SPECIMEN GRs

CHANGE IN WEIGHT
OF MORTAR SPECIMENS
IN 15% (CH₂)₂SO₄
AFTER
A PERIOD OF TIME
R.C.
MAY 1937

TIME IN DAYS



CHAPTER IV

NEAT CEMENT SPECIMENS IN AMMONIUM SULPHATE SOLUTION

Neat Cement Specimens in Ammonium Sulphate Solution

~~Willing~~ to prove that corrosion of mortar specimens depends upon the cement used for its preparation, and that it is perfectly independent of the shape of specimen, the author prepared neat mortar cubes $2 \times 2 \times 2 \text{ in}^3$ and put them in the ammonium sulphate solution.

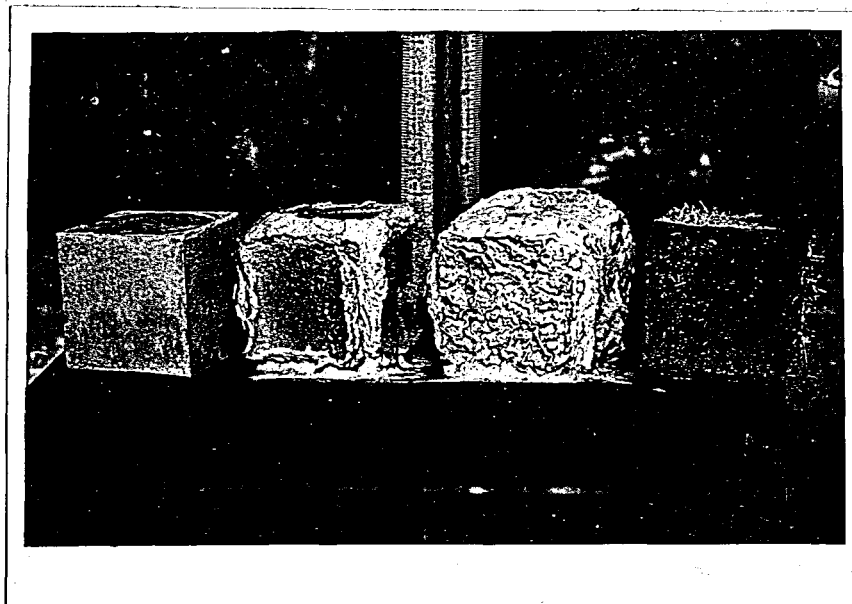


Fig.12 - Neat cement specimens
after being immersed for
6 months in 15% ammonium
sulphate solution.

After 6 months in solution, neat cement specimens appeared as shown in Fig.12. From left to right the first cube is a specimen kept in water. Observe the sharpness of its edges. The second one is that of Zeytin Burnu "Arslan" common cement specimen. Observe the expansion of edges and relatively good condition of faces. The third specimen is that of Daridja-Eskihisar "Aslan" common cement, badly corroded. The last one is that of alumina "Lafarge" cement covered with ammonium sulphate crystals, a sign

of its inactivity in that solution.

That picture shows that the results obtained by two different methods are perfectly applicable to neat cement specimens.

CONCLUSION

1. Resistive capacity to chemical aggression may be different for cements of similar physical character.
2. There is no relation between the ultimate strength of cement mortar and its resistance to corrosion.
3. Resistive properties of mortars depend on cements used for their preparation.
4. Corrosive activity of sulphate solutions is proportional to the concentration of solutions.
5. For Portland cement with or without silica admixture, ammonium sulphate solution is the most active among the three solutions used: that is, ammonium sulphate, sodium sulphate and magnesium sulphate solutions.
6. For alumina cement, sodium sulphate solution is the most active among the three solutions used.
7. Mortar specimens with common, super and blended Turkish Portland cements and French alumina cement, after staying immersed in 20% by weight magnesium sulphate solution for 7 months, were not affected by it.
8. Mortar specimens with common super and blended Turkish cements after staying immersed in 20% by weight sodium sulphate solution for 7 months, were not affected by it, except French alumina cement mortar which was slightly corroded.

9. Mortar specimens with common, super and blended Turkish cements were entirely disintegrated in ammonium sulphate solutions (20% and 15%); French alumina cement was not affected.
10. Cements according to the increasing resistive capacity to chemical corrosion in ammonium sulphate solution:
1. Darıdja-Eskihisar "Aslan", common Turkish cement
 2. Kartal "Yunus", common Turkish cement
 3. Darıdja-Eskihisar "Aslan", super Turkish cement
 4. Kartal "Yunus", super Turkish cement
 5. Darıdja-Eskihisar "Aslan", blended cement with German trass
 6. Zeytin-Burnu "Aslan", common Turkish cement
 7. Le Teil "Lafarge", alumina French cement
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APPENDIX

CEMENT ANALYSIS

Use samples passing 200-inch sieve.

Silica

Mix with the weighed sample (about 0.5 gr.) in a platinum crucible about 5.0 gr. of sodium carbonate, approximately weighed. Place the cover on the crucible but slightly toward one side so that the contents may be observed. Heat gently at first in order to avoid violent effervescence and consequent loss by spattering, gradually raising the temperature until the full heat of the burner fails to cause more than slight action. Place the crucible over the blast lamp and heat for 15 minutes after carbon dioxide has ceased to be evolved. Remove the lamp, lift the triangle by means of the tongs and slowly rotate the crucible in such a manner that the fused mass will be spread over the sides of the crucible as it solidifies.

After cooling, place the crucible and its contents in a Pyrex beaker, a platinum dish or a porcelain casserole and cover with hot distilled water. Digest until the entire mass has become disintegrated. Cover the vessel and add, gradually, from a pipette, concentrated hydrachloric acid until the carbonates are completely decomposed. Remove the crucible and cover by means of a stirring rod, rinsing well and using the policeman, if necessary, to remove adhering silicic acid. Crucible tongs should not be used.

The solution is now evaporated to dryness. If speed is essential and if a casserole has been used, the greater part of the liquid may be evaporated by holding over a free flame, giving a rotary motion to the casserole to prevent spattering or bumping. If other work may be carried on the same time, the solution should be evaporated over the steam bath.

When completely dry, heat for 15 minutes at about 110°C , cool and add 5 ml. of concentrated hydrochloric acid and 50 ml. of water; warm until soluble salts are dissolved and filter the residue of silica at once, washing until free from chlorides, adding the washings to the filtrate. Evaporate the solution again to dryness; heat at about 110° and repeat the treatment with hydrochloric acid and water filtering in a different paper.

Place both papers with their residues in a weighed platinum crucible, dry and burn the papers in the usual way, then ignite over the blast lamp or in the muffle furnace for 20 minutes, cool and weigh. Small quantities of metal salts will have been retained in the residue. In order to correct for their presence, the residue is moistened with 1 or 2 drops of sulphuric acid and about 5 ml. of hydrofluoric acid is added. The silicon tetrafluoride being volatilized, the acids are evaporated and the residue, which should be small is heated over the burner. The loss in weight is taken to represent silica. Calculate its percentage in the sample.

If the silica has been well washed, it will contain no calcium or magnesium and only the small amounts of other metals that are to be ignored, as already stated, in addition to oxides of iron and aluminum. As the crucible has been weigh-

ed, it may be set aside until the precipitate next to be obtained is ready.

Iron and Aluminium

Concentrate the combined filtrates and washings from silica to about 100 ml. add a drop or two of methyl red, and then make barely basic with dilute ammonium hydroxide. Boil shortly to flocculate the hydroxides of iron and aluminium and then filter and wash with hot water. On account of the large amount of precipitate usually obtained from silicates, and of its colloidal character, it is advisable to make a second precipitation in order to remove absorbed calcium and magnesium salts. Place the beaker in which iron and aluminium were precipitated under the filter and dissolve the precipitate in hydrochloric acid, using no more than is necessary. Thoroughly wash with hot water, then discard the paper. Re-precipitate iron and aluminum from the acid solution. Filter and wash with hot water, remove the paper from the funnel, fold, and burn in a weighed porcelain crucible. Burn the paper at a low temperature in presence of an excess of air, inclining the crucible to facilitate oxidation. Finally ignite at high temperature and weigh. Report as aluminum oxide and iron oxide.

Calcium

To the filtrates from iron and aluminum oxides, add drop by drop hydrochloric acid until the solution is slightly acid. Concentrate, if necessary, to about 100 cc. Heat to boiling, add 2 cc. hydrochloric acid (1:1) and 5 cc. of 15%

oxalic acid. Then continue to boil and stir the solution

with a stirring rod, adding drop by drop ammonia hydroxide (1:10) until the point when acid solution is changed to basic.

Ammonium hydroxide must be added in such a way that from the point when acid solution is changed to basic; ammonium hydroxide must be added in such a way that from the point when the precipitate is formed up to the end of formation of precipitate no less than 10 minutes passed. The change of reaction of the solution may be judged by means of a litmus paper, or by adding to the original filtrate few drops of methyl orange (1:1000). Then add 12.5 cc. of concentrated ammonium oxalate.

After 4 hours, add a few drops of ammonium oxalate to the clear liquid above the settled precipitate, if the precipitate is formed add some more ammonium oxalate; then filter and wash the filtrate with 1% solution of ammonium oxalate until the washing acidified by nitric acid, does not become cloudy by adding 1% solution of silver nitrate.

Weigh a platinum crucible and put into the wet precipitate and the filter paper, heat carefully by the burner until moisture is expelled, ignite during 30 minutes in the furnace. Cool and calculate the percentage of calcium oxide.

Magnesium

Concentrate the combined filtrates and washings from calcium to about 100 cc. if it is not very clear, filter, to the clear solution, make the solution faintly basic with ammonium hydroxide. Now add from a pipette slowly and with stirring, 15 cc. of a clear 10% solution of disodium orthophosphate. Allow to stand for 15 minutes or until a consider-

able part of the precipitate has appeared. Then, slowly and with continuous stirring add concentrated ammonium hydroxide solution (sp.gr. 0.90) equivalent to one-eighth of the volume of solution. Cover and allow to stand for 3 hours or stir continuously for 30 minutes at room temperature. Filter the precipitate on a filter of extracted paper and wash until free from solution containing 2% of ammonia, finally testing the washings with silver nitrate after acidifying with nitric acid. Place the filter paper, in a weighed platinum crucible, incline the crucible with cover leaned against it and heat gently over the burner until the paper is completely changed to ash. Calculate the percentage of magnesium oxide in cement.

Sulphur Trioxide

Weigh about 1 gr. of the sample into a 25 cc. beaker, add 5 cc. of water and 5 cc. of concentrated hydrochloric acid, and warm to complete the decomposition of the sample. Add 40 cc. of water and then filter and wash the residue with about 100 cc. of cold water.

Add a drop or two of methyl orange and carefully neutralize the excess of acid with any standard solution of a base or carbonate, then add 1 cc. of a normal hydrochloric acid solution, or an equivalent volume of a solution of any other normality. Heat to boiling and then precipitate by adding 10 cc. of 5% barium chloride solution, dropwise from a pipette. Digest on the steam bath for 30 minutes, then filter and wash free from chlorides with hot water.

Place the paper and washed barium sulphate in a weighed platinum crucible and heat with the ordinary burner until the paper is burned and the entire residue is white. High-temperature ignition is not necessary.

Calculate the percentage of sulphur trioxide in the cement.

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