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STUDIES ON THE PROPERTIES OF SOME BLENDED CEMENTS MADE WITH LOCAL MINERAL ADMIXTURE UNDER SULPHATE ATTACK

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ABSTRACT:

Three types of replacement materials were used in manufacturing of some blended cements. The characterization, durability and resistance of these prepared blended cements against sulfate aggressive media were studied. The replacement materials used in this study are metakaolin, sandy clay and limestone. Blended cement mortars were prepared with 15, 20, and 25% mineral admixtures replacement instead of the same percent of cement. The specimens were immersed in 5% magnesium sulfate and 5% ammonium sulfate solutions then compared with the samples dipped in distilled water as reference samples for 90 days curing. The compressive strength and expansion of cement mortars were investigated at different time intervals.

The result revealed that metakaolin can be used for resisting sulfate attack without any disadvantages in physical properties of cement. Sandy clay show good results against sulfate attack but causes side effect on physical properties of cement due to its high insoluble residue. However, limestone as mineral admixture not failed to resist o sulfate attack.

1. INTRODUCTION:

The degradation of cementitious materials by external sulfate attack is one of the most frequently cited causes of service life reduction of concrete structures. The importance of sulfate attack is attested by the multitude of experimental and theoretical studies on its origin and manifestations that have been published just in the last decade [1–6]. The formation of ettringite [7–9] and sometimes gypsum [10] are usually thought to be responsible for significant volumetric expansion and structural damage during sulfate attack.

The present work studied the effect of some replacement material on resistance of sulfate attack and its effect on physical properties of cement

2. EXPERIMENTAL

Blended Portland cements were prepared by mixing CEM I 42.5 N with 15, 20, and 25% of metakaolin, sandy clay and limestone as replacement materials.

The effect of these replacement materials on the water of consistency and setting times of the cement was carried out according to EN196-3:2016(11).

The cement was mixed with sand for preparing mortar samples with the ratio of 1:2, respectively with w/c ratio of 0.46. The Mixing process was performed in compliance to ASTM C 305-20(12). The mortar pastes were molded in 1x1x11.25 inches cm stainless steel molds with test method ASTM C 157 (13) and ASTM C 490 (14), stored 24 h in humidity chamber, demolded then cured in 5% $MgSO_4$, 5% $(NH_4)_2 SO_4$ solutions as well as distilled water as reference up to 3 months .The effect of the additives was performed by adding 15, 20, and 25% by weight replacement material to Portland cement then proceeding as described.

The compressive strength of the hardened mortar samples were measured up to 90 days curing according to B.S. EN 196-1:2016(15).

3. RESULTS:

3.1 Characterization of cements

Table 1 illustrates the oxide percentages of CEM I 42.5 N, metakaolin cements (K), sandy clay cement(S) and limestone cement (L).

Table (1): Oxide composition of CEM I 42.5N (m. %)

SAMPLE	SiO2	Al2O3	Fe2O3	CaO	MgO	K2O	Na2O	SO3	Cl	L.O.I	IR
OPC	**19.8**	**4.74**	**3.57**	**62.79**	**2.07**	**0.216**	**0.299**	**2.87**	**0.038**	**3.24**	**0.72**
L1	**17.98**	**4.21**	**3.12**	**63.58**	**2.05**	**0.204**	**0.261**	**2.69**	**0.037**	**10.28**	**1.12**
L2	**17.56**	**4.12**	**3.03**	**64.04**	**2.05**	**0.192**	**0.262**	**2.59**	**0.038**	**11.54**	**1.14**
L3	**16.77**	**3.89**	**2.9**	**64.44**	**2.07**	**0.185**	**0.249**	**2.72**	**0.04**	**13.08**	**1.6**
S1	**26.74**	**5.04**	**3.79**	**54.85**	**1.89**	**0.27**	**0.29**	**2.45**	**0.026**	**4.09**	**8.2**
S2	**29.09**	**5.08**	**3.86**	**52.16**	**1.85**	**0.286**	**0.29**	**2.5**	**0.029**	**3.93**	**11.5**
S3	**31.16**	**5.15**	**3.98**	**49.86**	**1.81**	**0.282**	**0.294**	**2.4**	**0.026**	**3.62**	**16.21**
K1	**23.87**	**7.44**	**4.96**	**54.07**	**1.92**	**0.279**	**0.296**	**2.55**	**0.024**	**4.32**	**4.2**
K2	**24.17**	**7.69**	**5.08**	**53.3**	**1.91**	**0.27**	**0.295**	**2.53**	**0.025**	**3.99**	**7.4**
K3	**25.86**	**8.93**	**5.81**	**49.7**	**1.83**	**0.31**	**0.299**	**2.35**	**0.022**	**3.87**	**10.5**

Samples legend: OPC (Ordinary Portland cement), L (limestone cements, L1, L2 & L3 are 15, 20 & 25% limestone replacement, respectively) . S (Calcined sandy clay cements S1, S2 &S3 are 15, 20 &, 25% replacement, respectively). K (Calcined kaolin clay cements K1, K2 & K3 are 15, 20 &25% replacement, respectively).

3.2 Water of consistency and setting time

Table2 exhibits the effect of replacement materials on the water of consistency and setting time of Portland cement. The results indicate a clear increase in the water of consistency due to the increase in surface area of cements with the increase of replacement materials. There is a retardation of the cements set with the increase of the replacement material percentage due to the increase of aluminate phases especially kaolin blended cements materials.

Table (2): Effect of replacement materials on water of consistency and setting time of Portland cement and blended cement pastes

cements	Consistency	I.S.	F.S.
OPC	28	140 min	185 min
SRC	27.75	135 min	180 min
L1	28.5	155 min	210 min
L2	28.25	150 min	210 min
L3	28.5	150 min	215 min
S1	30.2	161 min	225 min
S2	30.5	169 min	238 min
S3	31	174 min	247 min
K1	29.5	160 min	220 min
K2	29.8	168 min	227 min
K3	30	172 min	240 min

3.3 Expansion

The expansion results of OPC and blended cements immersed in (a) 5%$MgSO_4$ (b) 5 % ($NH4)_2SO_4$ solution (C) distilled water are showed in figure 1. The results indicate that expansion of meta kaolin cements (K1,K2,K3) as well as calcined sandy clay cements (S1,S2,S3) decreased while increases with limestone cements (L1,L2,L3) specially with 30% replacement for 90 days curing. Ammonium sulfate salt is more harmful than magnesium sulfate solution.

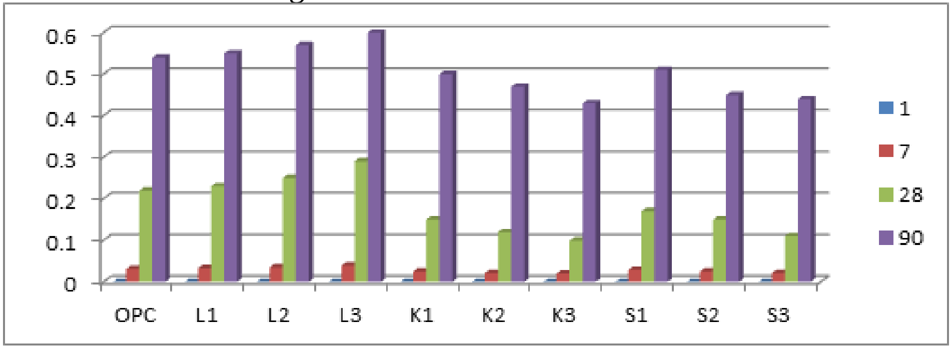

Figure 1 (a) Expansion of cements immersed in 5%$MgSO_4$

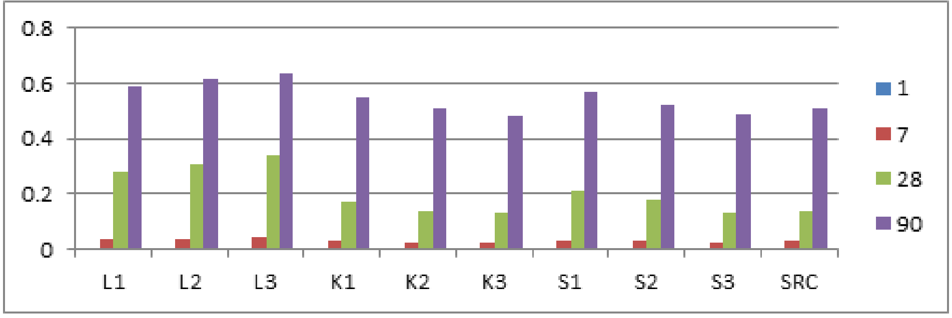

Figure 1 (b) Expansion of cements immersed in 5 %($NH4)_2SO_4$ solution.

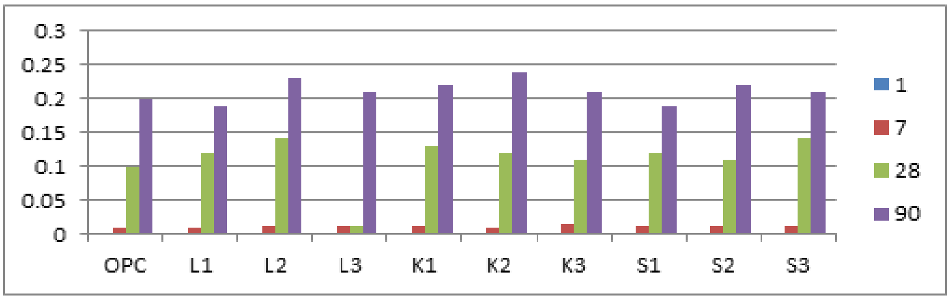

Figure 1 (c) Expansion of cements immersed in distillated water

3.4 Compressive Strength

The compressive strength of blended cements cured in distillated water, 5%MgSO$_4$ and 5 %(NH4)$_2$SO$_4$ solutions for 2, 7, 28, 90 days are shown in figure 2 (a, b &c). There is a clear reduction in compressive strength of k3 sample (30%) kaolin. This is may be due to the reduction of CSH phase. However, the results of K1 and K2 are agree with the specification B.S. EN 196-1:2016(15). Also reduction of compressive strength with increasing limestone content is due to reduction of the amount of hydraulic phases especially CSH phase. However, compressive strength with calcined sandy clay decreases because of high insoluble residue. 20% kaolin replacement shows the maximum value of compressive strength due to formation of additional hydrated phases resulted from pozzolanic reaction of kaolin.

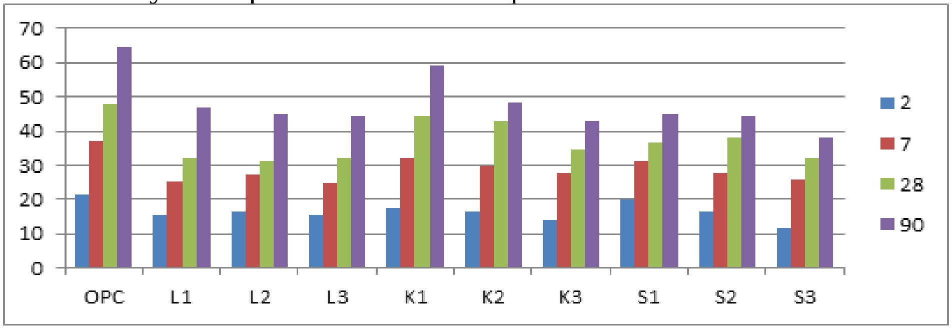

Figure 2 (a) Compressive strength of cements immersed in 5%MgSO$_4$

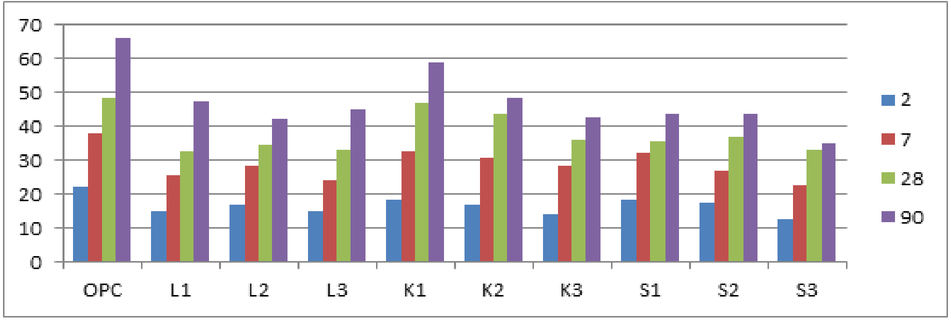

Figure 2 (b) Compressive strength of cements immersed in 5%(NH$_4$)$_2$SO$_4$ solution

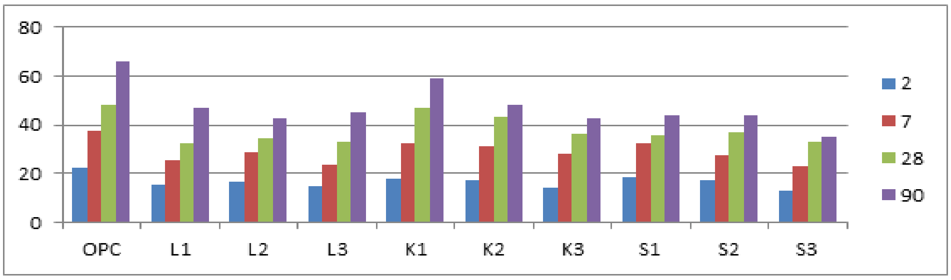

Figure 2 (c) Compressive strength of cements immersed in distilled wate

X ray diffraction

The X-ray diffraction patterns of Portland cement mortars mixed with 15% metakaolin cured in distilled water,5% magnesium sulfate solution and 5% ammonium sulfate solution for 3 months are represented in figure 3 (a,b&c), respectively. The figures show that the presence of $Ca(OH)_2$, quartz and traces of gypsum in samples treated with sulphate solutions.

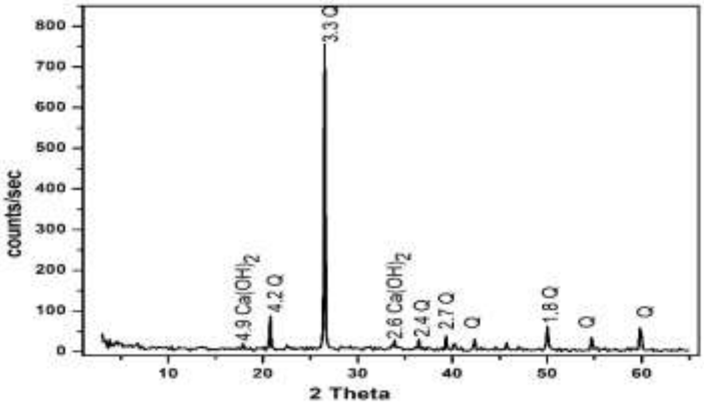

Figure 3 (a) Portland cement mortars mixed with 15% metakaolin cured in distilled water for 3 months

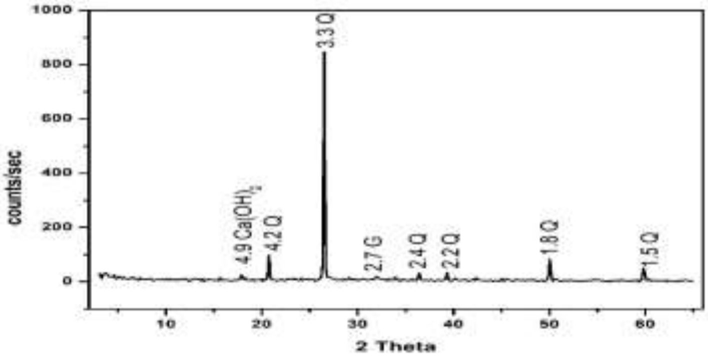

Figure 3 (b) Portland cement mortars mixed with 15% metakaolin cured in 5% magnesium sulfate solution for 3 months

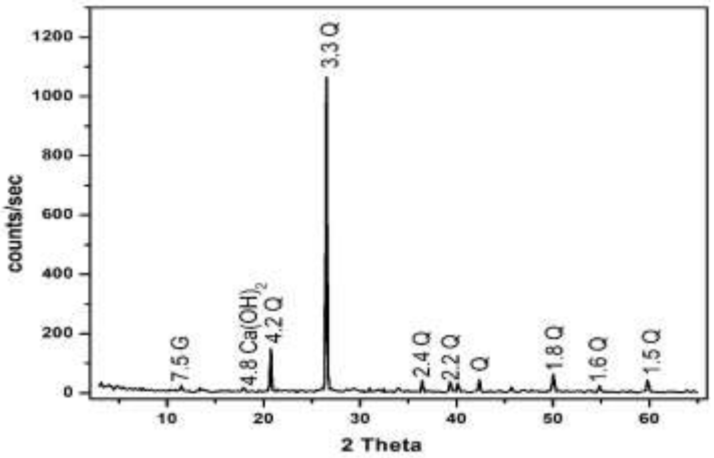

Figure 3 (c) Portland cement mortars mixed with 15% metakaolin cured in 5% ammonium sulfate solution for 3 months

4. DISCUSSION:

4.1 The delayed ettringite formation (DEF)

The delayed ettringite formation has a harmful effect on the hydrated cement systems, depending on its large volume. This large phase causes cracking and damage of hydrated cements or collapsing of concretes. Sulfate attack may internal or external from outside as sea water or sewage and ground water**.** The process takes place in the core of the cement or concrete causing expansion. This phase appears after 6 months curing, so this phase does not appear in x ray diffraction analysis.

4.2 Resistance of the sulfate attack.

The use of limestone as mineral admixture does not improve sulfate attack resistance because of excess amount of CaO and consequently free lime. On the other hand, metakaolin and sandy clay can resist sulfate attack due to its ability to form additional CSH phases during the hydration process. These precipitated phases decrease the porosity through filling up the space. Hence minimize the ettringite phase formation which need large space to be settled.

5. CONCLUSIONS

The resistance of sulfate attack of cementing materials can be taken by using replacement material suitable for this process. Metakaolin can be safely added to Portland cement to resist sulfate attack. On the other hand, sandy clay can resist attack successfully but with side effect on the physical properties of cement. Limestone as replacement material cannot be used to resist sulfate attack. Finally, 20% metakaolin replacement for 42.5 I cement can be used as mineral admixture for preparing blended cements used as resisting sulphate attack cements.

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دراسات على خواص بعض الاسمنتات المخلوطة المصنعة من اضافات معدنية محلية ومعالجة في اوساط كبريتية

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تتعرض بعض المباني لمهاجمة تفاعل املاح الكبريتات خاصة الموجودة في المناطق الساحلية او بجوار الصرف الصحي هذا التفاعل ينشأ عنه ملح الاترنجيت الذي يسبب تمدد وهدم في الخرسانة مع مرور الوقت لذلك فعلنا دراسة لايجاد طريقة لمقاومة مهاجمة هذه الاملاح .

تم خلط الاسمنت البورتلاندي العادي بمواد بديلة للاسمنت مثل الحجرالجيري و طفلة ميتاكاولينا وطفلة رمليه محروقة بنسب 15، 20 و25% وتم معالجتهم في املاح الكبريتات مثل املاح كبريتات الماغنسيوم واملاح 15، 20 و25% كبيرتات الامونيوم لمدة ثلاثة اشهر.

تم دراسة تأثير هذه الاملاح على الخصائص الفزيائية للاسمنتات المخلوطة بالمواد البديلة مثل التمدد وقوه تحمل الضغط ومقارنتها ايضا بالمعالجة في الماء.

واظهرت ان الاسمنت المخلوط بالميتاكاولينا كان جيد حيث انه حتى لم يتعدى المواصفات القياسية وكان مقاوم جيد لاملاح الكبريتات ونتائج قوة تحمل الضغط اثبتت انه في حالة خلط الاسمنت بنسبة 15، 20 و25% مع الميتا كاولينا لا تتجاوز المواصفات القياسية ولكن الخلط بنسبة 25% تتجاوزت الحد المسبوح به

وايضا وجد ان الاسمنت المخلوط بالطفلة الرملية المحروقة مقاوم جيد لاملاح الكبريتات لان نتائج التمدد كانت جيدة ولكن قوة تحمل الضغط كانت ضعيفة بسبب انها تحتوي على نسبة عالية من المواد الغير ذائبة .

بينما الاسمنت المخلوط بالحجر الجيري وجد انه لا يكون مقاوم جيد لاملاح الكبيرتات لانه حقق نتائج عالية في التمدد وقوة التحمل الضغط كانت ضعيفة .