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Statistical Analysis for Autoclave Expansion of Sulphate-Resisting Cement

تحليل إحصائي للتمدد المحمم (أوتوكلاف) لأسمنت مقاوم للكبريتات

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Abstract :

Excessive volumetric change may have great influence in collapse of hardened cement mortar. Autoclave expansion test provides an index of potential delayed expansion and thereby the soundness of cement mortar. This paper presents an effort to model autoclave expansion in relation with factors affecting soundness of cement mortar.

A statistical analysis is performed for a data base of 575 chemical and physical tests obtained from archive of quality control at Kerbala plant for SRC cement. These data sets are refined to 444 by excluding outliers to avoid errors in measurement, recording, and observations. Multiple linear regression by SPSS16 software is used to develop a statistical model relating autoclave expansion with some explanatory variables (MgO %, F. CaO %, C_3A %, C_3S %).

Stepwise regression shows that linear model explains 89.4 % of variation in autoclave expansion by percentage of free lime to 0.05 degree of significance, while excludes other proposed variables. If the degree of significance is changed to 0.1, C_3A may be included in the statistical model as second explanatory variable. The low percentage of MgO makes its effect insignificant for inclusion in the developed model. Also, the analysis shows that the restricted percentage of Tricalcium Aluminate C_3A in the sulphate resisting cement may serve positively in mitigating the expansion of hardened cement mortar. On the other hand, the developed relation may give indication to control a recommended percentage of free lime in the raw materials to assure allowable soundness of cement.

المستخلص

إن التغير ألحجمي الزائد له تأثير بالغ في تصدع عجينة الأسمنت المتصلبه. يوفر فحص التمدد المحمم (الأوتوكلاف) مؤشر للتمدد المحتمل على المدى الطويل وبالتالي مؤشر عن الثبات الحجمي لعجينة الأسمنت المتصلبه. يقدم البحث جهدا لنمذجة التمدد المحمم بالعلاقه مع عوامل مؤثرة في الثبات الحجمي لعجينة الأسمنت. تم أجراء التحليل الأحصائي لقاعدة بيانات لفحوصات كيميائية وفيزياوية بعدد ٥٧٥، تم استخراجها من ارشيف السيطرة النوعية في معمل كربلاء للأسمنت المقاوم. تم تصفية البيانات إلى ٤٤٤ باستبعاد الحائد منها لتفادي أخطاء القياس و التدوين والمشاهدة. تم استخدام الأنحدار الخطي المتعدد في برنامج (SPSS16) لاستحداث نموذج احصائي يوضح العلاقة بين التمدد المحمم مع بعض المتغيرات المرتبطة به مثل (MgO %, F. CaO %, C_3A %, C_3S %).

تبين تقنية الأنحدار المرحلي ان النموذج الخطي يوضح ٨٩.٤ % من التغير في التمدد المحمم بدلالة نسبة الجير الحر وبدرجة معنوية بقدر ٠.٠٥ ، بينما تم استبعاد بقية المتغيرات المقترحة. يمكن تضمين نسبة C_3A في النموذج الإحصائي إذا تم تغيير درجة المعنوية إلى ٠.١ كمتغير وصفي ثاني. إن النسبة القليلة لأكسيد المغنيسيوم جعلت تأثيره غير معنوي لكي يدخل في النموذج المستحدث. يوضح التحليل ان التحديد لنسبة C_3A في الأسمنت المقاوم للكبريتات يخدم في تخفيف تمدد عجينة الاسمنت المتصلبة. من جانب آخر، تعطي العلاقة المستحدثة مؤشر للسيطرة على نسبة الجير الحر التي يوصى بها ضمن المواد الخام لتأكيد ثبات حجمي مقبول.

1. General

Four compounds (minerals) which are usually considered as the major constituents of cement. They are; Tricalcium Silicate 3 $CaO.SiO_2$, Dicalcium Silicate 2 $CaO.SiO_2$, Tricalcium Aluminate

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$3CaO.AL_2O_3$,and Tetracalcium Alumina Ferrite $4CaO.Al_2O_3.Fe_2O_3$ [1]. These compounds are abbreviated to C_3S, C_2S, C_3A, and C_4AF respectively. Also cement contains a percentage of free lime which means uncombined part of CaO [1]. Cement differs from plant to plant due to changes in raw material properties, kiln temperature, fineness of grinding, and percentage of glass in clinker and presence of minor components.

All Portland cement is basically the same, but there are many types of cement are manufactured to meet the chemical and physical requirements for specific applications. Sulphate resisting Portland cement (SRPC) is a special type of cement manufactured to contain a high content of iron oxide in order to limit the amount of the mineral phase Tricalcium Aluminate (C_3A) and thereby increase its sulphate resistance. Additionally, SRPC is normally low alkali cement, which benefits cement paste or concrete in resisting the alkali silica reaction. This research aims at thorough investigation for the factors that affect expansion of SRPC cement paste. Further, statistical predicting models are developed to predict that expansion. There is no previous attempt to achieve statistical analysis of data involved cement expansion. Such models could be used in cement factories in quality control, which enable the manufacturer to make corrections in process within production stage. Moreover, it is useful to make adjustment to the raw mix design through the blend process of raw materials.

2. Expansion of Hardened Cement Paste

The expansion of the hardened cement paste may takes place due to the delayed or slow hydration or other reaction of some compounds present in the hardened cement, namely free lime, magnesia and calcium sulphate [2]. AL-Taii(2001) concluded that the excess of gypsum content leads to a deleteration reaction between gypsum, C_3A and water [3]. This reaction results in the formation of calcium sulphoaluminate hydrate (ettringite) which is accompanied by deleterious expansion causing cracks and deterioration of the cementitious materials.

Taylar (2000) studied effect of ettringite and concluded that in some cases it contributes to the formation of a strong and durable material [4]. But in other case, it is associated with expansion. Also, Taylor et. al.(2001) stated that the expansion from delayed ettringite formation is insignificant with sulphate-resisting Portland cement [5].

Table (1) demonstrates a summary of literature review for conclusions drawn about factors affecting cement expansion.

3. Autoclave Expansion of Hardened Cement Paste

Autoclave is apparatus used for conducting expansion test for Portland cement by increasing pressure and temperature of specimens under regulation of ASTM C151. The difference in length of the test specimen before and after autoclaving as percent of the effective length is reported to the nearest 0.01 percent. One of the most important characteristics of cement is soundness. Soundness is referred to the ability of the cement paste to retain its volume after setting. The Iraqi specification (IQS 5-1984) adopted autoclave test to determine the soundness because this test accelerates the slow reacting crystals of MgO by the application of high temperature.

ASTM C151 stated that, autoclave expansion test provides an index of potential delayed expansion caused by the hydration of CaO or MgO or both. Also, Neville (2000) stated that the expansion determined from the autoclave test is due to both MgO and free lime CaO [2]. AL-Aaraji (2003) stated that there are further factors that affect the expansion in the autoclave test such as the rapidity of cooling process of the clinker and C3A content [6]. In this paper, expansion of hardened cement paste is investigated due to data base of autoclave test records.

Table (1) A Summary of Literature Review for Conclusions Drawn about Factors Affecting Cement Expansion.

Author	Conclusion
Duda (1977) [7]	-Free **MgO** (periclase) reacts with the water to produce **$Mg(OH)_2$** that occupies a larger volume than **MgO**, it can split a part the binding of the hardened cement paste resulting in expansion crack. -Some times aggregates contain alkali-sensitive components, reacting with **alkali** (referred to **K_2O** and **Na_2O**) in the cement resulting expansion phenomena called alkali expansion. Therefore, to prevent this case, the total alkali should not exceed 0.6% by weight.
Popovics (1979) [8]	-undesirable negative effect of **C_3A** on the strength of cement paste when it is found in high contents. It reacts with sulphates forming ettringite, which causes expansion, and thus disruption of the hardened cement paste.
Lawrence (1995) [9]	find that the increase in **MgO** content may increase the delayed ettringite formation expansion.
Lawrence (1999) [10]	-increase in alite (**C_3S**) content or **fineness** and decrease in water/cement ratio, all tend to increase the ultimate expansion.
Harfort *et.al*.(1999) [11]	-cement contained clinker with **SO_3** up to 3% has shown that linear expansion at 10 months is negligible with no significant loss in strength.
Ricardo (1999) [12]	- Magnesium oxide **MgO** can cause delayed expansion of cement paste, and consequently reduce its soundness -Free lime (**F.CaO)** can cause unsoundness, which is simply defined as a volumetric change (expansion) after setting, causing appearance of cracks and deterioration of mortar strength.
Neville (2000) [2]	-when hardened cement paste is attacked by sulphate, expansion may result in a disruption of the hardened cement due to the formation of calcium Sulpho-aluminate from **C_3A**.

The investigation is undertaken through a data base of some variables that are proposed to affect autoclave expansion. Table (2) demonstrates some international standards for the autoclave expansion as well as some explanatory variables that are analyzed in this paper.

Table (2) International Standards Values for Data Used in Building Statistical Model

I.S. Code	MgO % (Max.) *	C_3A % (Max.) *	A.exp % **
B.S. 123 30-1988	6	Not specified	0.8
IQS 5 1984	5	3.5	0.8
ASTM C 150	6	5	0.8

*Percentage is by weight.

** A.exp % is Autoclave expansion (mm/mm)

As a previous attempt, Abdul-Latif (2001) developed a model to predict free lime from knowledge (15 observations) of autoclave expansion, MgO, C3A content as follows [13]:

(Auto)exp. = 0.0375 (MgO %) + 0.0927 (free lime %)……..(1)

(Auto)exp. = 0.157 (free CaO %)……..(2)

The developed model shows that free lime has the main effect on autoclave expansion relative to other observed independent variables.

4. Building of Statistical Model

In order to build a Statistical predictive model, there should be set of data (observations) that cover a wide range of variation of the independent variables. The data used in this study are taken from the archive of quality control of Kerbala cement plant for the period between 2001 and 2005. These data include the results of chemical analyses and physiochemical tests of (574) observations of law alkali sulphate resisting Portland cement at Kerbala cement factory.

It is intended to check the data set for outliers to avoid errors of; measurements, recording, and observations. Chauvernet criterion of outliers is used to exclude a data, which result in absolute value of (Max. – Av.) / St. and or (Min. –Av.) /St. of ≥ 2.54 [16]. Table (3) presents the refined data of 444 tests, used in building the statistical model. It can be seen that percentage of MgO is relatively low comparing with the specified standards in Table (2).

Table (3) Ranges of Data Used in Building Statistical Model

	MgO % (*)	F.CaO % (*)	C_3S % (*)	C_3A % (*)	A.exp % (**)
Min.	1.20	1.40	41.6	-1.08	0.08
Max.	2.00	1.81	56.8	2.40	0.45
Av.	1.62	1.59	49.04	0.74	0.24
St.	0.16	0.09	3.35	0.73	0.09
(Max. – Av.)/St.	2.33	2.34	2.32	2.27	2.52
Min. –Av./St.	1.82	2.04	2.22	2.49	1.82

*Percentage is by weight.

** A.exp % is Autoclave expansion (mm/mm)

Multiple linear regression analysis is chosen here to build up the model of cement expansion in percent, based on record data of autoclave expansion test. Multiple linear regression models have the following general form:

$$y = \beta x + \varepsilon \quad \text{.....(3)}$$

Where:

y = Expected dependent variable (in this study, autoclave expansion (A.exp) of cement paste in %).

x = Vectors representing the explanatory variables (in this study, C_3S %, C_3A %, MgO %, F.CaO %).

β = Vectors representing parameters to be estimated.

ε = Error term assumed to be normally distributed.

Selection of explanatory variables is based on literature review drawn in Table (1). Interco relation is avoided by using one predominant independent variable as the case of C3S % and fineness of cement. However the process is done with the aid of computer software SPSS –version 13-199, and stepwise regression method is applied. A comparison between two models with and without intercept is done for each dependent variable to prove that regression passing through the origin is suitable for our data or not.

To identify the best fitting model, F-value, R-square, and mean square error are used. Individual parameters in the β vector are tested to investigate the null hypothesis that a given parameter is zero using t- statistics. Also, the residual plots are demonstrated to detect the normality and presence of outliers.

5. Proposed Statistical Model

The statistical analysis is performed for two cases of models, with and without intercept. The results shows insignificant statistical model for the case of including intercept. On the other hand, Table (4) summarizes the out put of SPSS program for the case of linear model without intercept. Stepwise regression results in linear model that explains 89.4% of variation in autoclave expansion in relation with free lime, while excluding some explanatory variables according to a degree of significance of 0.05. However, if the degree of significance is changed to 0.1, C_3A may be included in the statistical model as second explanatory variable as shown in Table (4). It can be seen that the restricted percentage of Tricalcium Aluminate C_3A in the sulphate resisting cement may serve positively in mitigating the expansion of cement mortar.

Table (4) Summary of Developed Model of Cement Autoclave Expansion (A.exp)

Free lime F.CaO % as Independent Variable			
	Parameter	t-statistic	P-value
B	.148	60.939	0.000
No. of cases	444		
R^2	0.894		
F-value	3.714E3		
MSE	24.695		
SEE	0.08155		
P-v	0.000		
Excluded Independent Variables			
	Beta in	t-statistic	P-value
MgO %	0.016	0.126	0.900
C_3S %	-0.094	-0.567	0.571
C_3A %	0.039	1.787	0.075 *

* If the degree of significance is increased to 0.1 (degree of confidence is 90 %), the variable C_3A % may be included in the model.

The distribution of residuals for the model without intercept, as histogram, is shown in Figure (1). It is obvious that the residuals follow the normal distribution curve.

Furthermore, Figure (2) shows the observed plotted against the predicted values. By examining this plot, one can have impression that the predicted values are gathered around line concentrically. The plot confirms the linear regression analysis assumption, mentioned previously.

In Figure (3) the residuals are plotted against the predicted values. It is clear that the residuals gathered around zero concentrically as a horizontal band. This horizontal band indicates no abnormality and our regression analysis would not appear to be invalidated [14].

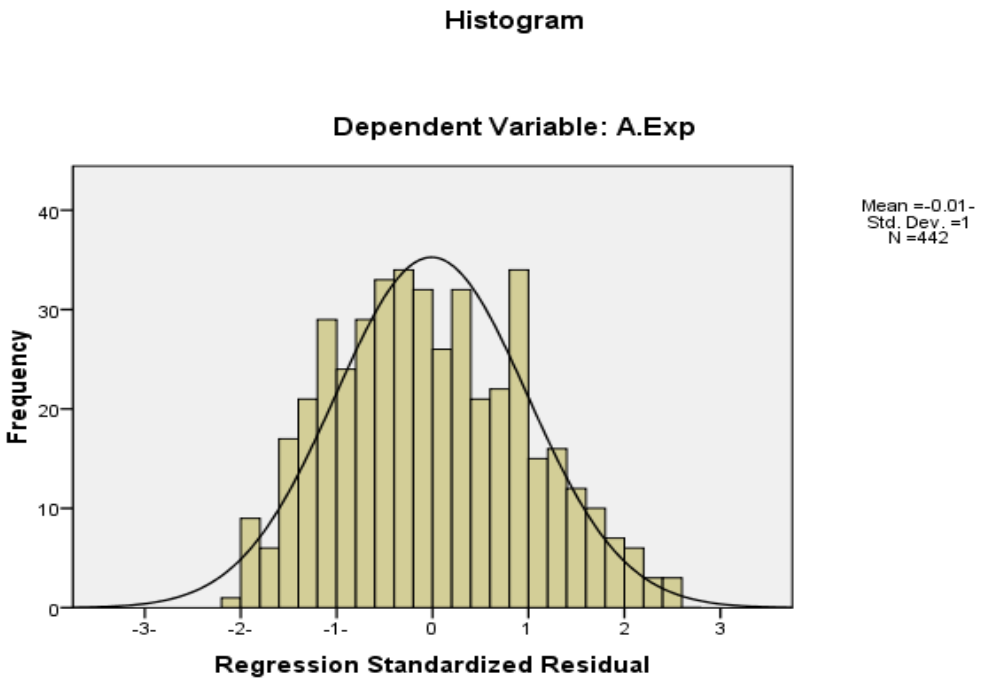

Figure (1) Distribution of Residuals in Model of Expansion.

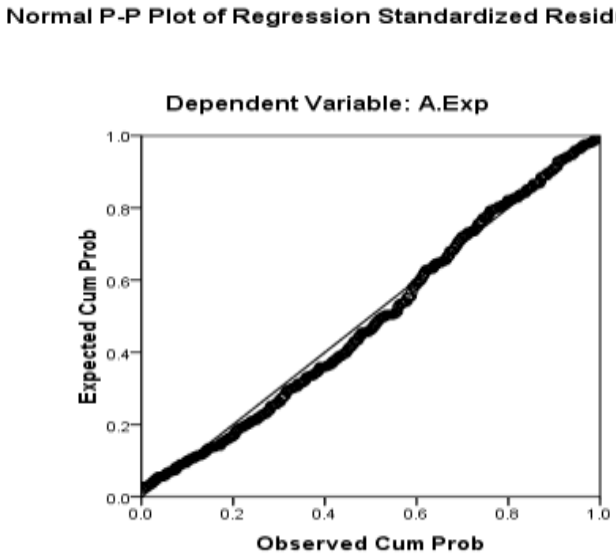

Figure (2) Observed Against Expected Values of Expansion Due to Model.

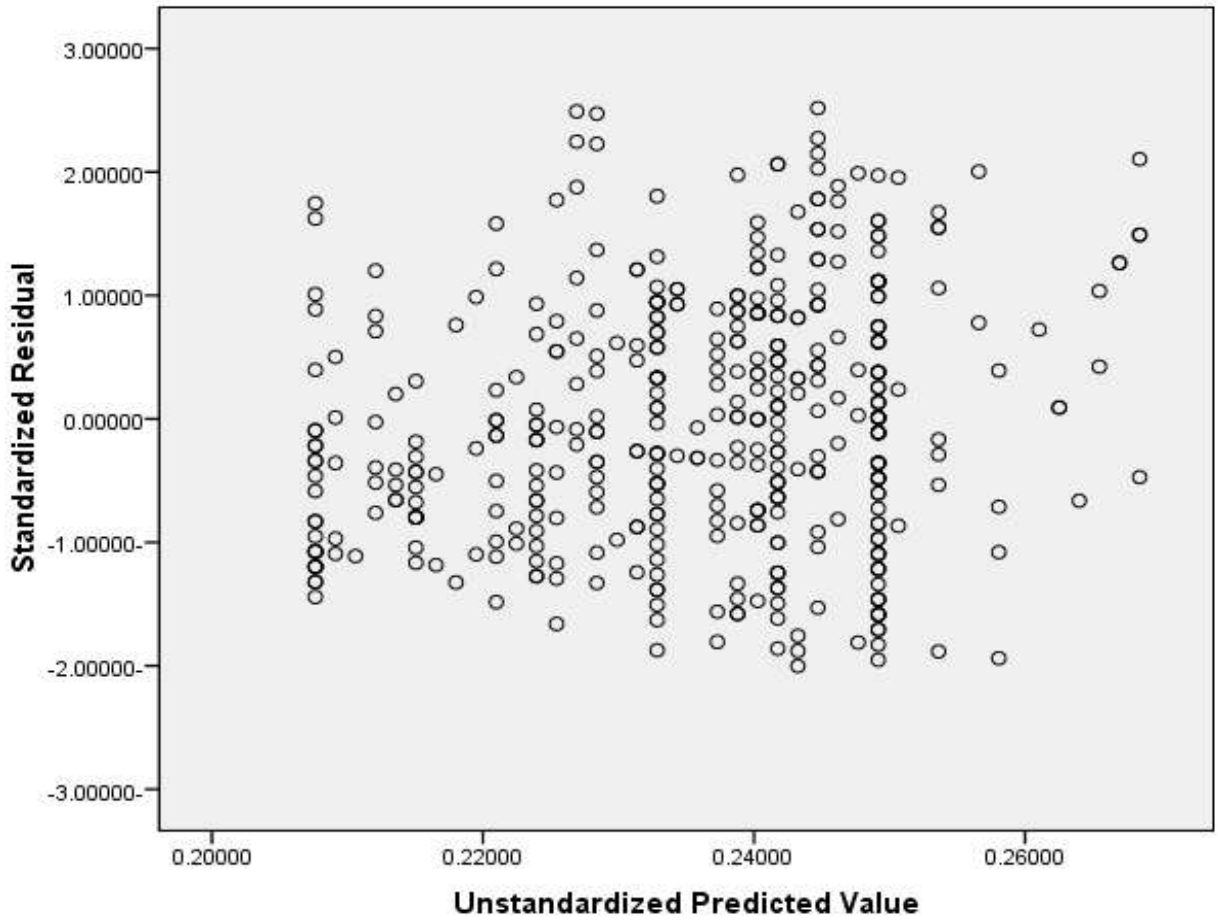

Figure (3) Predicted Values against Residuals of Expansion.

The main effect of free lime represented by the developed model may be discussed as follows:

- The expansion of hardened cement paste is due to the formation of $Ca(OH)_2$ resulting from hydration of free lime. This expansion may be interpreted to the effect of the expansive force built up due to the restriction and confinement of $Ca(OH)_2$ particles that do not try to fill up the pore space [15].
- It may be concluded that, the presence of free lime induces more expansion of cement mortar. This may be resulted from colloidal nature of ettringite formed due to hydration of cement in the presence of lime; thereby it develops large expansion [16].
- It can be seen that the expansion caused by MgO hydration is less than that caused by Cao hydration and this goes with the conclusion drawn by Mehta (1986) [17].
- Even the model developed by Abdul-latif (2001) is based on only 15 observations; there is agreement between the developed model in this paper and that in representing the main effect of free lime to explain the variation in autoclave expansion of cement mortar [13].
- The low percentage of MgO makes its effect insignificant for inclusion in the developed model.

6. Validation of Developed Models

A new data consist of (36) samples of sulphate resisting Portland cement are used in testing the applicability of the developed models. These data are not included in the building of models. A statistical χ^2 test is conducted to detect the significance of difference between the observed autoclave expansion and the corresponding value obtained from the developed model. As the χ^2

critical (49.76) for (d.f. 35 and α =0.05) is more than χ^2 calculated (3.755), it can be concluded that there is no significance difference between the predicted values and the corresponding observed values of autoclave expansion according to the developed model [18]. Thus, it may be concluded that the present models are appropriate to predict the expansion with a good accuracy.

7. Conclusions

The following are the main conclusions and recommendations that are reached throughout this research work:

1. Stepwise regression results in linear model that explains 89.4% of variation in autoclave expansion in relation with free lime, while excluding some explanatory variables according to a degree of significance of 0.05.
2. The low percentage of MgO makes its effect insignificant for inclusion in the developed model.
3. If the degree of significance is changed to 0.1, C_3A may be included in the statistical model as second explanatory variable.
4. The restricted percentage of Tricalcium Aluminate C_3A in the sulphate resisting cement may serve positively in mitigating the expansion of cement mortar.
5. The developed model is tested through the following criteria to assure valid analysis:

- The distribution of residuals for the model follows normal distribution curve.
- The observed plotted against the predicted values plot shows impression that the predicted values are gathered around line concentrically. The plot confirms the linear regression analysis assumption.
- The plot of residuals against the predicted values shows that the residuals gathered around zero concentrically as a horizontal band. This horizontal band indicates no abnormality and our regression analysis would not appear to be invalidated

Hence, the developed is adequate for prediction of autoclave expansion in relation with percentage of free lime (F. CaO).

6. Due to external data not used in building the developed model, there is no significance difference between the predicted values and the corresponding observed values of autoclave expansion according to the developed model.
7. The developed relation may give indication to control a recommended percentage of free lime in the raw materials to assure allowable soundness of cement.

8. References

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