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Statistical Analysis for optimum sulphate content of Sulphate Resisting Cement (SRC)

تحليل إحصائي لمحتوى الكبريتات الأمثل في السمنت المقاوم للكبريتات

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Abstract

It is impractical for cement producers to test the produced cement after manufacturing process, because it is very difficult to correct the final production. Moreover, it is useful to make adjustment to the raw mix design through the blend process of raw materials.

Calcium sulphate is added in small quantities to the other constituents of cement during its manufacture to control the setting time of the product.Using a large scale data base, this paper shows an effort to model optimum sulphate required to be expressed in term of some concerned variables.

Statistical analysis using SPSS16 software is performed for a data base of 362 chemical and physical tests obtained from archive of quality control at Kerbala plant for SRC cement. These data sets are refined to 322 by excluding outliers to avoid errors in measurement, recording, and observations.

Stepwise regression results in a linear model that explains (99.8%) of variation in required sulphate in relation with: C_4AF, C_3A, and K_2O, while excluding one explanatory variable (Na_2O) according to a degree of significance of (0.05).The developed model can be used as a guide for manufacturer to control the content of; K_2O, C_3A, and C_4AF that result in an optimum sulphate content of SRC cement.

المستخلص

يعد فحص السمنت بعد عملية التصنيع غير عملي بالنسبة للمنتجين وذلك بسبب صعوبة تصحيح الإنتاج النهائي. فضلاعن ذلك, فأن من المفيد أجراء التصحيح لتصميم خليط مواد الخام ضمن عملية التصنيع.

تضاف كبريتات الكالسيوم بكميات قليلة لباقي مكونات السمنت خلال عملية التصنيع لغرض السيطرة على وقت تجمد السمنت. باستخدام قاعدة بيانات واسعة, يوضح البحث جهد لنمذجة محتوى الكبريتات المطلوب بدلالة بعض المتغيرات ذات العلاقة.

باستخدام برنامج SPSS 16 تم إعداد تحليل إحصائي لبيانات 362 من الفحوصات الكيميائية والفيزيائية التي تم الحصول عليها من أرشيف السيطرة النوعية لمعمل السمنت المقاوم في كربلاء. تم تصفية البيانات الى 322 بعد استبعاد النقاط الشاذة لتجنب الأخطاء في القياس والقراءة والمشاهدة.

يمثل ناتج تحليل الانحدار المتدرج نموذج خطي يوضح 99.8 % من التغير في محتوى السلفات بالعلاقة مع مكونات (C_4AF, C_3A, K_2O) مع استبعاد مكون (Na_2O)وبمعنوية 0.05. يمكن استخدام النموذج المستحدث كدليل من قبل المنتجين للسيطرة على مكونات (C_4AF, C_3A, K_2O) لتنتج محتوى أمثل من الكبريتات في السمنت المقاوم SRC .

1. General

At the optimum calcium sulphate level, the early hydration products of the C_3A form ettringite which deposit as a fine-grained material on the clinker surface. This hydration product does not bridge the water-filled gaps between particles of clinker, and the paste becomes only slightly stiffer due to initial hydration during the early period [1]. Two cements produced from the same clinker with two different specific surface areas, show very different levels of of water demands and setting times [2]. It is argued that the quantity of sulphate in solution should be adjusted to the level of activity of C_3A in order to optimize fluidity: if there is too little sulphate present, then, in addition to ettringite, platy crystals of calcium aluminate hydrate or calcium monosulfoaluminate hydrate are formed. If there is too much sulphate, then secondary gypsum is formed during early hydration of the hemihydrates present. Both additional hydration products result in reduced fluidity and increased water demand and may lead to premature setting. Sulphate resisting cement is produced in an aim to resist external attack due to the chemical reaction between sulphates usually exisisting in ground water or soil and concrete or mortar. The main purpose of this research is to build up statistical models for the prediction of optimum sulphate required in sulphate resisting portland cement. Such models could be used in cement factories in quality control, which enable the manufacturer to make corrections in process within production stage.

2. Sulphate required in Cement paste

According to the Lerch (1946) the optimum gypsum content of cement is the amount of added gypsum, which results in the highest compressive strength and the lowest contraction on drying. This optimum content increases with the increase in C_3A content, alkalis content and fineness of cement. Table (1) demonstrates a summary of literature review for conclusions drawn about the factors governed optimum sulfate required.

Table (1) Factors affect sulphate required in cement.

Author	Conclusion
Lerch (1946)	the optimum sulphate required would increase with the increase of C_3A content of the cement.
Ost (1974)	reports that the Blainefineness is better estimator of the SO_3 requirement
Hobbs (1977)	the optimum sulphate required in cement is either related to cement fineness, alkali orC_3A content.
Older, Wonnemann (1983)	The higher the K_2O bound in the crystal lattice, the greater the reactivity and the greater the concentration of rapidly soluble sulphate required to control the setting and the fluidity reduction. In contrast toK_2O, The absorption of Na_2O into the lattice reduces the activity of the C_3A [3].
Harfort et. al.(1999)	using 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 .
AL-Attar (2001)	declares that the sulphate in concrete ingredients reacts with the aluminates, mainly C_3A and to a lesser degree C_4AF and water. This reaction results in the formation of sulpho-aluminates and it is accompanied by a significant increase in solid volumes.
Smidth (2006)	There is effect of SO_3 content on compressive strength at different ages

Gypsum, chemically, is a hydrated calcium sulphate $CaSO_4.2H_2O$ and it is a fairly common natural material,(AL-Attar,2001). In the chemical analysis of cement, the presence of gypsum refersto SO_3content. Table (2) summarizes conclusions of researchers who studied the effect of gypsum on cement properties.

Table (2) Summary of literature survey for effect of gypsum on some cement properties

Author	Conclusion
(Osback, 1980).	The effects on the early *strengths* in particular can be modified somewhat by varying the amount of gypsum added.
Soroka and Abayneh (1986)	They educed that addition of gypsum affects the *rate of hydration* and thereby the *strength* of cement.
AL-Rawi et. al. (1990)	the optimum gypsum under accelerated curing condition is found to increase with the increase in *fineness* of cement in similar trends to the trends observed under normal curing condition.
AL-Taii (2001)	the excess of gypsum content leads to a deleteration reaction between C_3A and water.
Abdul-Latif (2001)	-the effect of C_4AF on optimum gypsum content is less than that of C_3A, because the later is more active than C_4AF. -that in the ordinary cases, the increase in the alkali content increases the optimum gypsum required.

In order to control the setting time, cement needs a minimum amount of calcium sulphate. On the other hand, the maximum allowable SO_3 content in cement to prevent sulphate expansion is established according to the various standards between 2.5% and 4% (Duda, 1977).Table(3) demonstrates some international standards for allowed sulphate besides some explanatory variables related to it :

Table (3) International Standards values for data used in building statistical model.

I.S. Code	SO_3 %	C_3A%
B.S.123 30-1988	2.5	Not specified
IQS. 5-1984	2.5	3.5
ASTM C 150	2.3	5

3. Previous Models for optimum Sulphate required:

A statistical analysis of data allows the maximum SO_3 which causes zero further expansion to be expressed in term of cement fineness and Bogue composition [5] as follows:

$SO_3 = 0.035F^{0.34}$ ($\%C_3A+5C_4AF$) ………………………….(1).

Many attempts have been made to determine optimum sulphate content in cement, and many researches have been carried out in this area. Haskell (1959) develops an equation to correlate sulphate requirements of Portland cement with C3A, Na2O and K2O. This model is based on 12 cases only. Meissner et. al. (1950) proposes a similar model, but this model is based on a very little data (8) cases only, and Hobb (1977) also proposes other similar model. Abdul–latif (2001) selects only the factors that are expected to greatly influence the optimum gypsum content. This model is based on 44 cases only. Ost (1974) reports that the Blaine fineness is better estimator of the SO3 requirement, and extended Haskell's treatment. These models are shown in Table (4) as following:

Table (4)Linear regression coefficients for models of optimum sulphate

Factors	Meissner 1950	Haskell 1959	O.s.t 1974	bb 1977	Abdul-Latif 2001
Fineness			0.0017659		0.0003806
C_3A	0.1149	0.0933		0.10	0.09993
C_4AF					0.01669
F.CaO					-0.118
MgO					-0.0814
K_2O		0.9406			0.698
Na_2O		1.7105	0.556		1.449
Constant	0.789	1.228		1.14	
Equivalent Na_2O	1.872		-3.6002	1.8	
Fe_2O_3			-0.1072		

4. Building of a statistical model.

Based on the gained information from the literature survey, the following factors are selected to be included in this model as explanatory variables: K_2O, Na_2O, C_3A and C_4AF. In order to build a mathematical predictive model, there should be set of observations which cover a wide range of variation of the independent variables. The data used in this research are taken from the archive of quality control in karbala cement plant for the period between 2001-2005. These data include the results of chemical analyses and physical tests of (362) observations of law alkali sulphate resisting Portland cement at karbala cement factory.

It is intended to check the data set for outliers to avoid errors of: measurements, observations, and recording. Chauvernet criterion of outliers is used to exclude a data, which result in absolute value of: (max.-Av)/St. and or (min-Av)/St. 0f>=2.54 [6]. Table (5) displays the refined data of (322) cases, used in building the statistical model.

Table(5) ranges of data used in building statistical model.

	K_2O	Na_2O	C_3A	C_4AF	SO_3
max	0.54	0.47	2.26	14.93	2.17
min	0.39	0.11	1.43	14.21	1.78
Average	0.45	0.15	1.86	14.56	1.97
Standard deviation	0.032	0.034	0.17	0.15	0.08
(max-Av)/St	2.53	2.24	2.35	2.46	2.5
(min-Av)/St	2.13	1.03	2.53	2.33	2.38

Multiple linear regression analysis is chosen to build up the model of optimum sulphate required, which has the following general form:

Y=bX + e ………………………..(2)

Where:

Y= Dependant variable, in this research the percentage of sulphate.

X=Vectors representing the explanatory variables, in this research the percentage of:K_2O, Na_2O, C_3A and C_4AF.

b=Vectors representing parameters to be estimated.

e=Error term assumed to be normally distributed.

5. Proposed statistical model

By using the group of (362) observations as mentioned previously, the statistical analysis is performed for two cases of models with and without intercept. The results show insignificant statistical model for the case with intercept. On the other hand, stepwise regression results in linear model that explains (99.8%) of variation in required sulphate in relation with: C_4AF, C_3A, and K_2O, while excluding one explanatory variable (Na_2O) according to a degree of significance of (0.05)

Optimum SO3 = 0.096(C_4AF) + 0.147(C_3A) + 0.64(K_2O)……….(3)

R = 0.999

R^2 adj = 0.998

SEE = 0.08415

F = 65655.71

P-VALUE= 0

The normal distribution of residuals and validation of this model are very clear from Figures (1) and (2). Also, Figure (3) indicates that there is no evidence that the model is inadequate

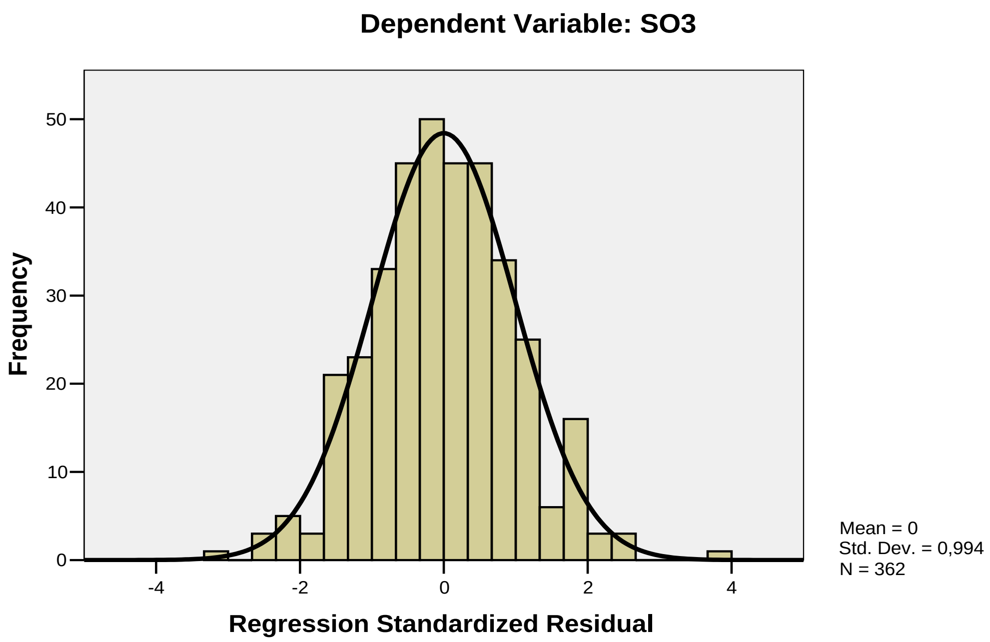

Figure (1) distribution of residuals of sulphate

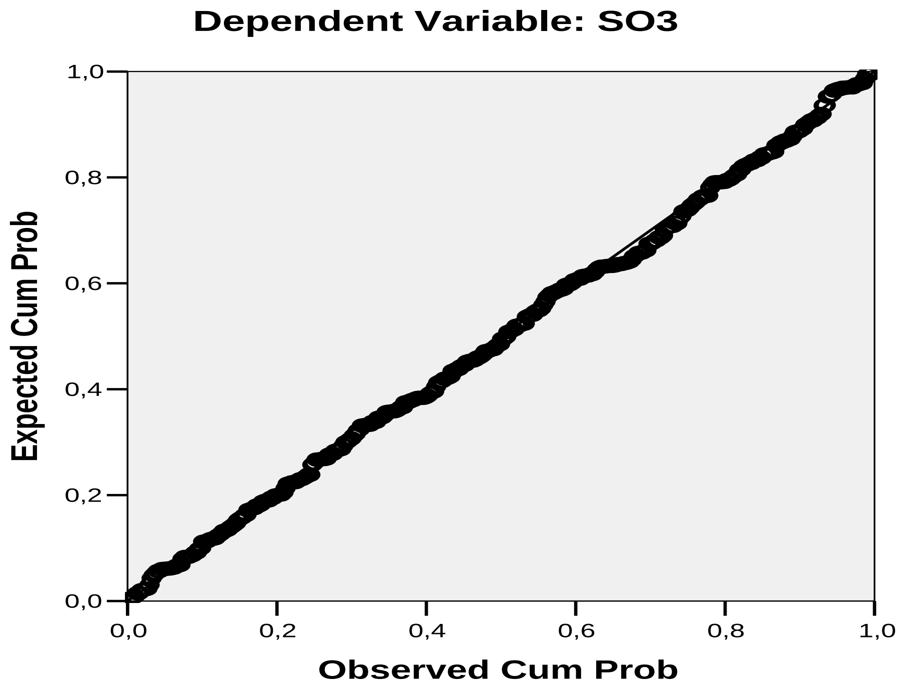

Figure (2) observed versus expected values of sulphate

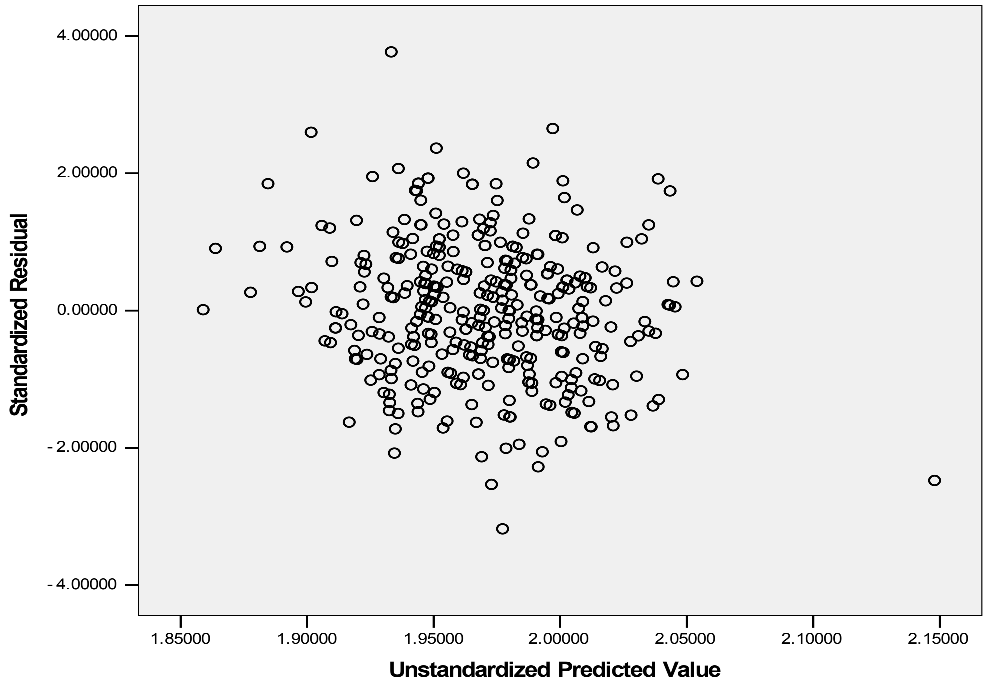

Figure (3) predicted values versus residuals of sulphate.

The aforementioned results are almost in agreement with the results of Abdul-Latif (2001) in table (2-6). It is clear that in both models each of C_3A, C_4AF and K_2O have a positive effect on optimum sulphate required. Many investigators are in agreement with this fact, the models of both Hobb (1977) and Meissner et. al. (1950) confirms the positive influence of C_3A. Also there is similarity with the Haskell's model (Haskell, 1959) that the C_3A and K_2O have a positive effect in both models.
The positive effect of C_3A, C_4AF and K_2O on optimum sulphate as well as the fact that effect of C_4AF is less than that of C_3A as found from this study is confirmed by the results of Jawed et.al. (1978), Lerch (1946) and Abdul-Latif (2001) who record that the optimum sulphate content is related positively to the alkali, C_3A and C_4AF content.

6. Validation of Developed models

In order to test applicability of the developed model, there are a new data consist of (18) samples from the same factory are used in this test. These data are not included in the building of model. This test shows that the maximum difference between the observed sulphate required and the corresponding value recorded from the developed model is (± 0.10), It may be concluded that there is no significance difference between the observed and predicted value according to the developed model[7]. Thus, it can be reported that the present model is appropriate to predict the optimum sulphate required with a good accuracy.

7. Conclusions

- Stepwise regression results in linear model that explains (99.8%) of variation in required sulphate in relation with: C_4AF, C_3A, and K_2O, while excluding one explanatory variable (Na_2O) according to a degree of significance of (0.05).
- Due to a validation test for the developed model, it may be concluded that there is no significance difference between the observed and predicted value according to the developed model.
- The developed model can be used as a guide for manufacturer to control the content of; K_2O, C_3A, and C_4AF that result in an optimum sulphate content of SRC cement.

8. References

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