A NEW STATISTICAL MODEL FOR THE ESTIMATION OF AUTOCLAVE EXPANSION OF PORTLAND CEMENT

Dr. Mohammed Mansour Kadhum, Assistant Prof.
Department of Civil Eng. College of Engineering/University of Babylon

Abstract

This paper presents the predictive functional control of an autoclave expansion of Portland cement, using non-linear regression equation. This is in order to save time and expense also for quality control assurance for produced cement (in cement factories). The autoclave expansion test (ASTM C151- 05) is one of the internationally used tests in detecting the unsoundness of Portland cement. The factors affecting test results were reviewed.

A statistical analysis was built and based on 50 different cement samples taken from 8 different Iraqi cement factories. Thirty three of the samples were ordinary Portland cement while the other seventeen samples were sulfate resisting Portland cement. The model examines different variables such as; chemical composition (phase composition and oxides percentages), and physical properties such as fineness. Regression analysis was performed to establish a mathematical formula. According to the analysis the model provide good estimation of autoclave expansion and yielded good correlations with the data used in this study.

It was found that the multiple linear regressions are very suitable for predicting the autoclave expansion of Portland cement. Study results indicate that the correlation coefficient may reach 0.9797, indicating that the proposed method has referential value. The model was tested with collected new raw data and the predictions were highly correlation to the experimental results (R^2=0.9535).

Keywords: Autoclave expansion, Soundness of cement, Fineness, Regression analysis

Introduction

Soundness of Portland cement means that it would not undergo large change in volume after setting. Such volume changes may result from the slow hydration of certain of its constituent's namely free lime, magnesia and calcium sulfate Lea's [1]. Autoclave expansion test ASTM C151-05 [2] is one of the internationally used tests in detecting the unsoundness of Portland cements. This test is, to some extent, complicated and needs time and professional staff. In addition to that, in Iraq, the equipment for test is not available in each laboratory.

Mathematical modeling process is a simplified representation of reality designed to fulfill a specific purpose. There are many reasons that made dealing with models preferable to dealing with real world. Often, the motivation is economic, to save money, time, or other valuable commodity Moscardini and Cross [3].

Cement industry in Iraq was established since mid forties of the last century. Iraqi cements are well complying with international standards [4] and [5]. This work is specified to build a statistical model for predicting autoclave expansion for Portland cements that are produced in Iraq.

The autoclave expansion test described by ASTM C151-05 [2] is used to detect soundness of neat cement paste. In this test a bar of 25.4 mm square in cross section and with 250 mm gauge length, is cured in humid air for 24 hours. The bar is then subjected to accelerated conditions (a steam pressure of about 2±0.07 MPa and a temperature of 216˚C) for 3 hours. The high steam pressure accelerates the hydration of both magnesia and lime Neville [6]. MgO and free lime are the effective components in cement that can cause delayed expansion. This expansion is due to the formation of $Ca(OH)_2$ and $Mg(OH)_2$ upon hydration of free CaO and MgO respectively. According to the ASTM C151-05, the expansion must not exceed 0.8 percent for all types of Portland cement.

The main factor which is governing the expansion is the free CaO and MgO contents in cement. The expansion is due to the formation of $Ca(OH)_2$ and $Mg(OH)_2$ upon the delayed hydration of free CaO and MgO respectively. Chatterji [7] stated that the mechanism of expansion for both oxides is the same, and its capacity for free CaO is more due to that $Ca(OH)_2$ is more soluble than $Mg(OH)_2$.

Moreover, as reported by Lea [8], it was found that there is an interrelationship between these two oxides on their effect on expansion. Lea quoted that cement with free CaO below 2% will pass the autoclave test when the total MgO content is low (1–2) %. But with high contents of MgO, the free CaO may need to be below 1 % to get a safe situation.

Neville [6] indicated that autoclave expansion test is sensitive to MgO and free CaO but not to CaSO4. In opposite to that, many researchers had pointed out that CaSO4 does affect the results of the autoclave test. Lerch [9] indicated, in many cases, that the sulfate content for highest strength was corresponding to that which yields lowest autoclave expansion. Messiner et al. [10] had confirmed the results obtained by Samdi et al. [11]

stated that the autoclave expansion, for mixes with different sulfate contents, increased with the increase of sulfates.

Fineness of cement containing free CaO and MgO is the most interesting factor affecting the soundness of cement. As reported by Al-Jabiri [12], Czernin [13] stated that little, but large, free lime particles in hardened paste will cause cracking and spalling, whereas, with increasing fine division of free lime the expansion will become less and more regular. He proved that by taking a neat cement prism with a high content of free lime 13 per cent and finely ground cement. The expansion which occurred was 20 percent in length but without causing disintegration of the test specimen. The extremely fine distribution of the free lime prevents destruction of the prism.

Abdul-Latif [14] proposed a statistical model for predicting autoclave expansion from MgO content, free lime content, C_3A content, and fineness in terms of Blaine specific surface. This model was as follows:

$$\text{Auto.} = 0.06811\times\text{Free CaO\%} + 0.04394\times\text{MgO\%} - 0.0000577\times\text{Blaine}\ (cm^2/gm) + 0.01943\times C_3A\%$$ **……..eq.(1)**

This model is based on 35 observations. The correlation coefficient, standard error, and F_{value} are 0.812, 0.1023, and 14.965 respectively.

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 [6] stated that the expansion determined from the autoclave test is due to both MgO and free lime CaO. AL-Aaraji [15] 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. In this paper, expansion of hardened cement paste is investigated due to data base of autoclave test records.

Research Significance

It is developing a statistical model for predicting the **Autoclave Expansion** that comprises most chemical factors and fineness of cement which affect this property. Such model helps to assess the degree of Soundness of cement which is a very substantial aspect of durability if the elaborate Autoclave test is unavailable.

Statstical Modeling

In statistical modeling, the overall objective is to develop a predictive equation relating a criterion variable to one or more predictor variables. 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 and Consultant Engineering Bureau of Babylon University of (50) different cement samples were tested, (33) of them were ordinary Portland cement while the other (17) samples were sulphate resisting Portland cement for the period between 2004-2012. Table 1 shows the names of cement factories and the types of their production with number of samples taken from each factory. Table 2 shows the chemical analysis and physical properties of the cements used in this study. And Table 3 shows the chemical analysis and physical properties limits of the cements used in this study. The autoclave test was used to determine the unsoundness of the cement samples used throughout the present study. The records comprised test results that required by the ASTM C150-02a (chemical composition and physical properties).

Table (1): Sources of the cement samples used in the present study.

No.	Factory	Type of cement	No. of samples
1	Kubaisa cement plant	Ordinary Portland cement- type I	7
2	Al-Najaf Al-Ashraf cement plant	Ordinary Portland cement- type I	7
3	New cement plant of Kufa	Ordinary Portland cement- type I	7
4	Al-Sada cement plant	Ordinary Portland cement- type I	6
5	South cement plant	Ordinary Portland cement- type I	6
6	Al-Qaim cement plant	Sulfate resisting Portland cement- type V	6
7	Kerbal Kerbala cement plant	Sulfate resisting Portland cement- type V	6
8	Karkuk cement plant	Sulfate resisting Portland cement- type V	5

Table 2. Chemical analysis and physical properties of the cement samples used in this study.

Physical Properties	AE	0.42	0.32	0.41	0.32	0.38	0.48	0.41	0.43	0.23	0.33	0.32	0.33	0.37	0.36	0.23	0.28	0.30
	Blain m^2/kg	320.0	298.0	301.5	298.2	295.1	321.0	315.4	305.4	292.7	328.0	381.2	328.6	349.6	338.5	320.0	328.5	337.5
	FST min	230	235	230	210	210	250	265	235	215	235	210	220	235	230	245	235	255
	IST min	130	135	140	115	130	140	165	160	120	155	110	135	120	115	130	100	125
Chemical Analysis %	L.S.F	0.876	0.908	0.899	0.866	0.897	0.907	0.908	0.904	0.92	0.898	0.906	0.866	0.878	0.886	0.913	0.871	0.892
	IR	0.53	0.91	1.01	0.72	1.28	0.87	0.82	1.28	0.57	0.63	1.23	1.42	1.36	1.30	1.27	0.89	0.93
	L.O.I	1.55	1.21	1.30	1.15	1.38	1.60	1.54	1.62	0.93	0.96	3.32	3.52	2.21	1.89	1.36	1.15	0.98
	Free Lime	1.19	1.24	1.37	1.10	1.15	1.17	1.34	1.60	0.87	1.10	1.34	1.29	1.36	1.56	1.47	0.98	2.02
	SO_3	2.42	2.51	2.50	2.41	2.56	2.44	2.61	2.56	2.74	2.32	2.76	2.41	2.38	2.56	2.49	2.43	2.46
	MgO	3.36	2.61	3.57	3.81	3.49	3.79	2.90	3.01	4.41	4.50	3.30	3.81	3.28	2.72	3.18	3.23	3.20
	Fe_2O_3	3.21	3.11	3.20	3.95	3.80	3.43	3.30	3.12	3.23	3.20	3.08	3.56	3.61	3.22	3.06	3.24	3.78
	Al_2O_3	5.43	5.10	4.52	4.58	4.60	4.93	5.76	5.20	5.81	5.46	4.47	4.65	4.81	4.87	4.76	5.32	4.46
	SiO2	21.55	21.10	21.32	21.65	21.10	20.98	20.63	20.88	20.10	20.80	20.78	21.67	21.36	21.23	21.05	21.35	21.21
	CaO	62.10	62.80	62.13	61.20	61.98	62.41	62.52	62.13	62.05	61.66	61.32	61.10	61.28	61.46	62.59	61.15	61.68
	Type	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C
	Factory	Kubaisa	Kubaisa	Kubaisa	Kubaisa	Kubaisa	Kubaisa	Kubaisa	Al-Najaf Al-Ashraf	Al-Najaf Al-Ashraf	Al-Najaf Al-Ashraf	Al-Najaf Al-Ashraf	Al-Najaf Al-Ashraf	Al-Najaf Al-Ashraf	Al-Najaf Al-Ashraf	Kufa	Kufa	Kufa
	No	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

Table 2. Continued.

Physical Properties	AE	0.33	0.30	0.35	0.32	0.32	0.29	0.40	0.31	0.29	0.36	0.24	0.23	0.32	0.34	0.37	0.26	0.23
	Blain m^2/kg	298.3	284.8	302.4	298.0	300.5	294.4	341.0	305.8	341.4	342.0	285.4	290.0	282.3	303.0	324.7	289.6	282.5
	FST min	230	265	235	215	205	240	245	235	235	205	220	245	260	240	255	215	225

	IST min	100	145	135	125	115	120	135	145	150	105	135	145	140	135	160	130	145
	L.S.F	0.905	0.913	0.901	0.896	0.886	0.881	0.860	0.889	0.911	0.917	0.878	0.919	0.911	0.898	0.862	0.872	0.906
	IR	1.12	1.39	0.92	0.51	0.52	0.32	0.96	0.89	1.00	0.94	0.88	0.89	1.37	0.79	1.21	0.97	0.92
	L.O.I	1.27	2.11	1.62	1.30	1.25	1.04	2.00	2.44	3.10	2.88	1.87	2.40	2.13	1.90	1.78	1.37	1.80
	Free Lime	1.22	1.24	1.04	0.95	0.98	0.97	1.40	1.21	1.20	1.79	1.30	1.15	1.23	1.35	0.92	1.11	1.51
Chemical Analysis %	SO_3	2.38	2.14	2.23	2.67	2.64	2.71	2.71	2.22	2.30	2.21	2.45	2.38	2.11	2.49	2.44	2.27	1.92
	MgO	4.21	3.39	2.89	2.53	2.66	3.75	3.72	3.31	3.45	4.10	2.10	2.30	2.43	1.85	2.84	3.20	1.40
	Fe_2O_3	4.12	4.11	4.20	3.72	3.68	4.32	3.33	3.40	3.55	3.41	4.00	4.10	4.00	4.16	3.76	3.50	5.20
	Al_2O_3	4.18	4.29	4.50	4.88	4.92	4.51	5.10	5.38	4.70	4.82	5.31	5.23	4.19	5.34	4.87	4.87	3.94
	SiO2	21.12	21.23	21.28	21.00	21.10	21.60	21.50	21.11	20.96	20.45	21.42	20.50	21.25	21.00	21.97	21.86	21.60
	CaO	62.18	62.89	62.59	61.96	61.57	62.44	60.79	61.80	62.30	61.40	62.24	62.61	62.63	62.71	61.89	62.06	63.47
	Type	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	O.P.C	SRPC
	Factory	Kufa	Kufa	Kufa	Kufa	Al-Sada	Al-Sada	Al-Sada	Al-Sada	Al-Sada	Al-Sada	South	South	South	South	South	South	Al-Qaim
	No	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34

Table 2. Continued.

	AE	0.24	0.22	0.23	0.22	0.23	0.23	0.22	0.22	0.24	0.27	0.26	0.25	0.24	0.23	0.24	0.26
	Blain m^2/kg	268.0	304.0	297.2	310.0	290.0	288.8	300.2	316.0	283.7	285.0	293.4	283.8	296.8	293.6	289.0	303.4
Physical Properties	FST min	285	260	230	215	265	275	245	185	225	265	270	265	275	270	275	270
	IST min	175	150	170	135	165	150	135	85	140	145	150	145	155	150	145	160
	L.S.F	0.901	0.905	0.899	0.888	0.898	0.894	0.895	0.891	0.899	0.888	0.889	0.906	0.896	0.898	0.896	0.884
	IR	0.74	1.38	1.08	1.30	0.97	0.80	0.89	0.60	0.50	0.60	0.52	0.70	0.68	0.60	0.59	0.75
	L.O.I	2.12	2.27	1.57	2.40	1.78	1.18	1.17	0.88	1.33	1.30	1.28	1.20	1.31	1.40	1.33	1.30
hemical Analysis	Free Lime	1.29	1.33	1.49	2.01	1.52	1.03	1.20	0.85	1.33	1.30	1.00	1.11	1.20	1.29	1.30	1.20
	SO_3	1.87	2.01	1.93	2.00	1.91	2.00	1.90	2.04	1.92	1.80	1.88	1.70	1.70	1.65	1.66	1.60
	MgO	2.00	1.91	2.20	2.81	1.40	1.90	1.72	2.00	1.71	1.73	1.74	1.83	1.80	1.76	1.83	1.90

	Fe_2O_3	5.16	5.10	4.97	4.30	5.10	5.33	4.87	5.23	5.33	5.00	4.88	5.30	4.87	5.10	4.90	4.88
	Al_2O_3	3.82	3.93	3.60	3.10	3.92	3.85	3.87	3.79	3.90	3.81	3.85	3.90	3.45	3.74	3.69	3.50
	SiO2	21.56	21.20	21.72	22.00	21.79	21.80	21.90	21.80	21.72	22.20	22.31	21.50	22.20	22.10	22.00	22.30
	CaO	62.87	62.40	62.83	61.89	63.33	63.20	63.18	62.88	63.31	63.40	63.80	63.10	63.40	63.70	63.20	62.80
	Type	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC
	Factory	Al-Qaim	Al-Qaim	Al-Qaim	Al-Qaim	Al-Qaim	Kerbala	Kerbala	Kerbala	Kerbala	Kerbala	Kerbala	Karkuk	Karkuk	Karkuk	Karkuk	Karkuk
	No	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50

Table 3. Chemical analysis and physical properties limits of the cement samples used in this study.

Physical Properties	AE	0.32 - 0.48	0.23 - 0.43	0.23 - 0.35	0.29 - 0.40	0.23 - 0.37	0.22 - 0.24	0.22 - 0.27	0.23 - 0.26
	Blain m^2/kg	295.1 - 321.0	292.7 - 381.2	284.8 - 337.5	294.4 - 342.0	282.3 - 324.7	268.0 - 310.0	283.7 - 316.0	283.8 - 303.4
Chemical Analysis %	L.S.F	0.886 - 0.908	0.886 - 0.920	0.871 - 0.913	0.860 - 0.911	0.862 - 0.919	0.888 - 0.906	0.888 - 0.899	0.884 - 0.906
	IR	0.53 - 1.28	0.57 - 1.42	0.51 - 1.39	0.32 - 1.00	0.79 - 1.37	0.74 - 1.38	0.50 - 0.89	0.59 - 0.75
	L.O.I	1.15 - 1.60	0.93 - 3.52	0.98 - 2.11	1.04 - 3.10	1.37 - 2.40	1.57 - 2.40	0.88 - 1.33	1.20 - 1.40
	Free Lime	1.11 -1.19	0.87 -1.60	0.95 -2.02	0.97 -1.79	0.92 -1.35	1.29 -2.01	0.85 -1.30	1.11 -1.30
	SO_3	2.41 -2.61	2.32 -2.76	2.14 -2.67	2.21 -2.71	2.11 -2.49	2.87 -2.01	1.80 -2.04	1.60 -1.71
	MgO	2.61 -3.81	3.01 -4.50	2.53 -4.21	2.66 -4.10	1.85 -3.20	1.40 -2.81	1.71 -2.00	1.76 -1.90
	Fe_2O_3	3.11 -3.95	3.08 -3.61	3.06 -4.2	3.33 -4.32	3.50 -4.16	4.30 -5.20	4.87 -5.33	4.87 -5.30
	Al_2O_3	4.52 -5.76	4.47 -5.81	4.18 -5.32	4.51 -5.38	4.19 -5.34	3.10 -3.94	3.79 -3.90	3.45 -3.90
	SiO2	20.63 -21.65	20.10 -21.67	21.00 -21.35	20.45 -21.60	20.50 -21.97	21.20 -22.00	21.72 -22.31	21.50 -22.30
	CaO	62.10 - 62.80	61.10 - 62.05	61.15 - 62.89	60.75 - 62.44	61.89 - 62.61	61.89 - 63.47	62.88 - 63.80	62.80 - 63.70
	Type	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC	SRPC
	Factory	Kubaisa	Al-Najaf Al-Ashraf	Kufa	Al-Sada	South	Al-Qaim	Kerbala	Karkuk
	No	1	2	3	4	5	6	7	8

Selection Of Predictor Variables

A set of all conceivable variables, that may be considered to have an effect on the autoclave expansion, was selected. Based on the descriptive statistical and graphical analysis which has assisted in the identification of the general trends in the data, the correlation coefficients are determined to identify the underlying from the relationship between the criterion variable and each of the predictor variables. Ideally, predictor variables are selected that have a high correlation with the criterion variable and low correlation with the other predictor variables.

A mathematical model is proposed and developed which is capable for predicting the autoclave expansion of Portland cement. In addition, attention has been made on the right choice for the variables involved in this model, especially the free CaO, MgO, SO_3 and fineness of cement. In addition, attempt has been made to use other variables, that are believed to affect autoclave expansion of Portland cement like the characteristics of the cement itself (phase composition) and other variables obtained from chemical analysis of the cement like LOI, IR, and LSF. The summary of descriptive statistics of all the variables is shown in Table 4. It is clear that the chosen data is covering wide ranges of variation for the selected variables.

Table 5 shows the correlation coefficients for each input parameter. Table 5 also lists the effects of ingredients on autoclave expansion. A positive correlation exists between chemical analysis parameters (free CaO, MgO, and SO_3), C_3A and fineness of cement; autoclave expansion is compared with correlation coefficients of regression analysis (Table 5). Table 5 shows the test results of the chemical analysis and physical properties of the cement - MgO, SO_3, free CaO, C_3A and fineness of cement are all positively correlated with autoclave expansion, and have correlation coefficients of 0.93, 0.76, 0.46, 0.83 and 0.93 respectively. The C3S IR and LOI are all negatively correlated with autoclave expansion, and have correlation coefficients -0.58 -0.23 and -0.10 respectively. Accordingly, some variables were omitted because they have no significant effect on the autoclave expansion of Portland cement.

The autoclave expansion was selected to be the dependent variable for the built model. The final set of variables used in the mathematical model prepared in this work was selected to be as the independent variables included:

i. Parameters from chemical analysis (free CaO, MgO and SO_3) %.
ii. Fin: Fineness of cement, m^2/kg (Blaine method).
iii. Phase composition (main compounds of Portland cement C_3A) which was calculated using Bogue`s equations.

Table 4: Statistical summary for predictor and criteria variables.

Variable	Minimum	Maximum	Sum	Mean	Standard Deviation
AE	0.2100	0.4300	15.49	0.3098	0.06304
FCaO	0.8500	2.0200	64.01	1.2802	0.19562
MgO	1.4000	4.5000	139.06	2.7812	0.86539
SO_3	1.6000	2.7600	112.40	2.2480	0.32830
FIN	281.5000	349.8000	15458.80	309.1760	21.22582
C_3A	0.9122	9.9378	252.7958	5.0559	2.91437
C_3S	37.2579	54.7850	2433.062	48.6612	4.76281
LOI	0.8800	3.5200	83.75	1.6750	0.61719
IR	0.3200	1.4200	45.32	0.9064	0.28795

Table 5: Correlation coefficients for each ingredient.

	AE	FCaO	MgO	SO_3	FIN	C_3A	C_3S	IR	LOI
AE	1.00								
FCaO	0.46	1.00							
MgO	0.93	0.30	1.00						
SO_3	0.76	0.24	0.75	1.00					
FIN	0.93	0.51	0.83	0.58	1.00				
C_3A	0.83	0.24	0.80	0.85	0.67	1.00			
C_3S	-0.58	-0.08	-0.60	-0.66	-0.50	-0.71	1.00		
IR	-0.23	0.36	-0.17	-0.18	0.21	-0.14	-0.05	1.00	
LOI	-0.10	-0.20	0.07	-0.11	-0.11	0.13	-0.06	0.56	1.00

Model Assessment

There are two approaches generally used to assess the adequacy of the proposed regression models, the first one is based on examining goodness of fit measures, whereas the second approach is based on the graphical analysis of the residuals, also called diagnostic plots.

1. Goodness of Fit Measures

The measures of goodness of fits aim to quantify how well the proposed regression model obtained fits the data and can make these results by same equation. The measure that is usually presented is the coefficient of multiple determinations (R2) Devore [16].

The R^2 value is the percent variation of the criterion variable explained by the suggested model and calculated according to the following equation:

$$R^2 = 1 - {SSE}/{SST} \quad \text{……..eq. (2)}$$

Where

SSE = the measure of how much variation in (y) is left unexplained by the proposed model. And it is equal to the error sum of squares $= \sum (y_i - y'_i)^2$

y_i = the actual value of criterion variable for the (i^{th}) case.

y'_i = the regression prediction for the (i^{th}) case.

SST= the quantities measure of the total amount of variation in observed (y) and it is equal to the total sum of squares $=\sum (y_i-y')^2$.

y'= the mean observed (y).

R^2 is bounded between (0) and (1); the higher the value of R^2 the more successful is the regression model in explaining (y) variation. If R^2 is small, and analyst will usually want to search for an alternative models (i.e., non-linear) that can more effectively explain (y) variation. Because R^2 always increases, a new variable is added to the set of the predictor variables and in order to balance the cost of using more parameters against the gain in R^2, many statisticians use the adjusted coefficient of multiple determinations adj R^2, which is calculated as follows:

$$\mathbf{adjR^2} = \left((n-1)R^2 - K \Big/ n-1-K \right) \qquad \text{……..eq. (3)}$$

Where:

n=the sample size.

K= the total number of the predictor variables.

Adjusted R^2 adjusts the proportion of unexplained variation upward [since (n-1)/ (n-k-1)>1], which results in $adjR^2 < R^2$.

The second measure, standard error of regression (SER), is calculated according to the following equation:

$$\mathbf{SER} = \sqrt{\frac{\mathbf{SSE}}{\mathbf{n-(K+1)}}} \qquad \text{……..eq. (4)}$$

The divisor n-(K+1) in the above equation is the number of degrees of freedom (df) associated with the estimation of (SER). In general, the smaller the (SER) value, the better the proposed regression model.

2. Diagnostic Plots

Another effective approach to the assessment of model adequacy is to compute the predicted criterion values, y'_i, and the residuals, e_i. Residuals are the difference between an observed value of the criterion variable y_i and the value predicted by the model, ($e_i=y_i-y'_i$), and then plot various functions of these computed quantities. Finally the plots are examine either to confirm the selected model or the model is not appropriate Devore [16].

- y'_i on the vertical scale versus y_i on the horizontal scale.
- e_i on the vertical scale versus y'_i on the horizontal scale.
- Histogram for the standardized residual versus the frequency.

Standardizing residuals is made by subtracting the mean value of residuals (zero) from each residual and then dividing by the estimated standard deviation. If the first plot yields points close to the 45° line [slope=1 through (0, 0)], then the proposed regression function gives accurate prediction of the values that are actually observed. Thus the first plot provides a visual assessment of model effectiveness in making prediction. If the model correct, the second plot of the residuals versus predicted (y) values should not exhibit distinct pattern. Also with the aid of the second plot, one can determine the extreme value of the (y'_i) can be determined, i.e., outliers. If the residuals plots indicate a distinct pattern, then the function structure should be changed to fit the data (if the residuals exhibit curved pattern, then a non-linear polynomial model can be fit). The histogram plot of the standardized residual should follow the normal distribution pattern if the underlying assumption for the proposed model is correct, with the mean value of zero. Any sequin in the distribution shape suggests further investigation in order to obtain the proper model.

The first plot enables immediate check of proposed model structure whether it is rational or not. The rational model is that model which gives rational predicted values.

Proposed Statstical Model

The multiple linear regression analysis was used to build the present model. The general purpose of regression analysis is to learn more about the relationship between one or several independent or predictor variables and a dependent or criterion variable. The regression equation or the best-fitting line is determined by minimizing the sum of squares of the residuals between the actual and predicted values of the dependent variables. The statistical analysis was done with the aid of computer software STATISTICA -2003 [17].

According to above-mentioned affecting factors, the general final form was decided to represent of this model is as follows:

$AE=a_0 \times ((FCaO + MgO)\ \hat{}a_1)/FIN\hat{}a_2 + (SO_3 + C_3A) \times a_3$ ……..eq. (5)

R = 0.9898 R^2 = 0.9797 S.E. = 0.05063 F_{value} = 90.3459

The reasons behind selecting such a form are:

- Choosing a linear would not represent the variation and behavior of the selected variables.
- The expansion mechanism is similar and interrelated for both free and magnesia, meanwhile, it is different for sulfate. Moreover, SO_3 and MgO are more effective on autoclave expansion than free CaO.
- The current form could be used efficiently in explaining the relationships between the dependent and independent variables.

The adopted model is nonlinear, and have a higher correlation coefficient was (R^2 =97.97%) and their 95% confidence intervals and acceptable diagnostic plot, in addition, based on the diagnostic plot shown in Fig. 1. This model is rational, the distribution of residuals are distributed normally, which represent goodness of fit measures. Fig. (1-a) shows the values obtained from the predicted model (obtained from the regression model) and the experimental testing (available actual values). The values show the coefficient of determination (R^2) equals to 97.97% of confidence. The proposed model shows its capability of generalizing between input and output variables with reasonable good predictions. Table 6 shows the parameters obtained from the statistical analysis.

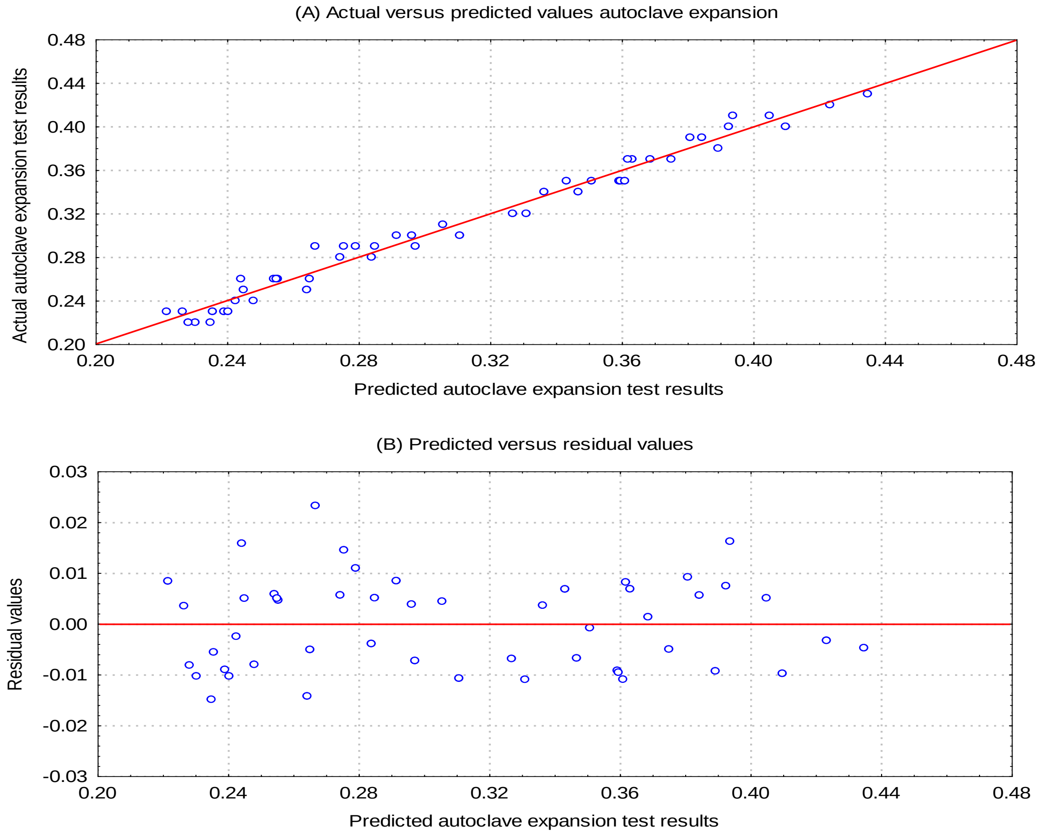

Figure 1: Diagnostic plot for the autoclave expansion obtained by the present

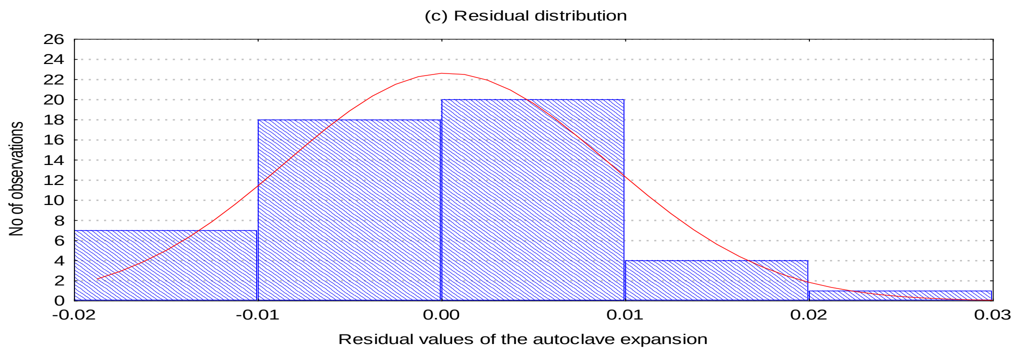

Figure 1: Continued.

Comparison With Other Data

To test the proposed model obtained from this study, it was decided apply the model using data from other sources or data from other researchers. This comparison is very important to check the validity of the proposed model for the prediction of autoclave expansion of cement for any set of data. A new data (consist of 20) cases were used for testing the applicability of the developed model. These data are not included in the building of model.

To check the validity of the proposed model to predict the autoclave expansion of cement, two samples of Portland cement were tested. One of them is Ordinary Portland cement while the other is sulphate resisting Portland cement. The correlation coefficient between experimental and predicted values was equal to (R^2=0.9535). Table 7 shows full details of the data imported and used to check the proposed model. The details of these cements and the values of the autoclave expansion observed and predicted are listed in this Table. From this Table it is clear that the maximum difference between the observed and predicted values is about +0.05. Thus, it may be concluded that the present model is appropriate to predict the autoclave expansion with a good accuracy.

The distribution of residuals is shown in Fig. 2. From this figure it is clear that the residuals are almost normally distributed. It is also clear that the residuals gathered around zero. This indicates that there are no evidences that the models are inadequate, or there is an error in analysis. Fig. 3 shows the relationship between experimental and predicted autoclave expansion of Portland cement. It is clear that the points roughly follow a straight line. This indicates that the model is appropriate for the data, and they are correctly specified.

Table 7: Chemical analysis and physical properties of cement used for checking the proposed model.

Factory	Type	Chemical Analysis %										Physical Properties		
		CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Free lime	L.O.I	IR	L.S.F.	Blaine (m^2/kg)	Autoclave Expansion	
													Observed	Predicted
Kubaisa	Type I	62.59	21.28	4.95	3.50	3.85	2.75	1.40	0.83	0.92	0.91	341.8	0.41	0.38
Kubaisa	Type I	61.96	21.0	5.10	3.21	3.31	2.23	1.23	1.96	0.51	0.90	347.0	0.34	0.39
Kubaisa	Type I	62.45	21.80	5.78	3.40	3.55	2.66	1.20	1.20	0.32	0.91	305.7	0.31	0.36
Kubaisa	Type I	60.79	20.52	5.40	3.60	4.28	2.21	1.68	1.52	0.95	0.89	342.0	0.40	0.39
Kubaisa	Type I	61.38	20.80	4.96	3.10	3.85	2.67	1.32	1.92	0.83	0.89	311.5	0.37	0.36
Factory	Type	Chemical Analysis %										Physical Properties		
		CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	Free lime	L.O.I	IR	L.S.F.	Blaine (m^2/kg)	Autoclave Expansion	
													Observed	Predicted
Kubaisa	Type I	61.10	20.96	5.20	3.44	3.87	2.47	1.19	1.77	1.00	0.88	323.0	0.36	0.37
Um-Qaser	Type I	62.71	21.00	5.70	3.30	2.93	2.63	1.35	0.38	1.09	0.89	314.8	0.38	0.39
Um-Qaser	Type I	62.50	20.30	5.90	3.28	3.11	2.57	1.60	0.74	0.79	0.91	306.1	0.38	0.38
Um-Qaser	Type I	61.57	21.10	5.82	3.24	4.43	2.75	0.88	0.81	0.90	0.87	290.9	0.40	0.37
Um-Qaser	Type I	62.61	21.26	5.80	3.20	4.41	2.33	1.17	0.72	0.88	0.91	327.0	0.39	0.40
Um-Qaser	Type I	62.22	20.5	5.56	3.18	2.56	2.18	1.18	2.62	0.52	0.90	297.0	0.38	0.36
Um-Qaser	Type I	62.12	21.10	5.48	3.23	2.37	2.39	1.32	1.99	0.90	0.89	305.7	0.40	0.37
Al-Muthana	TypeV	62.71	21.00	4.10	5.34	1.85	2.49	1.35	1.16	0.79	0.90	281.6	0.23	0.23
Al-Muthana	TypeV	62.98	21.53	3.55	5.40	2.00	1.89	1.29	1.36	0.73	0.90	303.0	0.24	0.22
Al-Muthana	TypeV	64.00	21.60	3.85	5.20	1.95	2.03	1.35	0.62	1.35	0.91	291.0	0.22	0.22
Al-Muthana	TypeV	61.18	22.00	4.00	5.68	2.14	1.85	1.47	1.68	1.05	0.85	309.0	0.23	0.23
Al-Muthana	TypeV	63.47	21.60	3.50	4.80	3.20	2.03	0.61	0.79	1.30	0.91	290.0	0.22	0.22
Al-Muthana	TypeV	63.75	21.42	3.80	5.32	1.40	1.92	1.51	0.88	1.17	0.90	281.0	0.21	0.21
Al-Muthana	TypeV	62.42	21.90	3.68	5.10	1.71	1.9	1.57	1.72	0.60	0.88	300.4	0.22	0.23
Al-Muthana	TypeV	63.50	22.10	3.48	4.84	2.00	2.05	0.96	1.07	0.54	0.89	316.0	0.23	0.25

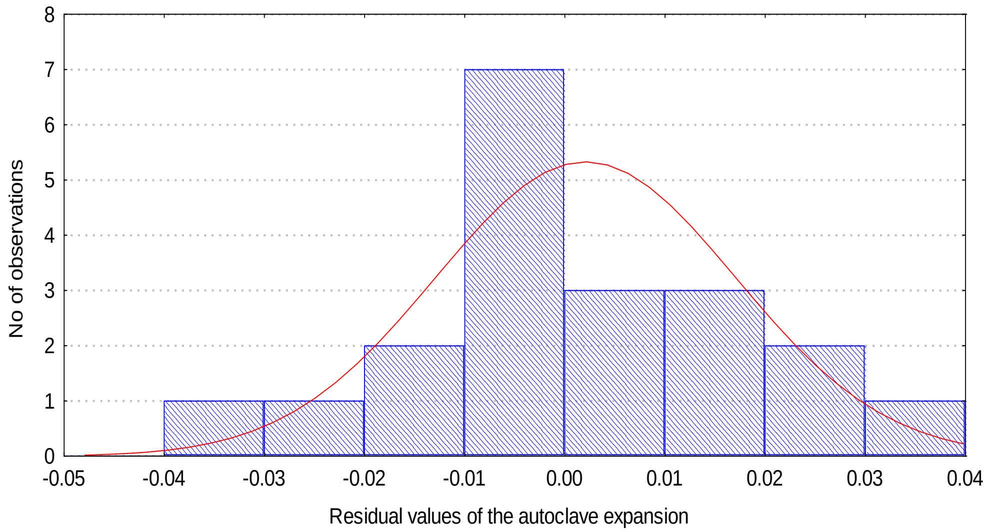

Figure 2: Diagnostic plot for the autoclave expansion obtained by the present model with new

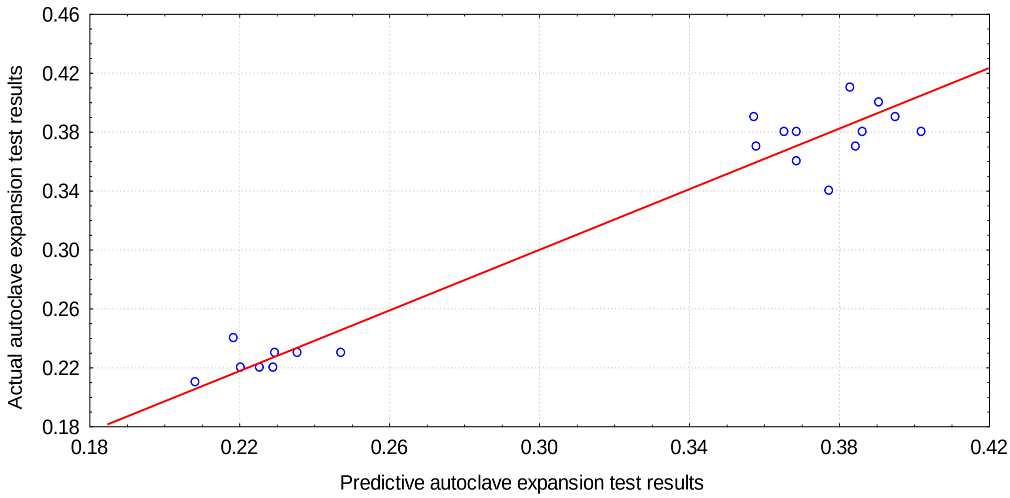

Figure 3: The Predicted values of the autoclave expansion against the predicted values obtained by the present model with new data.

Discussion

As mentioned earlier, the mathematical model based on the statistical regression analysis was developed in this study. This model obtained to obtain the autoclave expansion which pass through the origin (without intercept) is more suitable and recommended. From the present work the following points have been:

1. Previous models that deal with the prediction autoclave expansion of cement lack of including other variables affecting autoclave expansion gaining in cement.

2. It is obvious that the correlation coefficients, F_{value}, and the standard error of the model development in the present study are very close.
3. As explained earlier, fineness of cement is the most interesting factor affecting the soundness of cement. From the built model, it is clear that the autoclave expansion increases with the increase in cement fineness.
4. From built model, it can be deduced that the increase in MgO and SO_3 contents increase the autoclave expansion. The free CaO has the same effect but at a lesser degree. This result seems acceptable as they play a role in cement paste volume change as mentioned earlier.
5. The built model showed the ability to explain most of the known relationship between included variables.
6. On the basis of the present models, it is proven statistically that the autoclave expansion increases when the content of C_3A are increased. This behavior may be explained in the light of the fact that the hydration of Tricalcium Aluminates is associated with a volume increase.
7. As expected C_3A increase the autoclave expansion, this is obvious from the correlation coefficient in present model. This may be attributed to the fact that this compound cause expansion of cement paste as discussed earlier. This is online with what was demonstrated by Lea [16].

Conclusion

The following conclusions are based on analyses and discussions.

1. It is found that the mathematical model which passes through the origin (without intercept) is more suitable and recommended. This model possessed R^2 equal to 0.9797.
2. The increase in MgO and SO_3 contents increases the autoclave expansion intensively. The free CaO has the same effect but at a lesser degree.
3. The increase in fineness of cement increases the autoclave expansion remarkably.
4. This model proves to be used with any set of data in spite of variations in test results of the cement in question.
5. 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.
6. In this work, a mathematical model has been developed for predicting the autoclave expansion of cement. The presence of model would possibly obtain the hard balance and equality between controlling the quality (quality control process) and economics (saving time and expense), i.e. this model could be used in cement factories in quality control process to provide a

chance for the producer to make the necessary corrections during the process of cement production.

Acknowledgments

The author would like to thank the head and staff of the Consultant Engineering Bureau of Babylon University and quality control records for providing experimental data for this study.

References:

Lea's, P.H., 2004 "Chemistry of Cement and Concrete", UK, ELSEVER.

ASTM C151-05, 2006 "Standard Test Method for Autoclave Expansion of Hydraulic Cement", Annual Book of ASTM Standards, USA.

Moscardini, A.O., and Cross, M., 1983 "Issues Involved in the Design of a Mathematical Modeling Course", Proc. 4th int. Conf. of Mathematical Modeling in Science and Technology, pp.954-963.

ASTM C150-05, 2006, "Standard Specification for Portland Cement", Annual Book of ASTM Standards, USA.

BSI, BS 12:1996, "Specification for Portland Cements", (UK, BSI).

Neville, A.M., 2005, "Properties of Concrete", 4th and final Edition, Pitman publishing, London. 844 pp.

Chatterji, S., 1995, “Mechanism of Expansion of Concrete due to the Presence of Dead-Burnt CaO and MgO”, Cement and Concrete Research, 25, pp.51-56.

Lea, F.M., 1976, "The Chemistry of Cement and Concrete", 3rd Edition, Publisher: Edward Arnold, London, LTD. 727 pp.

Learch, W., 1946, "The Influence of Gypsum on the Hydration and Properties of Portland Cement Pastes", Proc., ASTM, 46, pp.1252-1292.

Meissner, H.S., Cook, H.K., and Gonnerman, H.F., 1950, "The Optimum Gypsum Content of Portland Cement", ASTM Bulletin, 139, pp.39-45.

Samdi, M.M., Haddad, R.H., and Akour, A.M., 1999, "Potential use of Phosphogypsum in Concrete", Cement and Concrete Research, 29, pp.1419-1425.

Al-Jabiri, T.M., 2002, "Concrete Strength Development Related to MgO and SO_3 Contents in Cement", M.Sc Thesis, University of Baghdad, College of Engineering, Baghdad, Iraq.

Czernin, W., 1980, "Cement Chemistry and Physics for Civil Engineering", English Edition, George Godwin LTD., London, 196 pp.

Abdul-Latif, A.M., 2001, "Mathematical Model for Optimum Gypsum Content in Cement Mortar and Concrete", Ph.D. Thesis, University of Baghdad, College of Engineering, Baghdad, Iraq.

Al-Aaraji, T.M., 2003, "Prediction of Compressive Strength of Cement", M.Sc Thesis, University of Babylon, College of Engineering, Babil, Iraq.

Devore, J., 2000, "Probability and Statistics for Engineering and Sciences", 5th Edition, Duxbury Thomson Learning, USA.

Stat Soft 2003, "Multiple Regressions", Electronic Text Book. http://www.statsoft.com/textbook/stnonlin.html#general