SUST
Journal of Natural and Medical Sciences
Journal homepage:
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The Effect of Alkalis on some Properties of Sudanese Cement

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Article history: Recieved: 28/10/2015 Accepted: 12/05/2016

ABSTRACT

The aim of this work was to study the effect of alkali metal oxides, (Na_2O and K_2O) on some properties of Portland Sudanese cements. The physical properties investigated were compressive strength at (2, 7 and 28 days), initial and final setting time, soundness and expansion. Three brands of cements (El Salam, Atbara and Berber) were analyzed by flame photometry to evaluate their alkali levels. It was found that Berber sample had the lowest alkali content (0.7%). Additive values of 2%, 4% and 6% alkalis (as sodium hydroxide solution), were performed to check the effect of increased alkalinity on strength, setting and soundness. The expansion test was performed on the three samples of cement with 5% alkali addition .Alkali addition reduced both, the compressive and flexural strength properties of Berber cement. Initial and final setting time, were more reduced, and soundness followed the same pattern. In contrast to Berber cement Atbara and Al salam, recorded greater expansion than the permitted maximum percentage of 0.6%. The high alkali content detected in the final product caused many difficulties and affected adversely its properties. Serious attempts to decrease alkali contents in Sudanese cement, hence, become necessary.

KEYWORDS**:** Alkalinity, Soundness, Schist, Setting time, alkali aggregate.

المستخلص

كان الهدف من البحث دراسة تأثير القلويات (أكسيدي الصوديوم و البوتاسيوم) علي خواص الأسمنت البورتلاندي السوداني. حيث جمعت ثلاث عينات من الأسمنت و هي بربر، عطبرة و السلام و تم أولا إجراء تحليل لمحتوى القلويات في المنتج النهائي بواسطة مضواء اللهب. أجريت تجارب مختبرية علي الأسمنت المجهز من مصنع أسمنت بربر بإضافة مزيد من القلويات في شكل هيدروكسيد صوديوم لمعرفة تأثير زيادة القلويات على الخواص الفيزيائية للأسمنت و هي تحديد القوة الانضغاطية (3 – 7 و 28 يوم) و تحديد زمن التصلب الابتدائي و النهائي ثم أجري اختبار التمدد بإضافة 5% من هيدروكسيد الصوديوم علي أسمنت بربر، عطبرة و السلام علي مدى ثلاث أشهر. أظهرت نتائج التحليل الكيميائي أن أسمنت بربر يحتوي علي أقل نسبة من القلويات و هي 0.7% وأظهرت نتائج الاختبارات الفزيائية ان زيادة محتوى القلويات فوق المعدل المسموح به (0.6%) تودي الي تدهور في العجينة الأسمنتية و الخرصانة حيث تقل القوة الإنضغاطية و يزيد التمدد بزيادة القلويات. لهذا نوصي بإستخدام مواد خام قليلة القلويات لتفادي النسبة العالية لأكسيدي الصوديوم و البوتاسيوم في المنتج النهائي .

INTRODUCTION

Portland cement consists mainly of major oxides which include: CaO, SiO_2, Al_2O_3 and Fe_2O_3. Optimum cement quality is obtained when the required proportions of these four oxides are consistent throughout the cement (1), and cement contents minor oxides which include: SO_3, TiO_2, Mn_2O_3, MgO, Na_2O and K_2O. Minor oxides must usually be less than a few percent of the mass of cement. Two of the minor compounds are of interest: the oxides of sodium and potassium (Na_2O and K_2O) known as the alkalis oxides (2).

These two compounds are invariably associated with cement raw materials and, if present in low quantities in the chemical composition of Portland cement, they are quite harmless. However، larger amounts of alkalis can cause difficulties on the mechanical properties of cement.

The raw materials which were used to control the four major compounds in cement industry of Atbara and Al Salam included Limestone and clay, while Berber cement raw materials consisted of limestone, schist, clay and iron ore, which give the flexibility in raw mix control for Berber cement rather than others.

Number of previous studies demonstrated that the effects of alkalis on various properties of cement paste, mortar, and concrete, including early hydration and setting, strength development and ultimate strength, drying shrinkage, susceptibility to cracking, microstructure of cement hydrates, and durability, have been a subject of concern since many decades. Stark (3) demonstrated that, the significant proportion of alkalis in clinker can cause quick setting, reduce the ultimate strength of concrete, and increase expansion under water and shrinkage under drying conditions. Blaine, et al, (4), Carlson,(5) and Burros(6) demonstrated that higher cement alkali content tend to increase the susceptibility to shrinkage under drying conditions in the case of cement pastes and mortars. This effect is not so clear in the case of concrete. Osbaeck(7) concluded that the higher alkali content in cement accelerates the strength development in short term but decreases the ultimate strength. Jawed and Skinny (8) also concluded that high alkali content in cement generally results in a higher strength at early age، but to lower strength after 28 days. Gouda (9) observed similar trend for concrete specimens made with both low alkali (0.58% Na_2O) and very high – alkali (1.76% Na_2O) cement. Avery low-alkali cement can result in abnormally low strength development at early ages. On the other hand، Odler and Wonnemann (10) observed that the alkalis incorporated into the cement clinker did not affect the compressive strength, whereas an external addition of alkali sulfate considerably reduces the strength at any age up to 28 days. Alexander and Davis (11) observed that the higher the alkali increase, the lower the compressive strength of cement pastes. Unfortunately, most studies on the effects of alkalis on the mechanical properties of hydraulic systems were performed on cement paste and mortar specimens. Shayan and Ivanuse (12) reported an increase in the expansion of mortar bars using sodium hydroxide doping. Vivian (13) showed no significant expansion to occur when the alkali content of the cement was increased to 4.08% using NaOH in the mixing water. One of the disadvantages of increasing alkalis is alkali - aggregate reaction (AAR) which is a mechanism of deterioration of concrete resulting from an interact-tion between alkali principally originating from the Portland cement and certain types of aggregates. The most common type of the reaction is the alkali silica reaction (ASR) which occurs with siliceous aggregates forming a calcium alkali-silica gel. This gel is of calcium silicate hydrate (C-S-H) imbibes water producing a volume expansion which disrupts the concrete [14]. The mechanisms that control this reaction are not well understood, and the measures to prevent or control the reaction have been based largely on empirical consideration. No known cure exists since the essential ingredie-nts of the reaction were irretrievably mated in the concrete during mixing and hardening processes. Now alkali silica reac-tion has received wide spread publicity and it has been described as a concrete cancer.

In Sudan, no example concerning deterioration of concrete due to ASR has been reported, and no investigations of cracked or otherwise deteriorated concrete, to establish whether it is a case of alkali-aggregate reaction, have been conducted until 1992. Nour-Allah El-Tilib[15] carried out a survey on Sudanese aggregates for their alkali-silica reactivity and reported that alkali-silica reaction has been found in some aggregates. His recommendations in all studies were very useful; they were considered and used in Merowe Dam which is the one of the biggest construction project in Sudan.

In the present work, the effect of increased alkalinity on strength, soundness, setting time and expansion of Sudanese cements is investigated.

METHODS:

Sampling: Three cement samples were randomly collected from Berber, Atbara and Al Salam cement factories, in the river Nile state. One rock aggregate sample (rhyolite) from the Seleit area north east of Khartoum, known of being potentially non-reactive, was used in the investigation.

Flame photometric determina-tion of sodium and potassium oxides: This test method covers the determination of sodium oxide (Na_2O) and potassium oxide (K_2O) by flame photometer.

2.0000g of any one of the samples was accurately weighed in a 100 ml beaker and stirred with distilled water, 5 ml of HCl added all at once, the beaker is filled half with distilled water and left for 15 minutes on a hot plate at 90-100°C. The solution is then filtered through a filter paper into a 250 ml volumetric flask. The beaker and filter paper were washed with hot distilled water and filled to the mark with boiled distilled water, then after cooling to room temperature, a 100 ppm solution was prepared from 1000 ppm (in-volumetric flask), then a 2, 4, 6, 8 and 10 ppm standards were prepared from 100 ppm. Standard and samples were determined and calculated from recorded averages for Na_2O and K_2O in the unknown samples (Table 1).

Table 1: Alkali Content of Berber, Alsalam and Atbara Portland cement used

Cement	K_2O%	Na_2O%	Alkalis as Na_2O equivalent
Berber	0.3640	0.5422	0.77
Salam	0.3951	0.7089	0.97
Atbara	0.4254	0.7093	0.99

Determination of Strength: In order to assess the effect of cement alkalis on the cement strength property Berber cement product was chosen. The strengths were measured at 2 - 7 and 28 days. Four series of tests were performed. In one series the tests were carried out without alkali addition. In the other three series, the alkali content was increased using sodium hydroxide pellets at concentration of 2%, 4% and 6%. The procedure used for determination of the compressive and flexural strength followed to a large extent that described in the European standard EN 197-1. (The minimum compressive strength should be 10 MPa in 2days, 30 MPa in 7 days and 42 Mpa for 28 days.)

Prismatic test specimens 40mm x 40mm x160mm in size were casted from a batch of plastic mortar containing one part by mass of cement and three parts by mass of standard sand with water/cement ratio of 0.5. The mortar is prepared by mechanical mixing and is compacted in a mold using a standard jolting apparatus. The specimens in the mold are stored in a moist atmosphere for 24 h at a temperature of 20 ±1^{o}C, relative humidity of 95% ±1and then the remolded specimens were stored under distilled water in standard environment of temperature of 20±1^{o}C, and relative humidity of 50%±1 in until strength testing. At the required age, the specimens are taken from their wet storage, broken in flexure into two halves and each half tested for strength in compression (Table 2).

Table 2: Compressive and flexural strength properties of Berber cement in the presence and absence of alkali additions

Test duration(day)	Alkali addition%	Average Compressive strength (MPa)	Flexural strength (MPa)
2	0	19.8	4.1
	2	16.8	4.35
	4	8.4	2.6
	6	5.0	3.05
7	0	32	5.8
	2	25.7	4.8
	4	13.6	4.3
	6	7.6	4.2
28	0	45.9	7.75
	2	37.3	7.75
	4	22.3	4.6
	6	11.5	2.8

Determination of setting time: 500g of cement was weighed accurately, required percentage of sodium hydroxide has been added to the cement (0%, 2%, 4% and 6%), 125 ml of distilled water added in the mixer. Cement was added carefully within 10 seconds to the water in order to avoid loss of water or cement. Zero time for addition is registered The mixer was started at low speed for 90 seconds, stopped for 15 seconds to scrap the mixer paddle, and then again started for 90 seconds with high speed. Then cement paste was removed from mixers jug and transferred into Vicat apparatus, The paste and the mould were stored in a moist atmosphere with a temperature of 20±1^{o}C, and relative humidity of 95% ± 1 (EN 196-4 specification limited the minimum value of initial setting time should be 60 minutes and the maximum final setting time should be 390 minutes). Initial setting time needle has been fitted to Vicat apparatus and zero reading adjusted using base plate and then after every 5 minutes penetration of needle is observed till the height of needle from the base plate has reached 4~6 mm, initial setting time was registered, then final setting time needle fitted and the test continued till the impression of the needle for cement paste gone and final setting time registered, (Table 3 and Figures 1 and 2).

Table 3: Setting time of Sudanese cement

Alkali content	Initial setting time	Final setting time
0%	185 min	275 min
2%	175 min	235 min
4%	45 min	75 min
6%	10 min	20 min

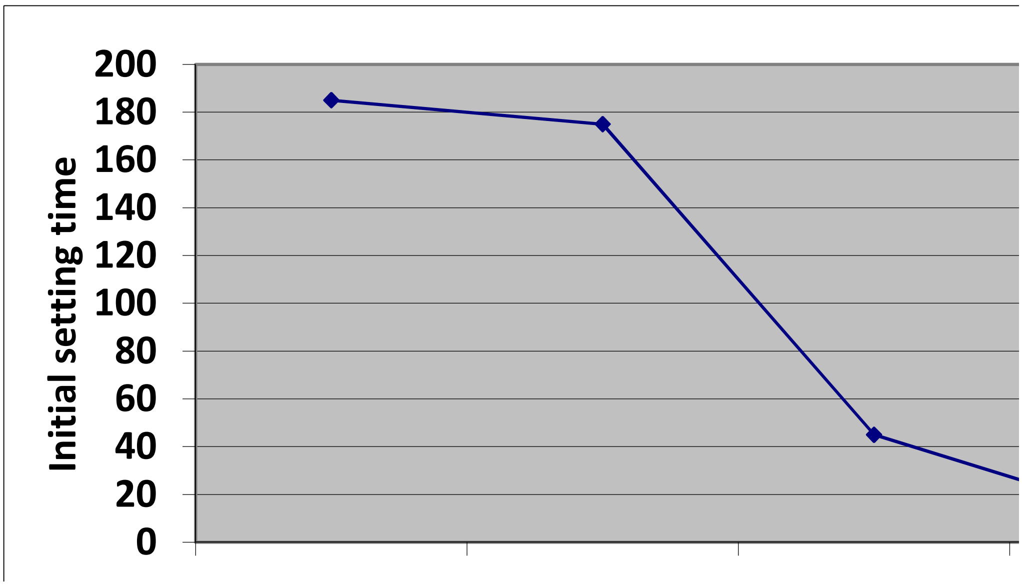

Figure 1: Relation between initial setting time and alkali content of Sudanese cement

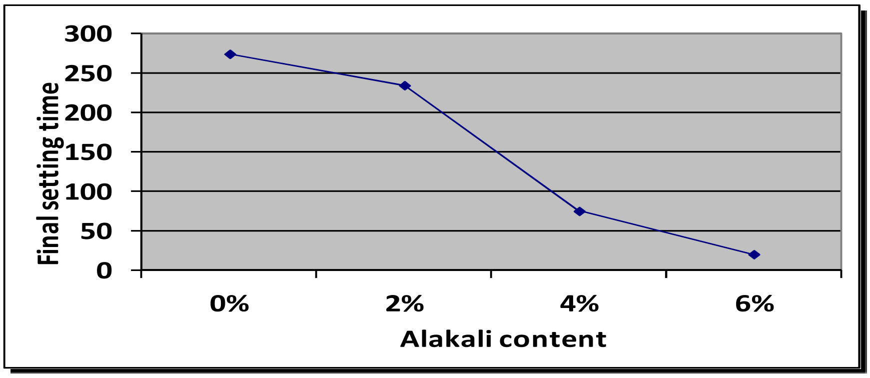

Figure 2: Relation between final setting time and alkali content of Sudanese cement

Determination of soundness: A cement paste from the above setting time test was taken, and transferred into Le Chatelier apparatus and compacted well to remove any air gap, Le Chatelier apparatus had been covered from top side and bottom side with glass sheet (4mm thickness), kept for 24 hours at same standard environment. After 24 hours distance between Le Chatelier apparatus legs has been measured, paste and apparatus has been immersed into hot distilled water (100^{o}C) for three hours and half. Cooled down to room temperature and gap between both legs again measured, difference has been registered, (Table 4 and Figure 3).

Table 4: Soundness property of Sudanese cement

Alkali content	Initial	Final	Value of soundness
0%	7.5	9.5	2.00
2%	9.7	11.5	1.8
4%	9.8	10.7	0.9
6%	7.4	8.2	0.8

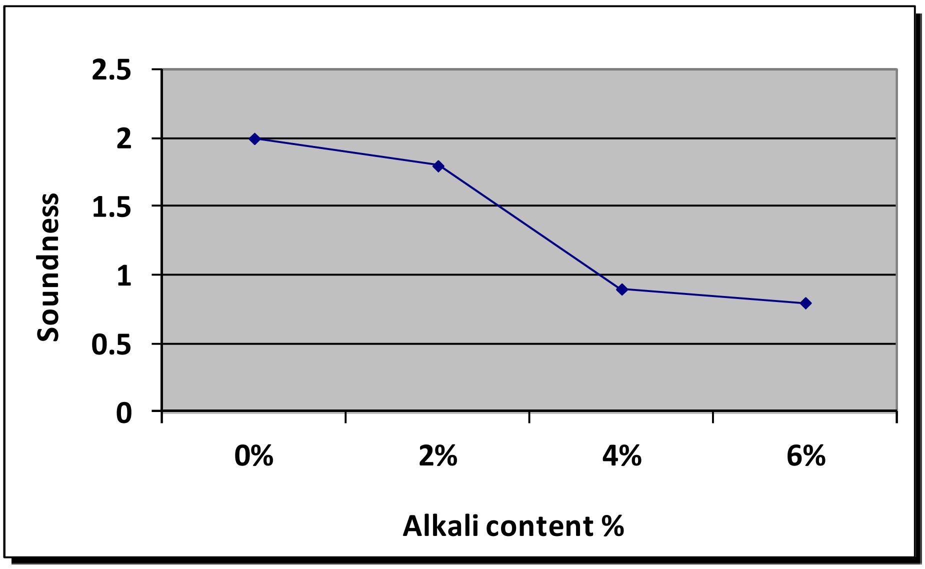

Figure 3: Relation between soundness and alkali content of Sudanese cement

Determination of mortar bar -expansion: In this test the mortar-bars 25x25x280mm in size are prepared with an aggregate/cement ratio of 2.25 by weight. The specimens remained in the moulds for 24 hours, then they were removed for initial length measurement. The specimens were stored above water at 38°C in a closed container with blotting paper on the inside walls to act as a wick to maintain a high humidity throughout the container. The specimens were removed periodi-cally for length measurement. The average expansion at 3 months is taken as a measure of the potential alkali-reactivity, (Table 5, 6 and Figure 4, 5).

Table 5: Mortar-bar expansion property of Sudanese cement without alkali addition

Cement Time (days)	**Berber**	**ALSalam**	**Atbara**
0	0	0	0
15	0.02	0.021	0.022
30	0.027	0.029	0.031
60	0.038	0.038	0.039
90	0.040	0.043	0.044

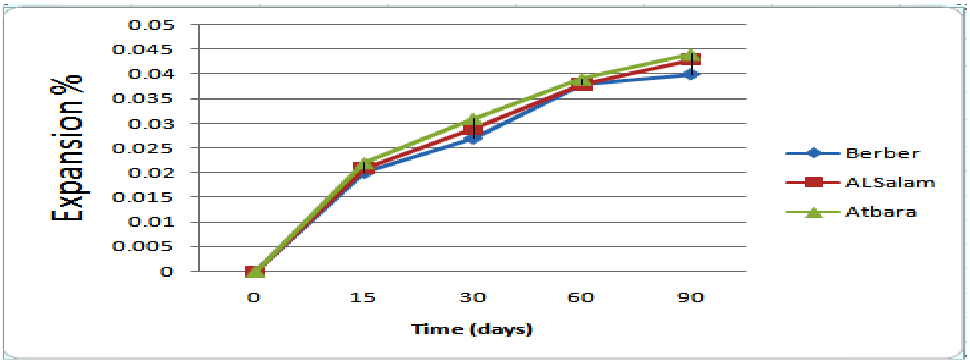

Figure 4: Mortar bar expansion property of Sudanese cement without alkali addition.

Table 6: Mortar-bar expansion property of Sudanese cement with 5% alkali addition

Cement Time (days)	**Berber**	**Alsalam**	**Atbara**
0	0	0	0
15	0.02	0.021	0.023
30	0.027	0.033	0.034
60	0.037	0.043	0.045
90	0.045	0.052	0.053

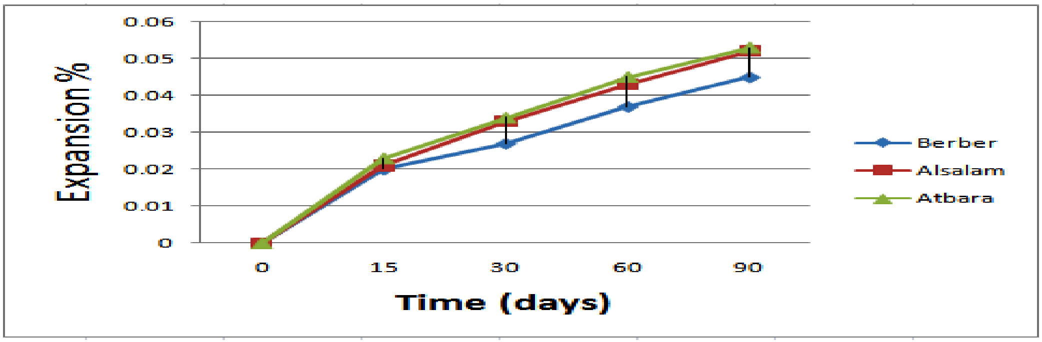

Figure 4: Mortar bar expansion property of Sudanese cement with 5% alkali addition.

RESULTS and DISCUSSION

Alkali content of Sudanese cement are given in Table 1. The results show that Berber cement is relatively of a lower in alkali level than Al Salam cement which, in turn, is of a lower alkali than Atbara cement. The three cements, however, are of alkali contents greater than the ASTM C150 [16] specifications of 0.6%, if the cement is to be used with potentially reactive aggregate for concrete. The alkali content of Portland cement is expressed, according to ASTM C150 [16], as sodium oxide equivalent ($Na_20+0.658K_20$).

Results of strength test show that with more alkali addition there was more reduction, in both, the compressive strength and flexural strength. Furthermore, the reduction in strength was more pronounced at the 28th day strength, particularly, the compressive strength. The obtained test results are in agreement with the findings of Smaoui [17], Osbaeck [7] and Alexander and Davis [11] .From the results obtained it can be deduced that a high alkali cements produce, especially in the long term, lower compressive and flexural strength than a low alkali cement.

Results of setting time and soundness shows that with more alkali addition there was more reduction in both tests values.

Result of mortar-bar expansion test shows that Berber cement which have a lower amount of alkali gave expansion less than ASTM failure criterion of 0.05%.

CONCLUSION:

The alkalis content generally affected the mechanical properties of cement. Optimum alkali content was about (0.6 %). Addition of alkali made the structure of cement more weak (strength, setting time and soundness tests). Any addition of more than 0.6% alkali content could increase expansion in cement paste.

RECOMMENDATIONS:

Owing to their high alkali oxides content, we recommend that Atbara and Alsalam factories vary their sources of raw materials to obtain the principal oxides for the manufacture of cement with less quantity of alkali oxides as does Berber factory by adding schist mineral to the main minerals of clay and limestone.

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