CHEMICAL AND PHYSICAL PROPERTIES OF SOME TYPES OF CEMENT AVAILABLE IN LOCAL MARKET

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الخلاصة: -

ممالا شك فيه إن لنوعية الاسمنت وخواصه تأثير كبير على خواص الخرسانة حيث انه من المكونات الرئيسة للخلطة الخرسانية ويشكل جزءا مهما من احد أطوار الخرسانة الرئيسة وهو طور عجينة الاسمنت التي تؤثر بصورة كبيرة على خواص الخرسانة المنتجة. في هذا البحث تم دراسة الخواص الكيميائية والفيزيائية لأربعة أنواع من الاسمنت منها نوعين من الاسمنت البورتلاندي الاعتيادي وهي اسمنت معمل كبيسة العراقي واسمنت شركة الاسمنتة الأردنية ونوعين آخرين من الاسمنت البورتلاندي المقاوم للكبريتات وهي اسمنت معمل القائم العراقي واسمنت شركة تراب السبع اللبنانية اجري التحليل الكيميائي للأنواع الأربعة في مختبر بغداد المركزي التابع للمركز الوطني للمختبرات والبحوث الإنشائية و المختبر التابع لمعمل اسمنت القائم وأجريت الفحوصات الفيزيائية الأخرى مثل القوام القياسي لعجينة الاسمنت وزمن التجمد الابتدائي والنهائي ومقاومة مونة الاسمنت في مختبر تكنولوجيا الخرسانة التابع لكلية الهندسة جامعة الأنبار.

أشارت النتائج المستحصلة من الدراسة إلى أن الاسمنت المحلي بنوعيه الاعتيادي والمقاوم للكبريتات أبدى نتائج أفضل من الاسمنت المستورد الأردني واللبناني في معظم الخواص الفيزياوية والكيماوية التي تم فحصها مختبريا حيث أشارت النتائج إلى أن سمنت كبيسة أبدى زيادة ملحوظة في مقاومة الانضغاط مقدارها (34.1% و 35.5%) بعمر و 7 أيام على التوالي مع نقصان في الفقدان بالحرق والمواد الغير قابلة للذوبان كما كانت نسب مركباته الرئيسة اقرب إلى الاسمنت النموذجي مقارنة بالاسمنت الأردني .بالنسبة للاسمنت المقاوم للكبريتات كان هناك زيادة في مقاومة الانضغاط بمقدار 13.3 % بعمر 7 أيام بالنسبة لاسمنت القائم مقارنة بالاسمنت اللبناني إضافة إلى تجاوز نسبة المركب C3A للمواصفة العراقية رقم 5 لسنة 1984 للنوع الأخير .

Abstract

There is no doubt that the type and properties of cement extremely affect the general properties of produced concrete. Cement is one of the main ingredients of cement past phase in concrete. In present study chemical and physical properties of four types of Portland cement available in Iraqi local market were studied ,these types as follow: two types of ordinary Portland cement Kubaisa (Iraqi cement) and Ismnta (Jordanian cement) and the others of sulfate resisting cement Torab alsabia (Lebanese cement) and Al-qaim (Iraqi cement). Chemical analysis of the four types of cement were conducted in Baghdad central laboratory in National Center for Constructional Laboratories and Researches (NCCLR) and

Al-qaim factory laboratory .The physical tests were conducted in the concrete laboratory of Al_anbar university-college of engineering including standard cement paste ,initial and final setting and compressive strength of cement mortars.

The results indicate that the local cement (Kubaisa and Al-qaim) showed better performance than imported cement (Ismnta and Torab alsabia) in most tested chemical and physical properties .Kubaisa cement showed 34.1 % , 35.5 % higher compressive strength compared with Ismnta cement at 3 and 7 day respectively and lower loss on ignition and insoluble residue . The major compounds of Kubaisa cement were nearest to those in typical cement. For sulfate resisting cement , Al-qaim cement showed 13.3 % higher compressive strength at 7 day and lower percentage of C3A (1.95%) . Torab alsabia cement exceed the limits of Iraqi standard I.O.S No.5 1984.

1-Background

Directly or indirectly, our life is affected by cement, which is the fundamental ingredient of concrete. Cement, in general sense of the word, can be described as a material with adhesive and cohesive properties, which makes it capable of bonding mineral fragments into compact whole

[1]. Perhaps one of the greatest challenges facing the cement and concrete industry is to produce materials that are both highly durable and economic. Some of the latest developments in cement and concrete materials used for infrastructure are cement-based composites, concrete admixtures, fiber-reinforced concrete, polymer concretes, and high-strength concrete [2]. To assure high quality and avoid problems in performance throughout the life of concrete, it is essential to have reliable information about cement and its properties.

As it is well known that, cement test falls into two main areas: chemical and physical tests .Therefore, cement is tested to fulfill the following objectives [3]:

- 1- provide information about cement properties
- 2- Give chemical and physical test results on cement to permit comparison with standards and/or previous tests results for historical evaluation.

3- Provide guide lines (for example concrete results) for field utilization of products.

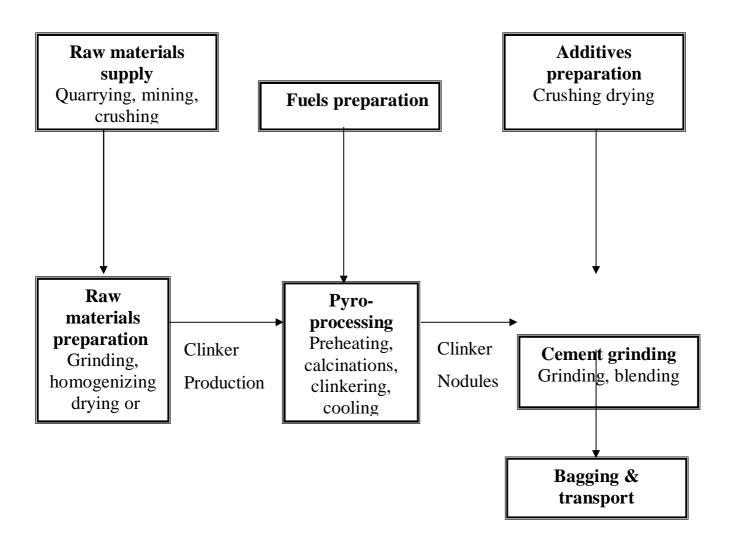
In general, cement chemists use the following the abbreviations: C = CaO; $S=SiO_2$; $A=Al_2O_3$; $F=Fe_2O_3$; $S=SO_3$; $H=H_2O$. Anhydrous Portland cement is a gray powder composed of angular particles typically ranging in the size from 1 to 50 µm. It is produced by pulverizing the clinker being a heterogeneous mixture of several compounds produced by high-temperature reactions between calcium oxide (CaO), silica (SiO_2), alumina ($Al_2 O_3$), and iron oxide (Fe_2O_3) with a small amount of 6 % calcium sulfate (gypsum: CaSO4.2H2O). The major compounds of Portland cement are C3S (tricalcium silicate called as **alite** phase), C2S (dicalcium silicate called as **belite**), C3A (tricalcium aluminate called as aluminate phase), and C4AF (tetricalcium aluminoferrite called as ferrite phase). The actual properties of various compounds vary considerably from cement to cement, and indeed different types of cement are obtained by suitable proportioning of raw materials [4]. Nowadays, Iraq imports many types of cement from different sources. The investigations presented in this paper is aimed to show the validity of two exports cements which is more available in Iraqi local markets and compared them with Iraqi cement

2-Manifucturing process of cement

The basic chemistry of cement manufacturing process is with the decomposition of calcium carbonate $CaCO_3$ at about 900 C to leave calcium oxide CaO and librates gaseous carbon dioxide CO_2 . This processes is known as calcinations. This followed by clinking process in which the calcium oxide reacts at high temperature (typically 1400-1500 C) with silica, alumina and ferries oxide to form the silicates, aluminates and ferrites of calcium, which comprise the clinker. The clinker then ground or milled together with gypsum and other additives to produce cement [5].

There are three main steps in cement production as shown in Flow chart (1) which are [6]:-

- 1. Preparing the raw materials.
- 2. Producing clinker, an intermediate.
- 3. Grinding and blending clinker with other products to make cement.



Flow chart.(1) Process steps in cement manufacturing [6]

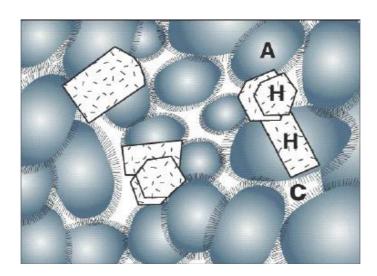
3-Hydration of cement

In cement chemistry, the term 'hydration' denotes the totality of the changes that occur when anhydrous cement, or one of its constituent phases, is mixed with water. The chemical reactions taking place are generally more complex than simple conversions of anhydrous compounds into the corresponding hydrates. A mixture of cement and water in such proportions that setting and hardening occurs is called a paste, the meaning of this term being extended to include the hardened material. The water to cement (w/c) or water/ solid (w/s) ratio refers to proportions by weight; for a paste, it is typically 0.3-0.6. Setting is stiffening without significant development of compressive strength, and typically occurs within a few hours. Hardening is significant development of compressive strength, and is normally a slower process. Curing means storage under conditions such that hydration occurs; conditions commonly employed in laboratory studies include storage in moist air initially and in water after the first 24 h, storage in air of 100% relative humidity and, less favorable for reaction, storage in a sealed container. Because Portland cement is a relatively complex mixture, many studies having the aim of elucidating its hydration chemistry have been made on its constituent phases. For a given particle size distribution and w s ratio, tricalcium silicate or alite sets and hardens in a manner similar to that of a typical Portland cement. Using XRD and other methods, it may be shown that about 70% of the C₃S typically reacts in 28 days and virtually all in 1 year, and that the products are calcium hydroxide (CH) and a nearly amorphous

calcium silicate hydrate having the properties of a rigid gel. C2S behaves similarly, but much less CH is formed and reaction is dower, about 30% typically reacting in 28 days and 90% in I year. In both cases, reaction rates depend on particle size distribution and other factors. Development of compressive strength runs roughly parallel to the course of the chemical reactions, and the strengths at 1 year are comparable to those of Portland cements of the same w/s ratio and cured under the same conditions. The calcium silicate hydrate formed on paste hydration of C3S or C2S is a particular variety of C-S-H, which is a generic name for any amorphous or poorly crystalline calcium silicate hydrate. [7]

Calcium sulfoaluminate hydrates (C3A +water) occupy 15 percent to 20 percent of the solids volume in the hydrated paste. Thus, it takes part in only a minor role in the microstructure-property relationships. During the early stages of hydration, the sulfate/alumina ionic ratio of the solution phase is generally the formation of trisulfate hydrate (C6 AS3 H32), which also called ettringite. Ettringite forms into long rods or needles with parallel sides that have no branches. In pastes of ordinary Portland cement, ettringite eventually transforms to the monosulfate hydrate (C4 ASH18), which forms hexagonal-plate crystals. The presence of the monosulfate hydrate in Portland cement concrete makes the vulnerable concrete to sulfate attack. It should be noted that both ettringite and the monosulfate contain small amounts of iron, which can substitute for the aluminum ions in the crystal structure. Depending on the particle size distribution of the anhydrous cement and the degree of hydration, some anhydrates clinker grains may be found in the microstructure of hydrated cement paste, even long after hydration. The clinker particles in modern Portland cement generally conform to the size range 1 µm to 50 µm. With the progress of the hydration process, the smaller particles dissolve first and disappear from the system, then the larger particles become smaller. Because of the limited available space between the particles, the hydration products tend to crystallize

in close proximity to the hydrating clinker particles, which gives the appearance of a coating formation around them. At later ages, hydration of clinker particles due to the lack of available space results in the formation of a very dense hydration product, the morphology of which may resemble the original clinker particle. Plot (1) shows a model of well-hydrated Portland cement paste [4].



Plot (1) Model of a well-hydrated Portland cement paste [4]

In Plot (1), **A** represents aggregation of poorly crystalline C-S-H particles which have at least one colloidal dimension (1 μ m to 100 μ m). Inter-particle spacing 10 within an aggregation is 0.5 nm to 3.0 nm (average 1.5 nm). **H** represents hexagonal crystalline products such as CH, C4 ASH_{18} , C4 ASH_{19} . They form large crystals, typically 1 μ m wide. **C** represents capillary cavities or voids which exist when the spaces originally occupied with water do not get completely filed with the hydration products of cement. The size of capillary voids ranges from 10 nm to 1 μ m, but in well-hydrated pastes with low water ratio to cement, they are less than 100 nm.

4- Experimental work

4-1 Materials

4-1-1 Cement

Four types of Portland cement produced by Kubaisa cement factory (Iraqi cement) ,Ismanta company (Jordanian cement) ,Al-qaim cement factory (Iraqi cement) and Toraba company (Lebanon cement) were used throughout this study .

4-1-2 Standard fine aggregate

A normal weight sand from Al_bokirbeet quarry of 4.75 mm maximum size was used to obtain standard fine aggregate. The following condition should be afford in such sand according to BS:part 12: 1970 [8]:-

- 1- Saturated surface dry (SSD).
- 2- Loss in HCl acid not exceed 0.25 %.
- 3- Completely pass from sieve 850μ .
- 4- Pass from sieve 600 μ not exceed 10 %.

4-1-3 Water

Potable water without tests was used with all types of cement.

4-2 Mixing of Samples

All samples of cement paste used in standard cement paste, initial and final setting tests were mixed manually for $4\pm 1/4$ minutes. In compressive strength of cement mortar specimens ,the dry mixed ingredients 1:3 (cement +standard sand) were mixed for one minute to ensure the homogeneity and to split the agglomerations of cement particle .The required quality of water was added to the mix and the whole constitutes were mixed for $4\pm 1/4$ minutes .

4-3 Preparation, casting, curing and types of the test specimens

Steel molds 70X70X70 mm were used for casting the compressive strength specimens of cement mortar .Before casting the molds were cleaned and oiled to avoid the adhesion of hardened mortar to the inside faces of molds. The fresh mortar was placed inside the molds with and consolidated by the mean of vibrating table for a sufficient period . .After casting ,the mortar surface was leveled and covered with nylon sheets to prevent evaporation of water so as to avoid the plastic shrinkage cracks. On the second day the specimens were demolded, marked and immersed in tap water until the test age..

4-4 Testing program

4-4-1 Chemical analysis

For the cement sector, cement is usually tested as a composite sample basis which is particularly true for the high consumption types. Thus samples are taken during the quality control testing operation. A composite sample is prepared from these operation, weighed according to the production rates of different production lines. In present study the samples are taken from different batches of cement.

The test was performed in Baghdad central laboratory in National Center for Constructional Laboratories and Researches (NCCLR) and laboratory of Al-qiam cement factory.

4-4-2 Physical properties

Standard cement paste, initial and final setting and compressive strength of cement mortar tests were performed according to BS: part 12:1970 [8].

The compressive strength of cement mortars were conducted on 70 mm cubes. The test was performed at ages 3 and 7 days. The recorded value represents an average of three readings measured on three specimens.

5-1 Results and discussion

5-1-1 Chemical analysis

The chemical analysis of the four types of cement tested in present study are listed in Tables 1, 3, 5 and 7. From these tables, it can see that the major oxides of Kubaisa cement were near those in typical cement Table 9 [9] more than Ismnta cement due to the quality control of mixing raw materials during manufacturing process. This inflected on the calculation of major compounds of cement using Bogue equations .The Ismnta cement showed less percentage of C₃S compared with the Kubaisa cement which was nearest to the typical cement .On the other hands, the loss on ignition and insoluble residue of Ismnta cement were exceed the limits of I.O.S No.5 1984 [10]. The loss on ignition is increased when the cement stored for a long periods and this is more likely occurred in imported than local cement .The percentage of C3A was more in the Jordanian cement compared with the local cement. This is because the higher percentage of alumina oxide in the first type of cement .The opposite results obtained for the percentage of C4AF and that may be related to the high ferrite oxide on the raw materials of cement on Jordon .The sulfates content in Ismanta was equal to the upper limit of I.O.S No.5 1984 and on the same time higher than Kubaisa cement.

On the other sides for sulfate resisting cement, Al-qaim cement showed higher percentage of C3S and less percentage of C2S compared with Torab Alsabia cement. This is surly affected the strength properties of cement where the silicates in cement are responsible on such properties.

The calcium silicate hydrate formed on paste hydration of C2S or C3S is a particular variety of C-S-H, which is a generic name for any amorphous

or poorly crystalline calcium silicate hydrate. Alite is the most important constituent of all normal Portland cement clinkers, of which it constitutes 50-70%. It is tricalcium silicate (3CaO.SiO2) modified in composition and crystal structure by incorporation of foreign ions, especially Mg^{+2} , Al^{+3} and Fe^{ff} reacts relatively quickly with water, and in normal Portland cements is the most important of the constituent phases for strength development; at ages up to 28 days, it is by far the most important. [7]

It is very important to noticed that the Torab Alsabia cement exceed the limits of I.O.S No.5 1984 standard in C3A content where the C3A must be less than 3.5 % to avoid chemical reaction with the salts causing an increase in the volume of cement paste .Moretheless, causing more cracking in cement paste which allow the salts effect on decreasing the strength properties and perhaps causing the corrosion of steel reinforcement in concrete.

The sulfate oxide which represents the quantity of gypsum added to the cement to control the setting of cement was less in Al-qaim cement compared with the Torab Alsabia cement due to the higher percentage of C3A in the last one. It is very important to control the quantity of gypsum because the gypsum in cement affects not only the setting time. but also the strength development and the volume stability [7]. The insoluble residue and loss on ignition of Al-qaim cement were less than Torab Alsabia cement this may be related to the same factors mentioned in ordinary Portland cement. Al-rawi et al [11] recommended to reduce the upper limit of SO3 in sulfate revisiting cement from 2.5 % to 2% and to increase the upper limit of C3A from 3.5% to 5%.

Table (1) Chemical analysis of Kubaisa cement

Item	Chemical	Content	Limits of
	Composition	%	I.O.S No.5
			1984

Lime	CaO	62.12	
Silica	SiO_2	22.56	
Alumina	Al_2O_3	4.72	
Iron Oxide	Fe_2O_3	2.96	
Magnesia	MgO	291	< 5
Sulfates	SO_3	2.26	< 2.8
Loss on ignition (L.O.I)		1.64	< 4
Insoluble residue (I.R)		1.09	< 1.5
Lime saturation factor (L.S.F)		0.86	(0.66-1.02)
Main compounds	% by weight of cement		
C_3S	38.9		
C_2S	35.4		
C_3A	7.51		> 5
C_4AF	8.99)	

Table (2) Physical properties of Kubaisa cement

Property	Result	Limits of I.O.S No.5 1984
Water cement ratio (standard cement paste) Vicat	0.334	
Initial setting (Vicat) min.	100	> 45
Final setting (Vicat) hr:min.	3:40	< 10
Compressive strength (MPa) 3-day 7-day	16.1 23.3	>15 > 23

Table (3) Chemical analysis of Ismanta cement

Item	Chemical Composition	Content %	Limits of I.O.S No.5 1984
Lime	CaO	55.64	
Silica	SiO_2	20.77	
Alumina	Al_2O_3	6.41	
Iron Oxide	Fe_2O_3	4.24	
Magnesia	MgO	3.00	< 5
Sulfates	SO_3 2.80		< 2.8
Loss on ignition (L.O.I)		4.35	< 4
Insoluble residue (I.R)		2.63	< 1.5
Lime saturation factor (L.S.F)		0.78	(0.66-1.02)
Main compounds	% by weight of cement		
C_3S	11.48		
C_2S	50.95		
C_3A	9.82		> 5
C_4AF	12.89		

Table (4) Physical properties of Ismanta cement

Property	Result	Limits of I.O.S No.5 1984
Water cement ratio (standard cement paste) Vicat	0.354	
Initial setting (Vicat) min.	70	> 45
Final setting (Vicat) hr:min.	3:10	< 10
Compressive strength (MPa) 3-day 7-day	12 17.2	>15 > 23

Table (5) Chemical analysis of Torab alsabia cement

Item	Chemical Composition	Content %	Limits of I.O.S No.5 1984
Lime	CaO	61.3	
Silica	SiO_2	21.85	
Alumina	Al_2O_3	5.93	
Iron Oxide	Fe_2O_3	3.41	
Magnesia	MgO	1.99	< 5
Sulfates	SO_3 2.75		< 2.8
Loss on ignition (L.O.I)		2.2	< 4
Insoluble residue (I.R)		0.88	< 1.5
Lime saturation factor (L.S.F)		0.84	(0.66-1.02)
Main compounds	% by weight of cement		
C_3S	30.9		
C_2S	39.4		
C_3A	9.94		< 3.5
C_4AF	10.36		

Table (6) Physical properties of Torab alsabia cement

Property	Result	Limits of I.O.S No.5 1984
Water cement ratio (standard cement paste) Vicat	0.36	
Initial setting (Vicat) min.	110	> 45
Final setting (Vicat) hr:min	3:50	< 10
Compressive strength (MPa) 3-day 7-day	17.6 21.0	>15 > 23

Table (7) Chemical analysis of Al-qaim cement

Item	Chemical Composition	Content %	Limits of I.O.S No.5
* ·		- 1 - 5	1984
Lime	CaO	64.67	
Silica	SiO_2	21.86	
Alumina	Al_2O_3	4.04	
Iron Oxide	Fe_2O_3	5.18	
Magnesia	MgO	1.30	< 5
Sulfates	SO_3 2.23		< 2.8
Loss on ignition	0.44		< 4
(L.O.I)			
Insoluble residue (I.R)	0.18		< 1.5
Lime saturation factor		0.91	(0.66-1.02)
(L.S.F)			
Main compounds	% by weight of cement		
C_3S	56.16		
C_2S	20.39		
C_3A	1.95		< 3.5
C_4AF	15.75		

Table (8) Physical properties of Al-qaim cement

Property	Result	
		Limits of I.O.S No.5 1984
Water cement ratio (standard cement paste) Vicat	0.332	
Initial setting (Vicat) min.	155	> 45
Final setting (Vicat) hr:min.	4:00	< 10
Compressive strength (MPa) 3-day 7-day	17.8 23.8	>15 > 23

Table (9) Chemical analysis of typical cement [8]

Item	Chemical Composition	Content %	Limits of I.O.S No.5 1984
Lime	CaO	63	
Silica	SiO_2	20	
Alumina	Al_2O_3	6	
Iron Oxide	Fe_2O_3	3	
Magnesia	MgO	1.5	< 5
Sulfates	SO_3	2	< 2.8
Loss on ignition (L.O.I)		2	< 4
Insoluble residue (I.R)		0.5	< 1.5

Lime saturation factor (L.S.F)		(0.66-1.02)
Main compounds	% by weight of cement	
C_3S	54.1	
C_2S	16.6	
C_3A	10.8	> 5
C_4AF	9.1	

5-1-2 Physical properties

The results of standard consistence of cement paste and initial and final setting for the four types of tested cement are illustrated in Figs. 1, 2, 3 and 4 and listed in Tables 2, 4, 6 and 8. The results indicate that the Torab alsabia cement showed the higher value of water cement followed by Ismanta cement then Kubaisa and Al-qaim cements respectively. In initial and final setting results Al-qaim provided a higher initial setting time compared with Torab alsabia cement due to the lower percentage of C3A which play an important rule in setting of cement .For ordinary Portland cement Kubaisa showed higher initial time compared with Ismanta cement in spite of the higher percentage of C3A for the last one .This may be related to the higher content of C3S in kubaisa cement which participate in setting of cement at early ages. The final setting behavior is similar to the initial setting where Al-qaim cement had along time to achieve the final setting for the two type of sulfate resisting cement and Kubaisa provided higher final setting for ordinary Portland cement compared with Ismanta cement. Fig 7 represent the result of compressive strength of cement mortar .It is clearly from the figure that the Iraqi cement ordinary or sulfate resisting showed a higher compressive strength compared with the to imported cements. This is as a result of the high percentage of silicates (C2S & C3S) in Iraqi cement which were 74.3 % and 76.55% for Kubaisa and Al-qaim cements respectively compared with 62.43 % for Ismanta and 70.3 % for Torab alsabia cement. In addition to the higher percentage of C3S in the two type of Iraqi cement compared with the two imported cement where C3S is one of the important major compounds in cement to achieve a higher strength at early ages of cement more than the other major compounds C2S.

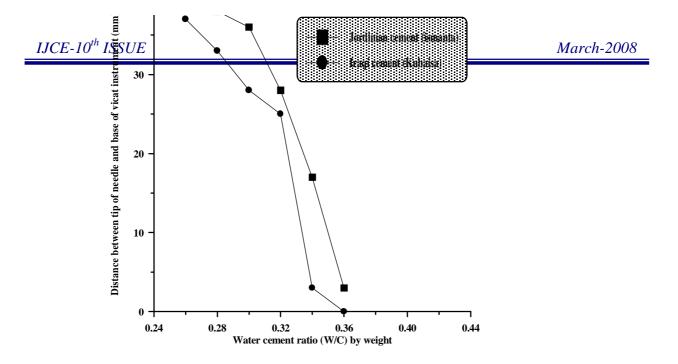


Fig.(1) Results of standard consistence of Kubaisa and Ismanta cement

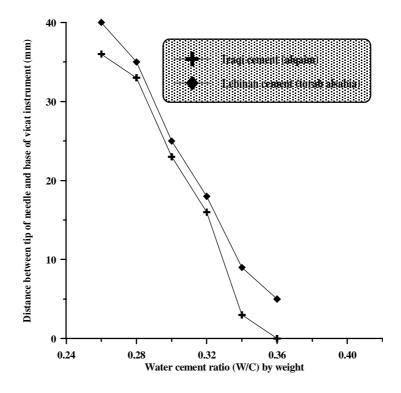


Fig.(2) Results of standard consistence of Al-qaim and Torab alsabia cement

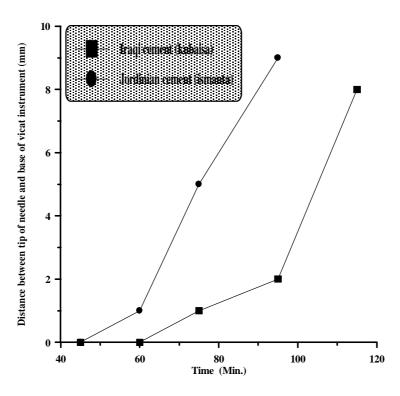


Fig.(3) Results of initial setting of Kubaisa and Ismanta cement

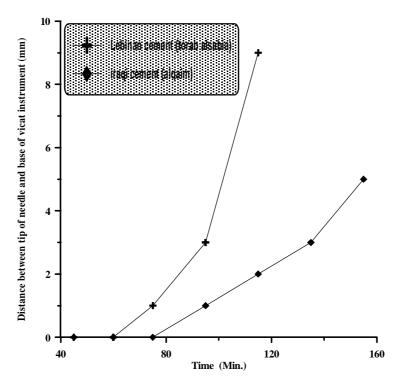


Fig.(4) Results of initial setting of Al-qaim and Torab alsabia cement

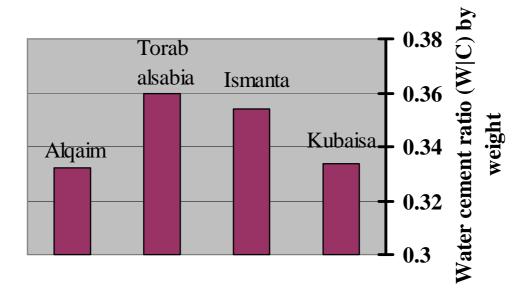


Fig.(5) W/C ratios to obtain standard consistence for the different type of tested cement

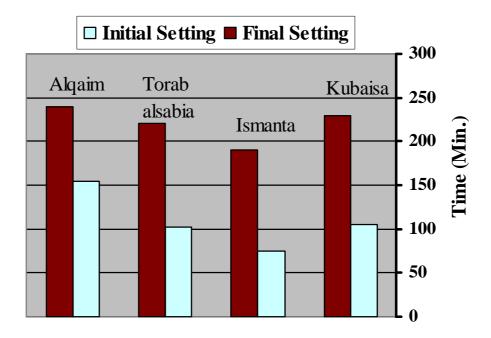


Fig.(6) Initial and final setting time for the different type of tested cement

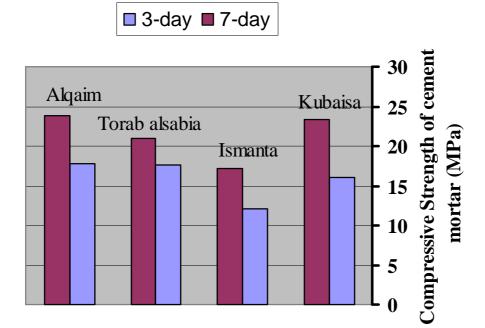


Fig.(7) Compressive strength of cement mortar for the different type of tested cement

Conclusions

Based on the results of present study the following conclusions can be drawn :

1-For ordinary Portland cement:

- The major oxides of Kubaisa cement were near to those in typical cement more than Ismanta cement.
- The loss on ignition and insoluble residue of Ismanta cement were exceed the limits of I.O.S No.5 1984.
- The Ismanta cement showed less percentage of C3s compared with the Kubaisa cement.
- Kubaisa cement showed higher initial time compared with Ismanta cement.
- The compressive strength of Kubaisa cement was 23.3 MPa at 7-day while it was 17.2 MPa for Ismanta cement.

2- For sulfate resisting cement:

- Torab Alsabia cement exceed the limits of I.O.S No.5 1984 standard in C3A content.
- The insoluble residue and loss on ignition of Al-qaim cement were less than Torab.
- silicates (C2S & C3S) in Al-qaim cement were 76.55% while it were 70.3 % for Torab alsabia cement
- In initial and final setting results Al-qaim provided a higher initial setting time compared with Torab alsabia cement.
- The compressive strength of Al-qaim cement was 23.8 MPa at 7-day while it was 21 MPa for Torab alsabia cement

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