



Compressive Strength in Sulphate Resisting Portland Cement (SRPC)

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Abstract

The compressive strength of cement is regarded as a principal indicator to determine the quality of cement. Therefore, efforts were focused to combine the factors which affect compressive strength together in such a form to develop suitable statistical models for predicting strength of cement at various ages (3 and 7 days).

Using SPSS16 software, a statistical analysis is performed for (574) observations taken from archive of quality control at Kerbala Cement Plant, which produces low alkalis sulphate resisting Portland cement. These data sets include compressive strength at 3 and 7 days with various independent variables.

Stepwise regression results in multiple linear models that explain (99.7 %) and (99.9 %) of variations in 3-days and 7-days compressive strength respectively in function of; C_3S , C_2S , C_3A , SO_3 contents, and Insoluble residue (IR). The developed models show that these contents positive effect on strength, but (I.R) content has a negative one. Such models could be used in quality control of SRPC factories to enable the manufacturer to make corrections in process within production stage. The sufficient data used in the analysis assures confidence of the developed statistical model.

مقاومة الانضغاط الاسمنت البورتلاندي المقاوم للسلفات

تعد مقاومة الانضغاط للإسمنت مؤشرا رئيسا لتحديد نوعية الإسمنت. لذلك تركزت الجهود لربط عوامل تؤثر في مقاومة الانضغاط لعمل نماذج إحصائية مناسبة للتنبؤ بمقاومة الاسمنت في أعمار ٣، ٧، أيام. باستخدام برنامج SPSS تم انجاز تحليل احصائي لبيانات ٥٧٤ من ارشيف السيطرة النوعية في معمل اسمنت كربلاء الذي ينتج أسمنت مقاوم للسلفات منخفض القلويات. تتضمن البيانات مقاومة الانضغاط بعمر ٣، ٧ أيام مع عدة متغيرات مستقلة.

نتج عن تحليل الانحدار المتدرج نماذج توضح ٩٩.٧ % من التغير في مقاومة الانضغاط لعمر ٣ أيام و ٩٩.٩ % لعمر ٧ أيام بدلالة محتوى مركبات (C_3S , C_2S , C_3A , SO_3) والمتبقي غير الذائب. النماذج المتحدثة تبين ان محتوى تلك المركبات له أثر ايجابي بينما كان المتبقي غير الذائب له أثر سلبي. هذه النماذج يمكن استخدامها في السيطرة النوعية لمعامل الاسمنت المقاوم للسلفات لتمكين المصنع من اجراء التصحيحات في المرحلة الاولى من عملية الإنتاج. البيانات الكافية المستخدمة في التحليل الاحصائي تؤكد الموثوقية بالنموذج المستحدث.

1. Introduction.

The most important characteristics of cement are: compressive strength. Compressive strength is taken as the maximum compressive load carried per unit area. Differences in compressive strength of various Portland cements are mainly attributed to their chemical composition and fineness. Also it can be seen that the rate of cooling of clinker, as well as, possibly other characteristics of the process of cement manufacture such as: the burning temperature, loss on ignition and the amount of added gypsum affect the strength of cement (AL-Attar, 2001). Never the less, if one process is used and the rate of cooling is kept constant, there is a definite relation between compound composition and strength (IQS No-5:1984). The effects of both chemical composition and fineness on the strength of cement mortars are considered here.

The strength of cement is judged by its performance in combination with water. The chemical reaction between cement compounds and water, known as hydration, produces very hard and strong binding medium. The rate of hydration depends on the relative properties of silicate and aluminate compounds, the cement fineness and the ambient condition particularly temperature and moisture.

The two silicates C_3S and C_2S , together form 70-80 percent of the constituents in the cement, and contribute significantly to the mechanical and physiochemical properties of cement mortar and concrete. The hydration of C_3A takes place very quickly, producing little increase in strength after about 24 hours. Tetracalcium aluminoferrite (C_4AF) is of less importance than the other three compounds when considering the properties of hardened cement mortar (Neil, 1995). In addition to the four principal compounds, Portland cement may also contain several minor constituents such as: sulphate, insoluble residue, alkalis and free lime, but they will be less to contribute strength development. As well as fineness plays a positive important role in cement strength.

2. Strength required in Cement paste

AL-Attar (2001) explained that the strength of cement paste derives to a large degree from the bonds formed between the very small particles that compose cement gel. Generally, the greater the number of such particles and the denser the gel structure, the stronger the gel mass. A survey of the most important factors influencing the strength of Portland cements are shown in Table (1).

Furthermore, many attempts have been made to determine the explanatory variables related to the force in cement, and many researches have been carried out in this area. Table (2) shows a summary of literature review for conclusions drawn about the factors governed strength in cement.

Table (1) Most factors affect compressive strength (Smidth,2006).

		<i>Compressive Strength(EN)</i> <i>N/mm²</i>			
		1-day	3-days	7-days	28-days
<i>Influencing Factors</i>	<i>Normal Range for OPC</i>	5 -15	20 - 35	30 - 45	45 - 60
C_3S	45 – 65%	+	+	+	+
C_3A	6 – 12%	+	+	+	+
K_2O	0.2 – 1.5%	+	+	0/-	-
SO_3	2 – 4%	-/0/-	+/0/-	+/0/-	+/0/-
<i>Fineness (Blaine)</i>	280–350m ² /kg	+	+	+	+

To prevent collapse in hardened cement some international standards limited the minimum strength wanted in cement paste, as well as the limits allowed for some explanatory variables related to it. Kiattikomel et.al.(2000) found that the reduction of the compressive strength at 1 day is about two

times of 60 days for the same percentage of insoluble residue. Therefore its value has limited in the specifications to be not to exceed a certain limit (Soroka, 1979), such as: ASTM 0.75%, B.S 1.5% and IQS 1.5%. Table (3) demonstrates the limits of strength and some explanatory variables related to it according to international standards:

Table (2) A Summary of literature review for conclusions drawn about factors that affect strength in cement.

Author	Conclusion
Johansen, 2005	Di-calcium silicate (C_2S) reacts slowly and contributes to long-term strength gain.
AL-Attar, 2001	The more <i>finely</i> cement is the greater the strength and particularly the early strength.
AL-A'araji (2003)	The C_3A has a positive effect on the strength of sulphate resisting Portland cement for the ages of (3days ,7 days and 28 days) due to its effect as a catalyst, the positive effect of C_3A is more pronounced at early ages .
Neville (2000)	<i>The fineness</i> has little effect on the later-age strength.
AL-A'araji (2003)	There is a negative effect of the compound C_2S on the strength at age 3, 7 and 28 days and it is more pronounced at early ages.
Popovics (1979)	The compound C_3A alone contributes very little to strength, but it shows a favorable effect on the setting and strength development at early ages in mixes with calcium silicates (C_nS).
Celani et.al.(1968)	The results of compressive strength of mortars produced from four different cement with a different content of C_3A , they educe that the C_3A has a positive effect on strength until 10% especially at early ages.
Neville (2000)	Cement with high (C_3A+C_4AF) content, it causes retrogression.
AL-A'araji (2003)	The compressive strength of cement increases with the increase of the percentage of C_4AF at the ages 3, 7 and 28-Days.
AL-Ta'ii (2001)	There is a negative effect of C_4AF at the ages 1 , 7 and 28-Days normal curing .
Osback,1990	<i>Alkalies</i> are important to the strength properties of the finished cement, as increased <i>alkali</i> content makes for more rapid development of the strength, while there is a reduction in the ultimate strength.
Smidth, 2006	Increased contents of <i>alkali</i> will increase early strengths, but decreases late strengths.
AL-A'araji(2003)	The compressive strength of cement is negatively affected by the increase in <i>free lime</i> content.
(Osback, 1980).	The effects on the early strengths in particular can be modified somewhat by varying the amount of <i>gypsum</i> added.
Soroka and Abayneh (1986)	They educed that addition of <i>gypsum</i> affects the rate of hydration and thereby the strength of cement.
Kiattikomol et. al. (2000)	They educe that the <i>insoluble residue</i> reduces the strength of cement mortar, but it is not the main factor affecting the strength of cement mortar.
Smidth (2006)	There is effect of SO_3 content on compressive strength at different ages

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

I. S. Code	Loss on ignition (%) <i>max</i>	Sulphuric anhydride (%) <i>max</i>	MgO (%) <i>max</i>	Insoluble Residue (%) <i>max</i>	C ₃ A (%) <i>max</i>	Fineness M ² /kg <i>min</i> ,	3-day MPa <i>min</i> .	7-days MPa <i>min</i> .
B.S.123 30-1988	5	2.5	6	1.5	N.A.	225	10	16
IQS. 5-1984	4	2.5	5	1.5	3.5	250	15	23
ASTM C 150	3	2.3	6	0.75	5	280	8	15

3. Previous Models for compressive strength:

The main purpose of this research is to build up statistical models for prediction the compressive strength at 3 and 7 days. There are some well- known mathematical models, developed previously by many researchers for modeling compressive strength of cement paste. Alexander (1972) proposed a simplified two component linear models to relate the strength to the composition and specific surface of cement. Blaine et. al. (1968) proposes a series of equations using multiple linear regression. Egorove et. al. (1975) derives an equation to express the relationship between compressive strength and clinker phase compositions. Tables (4) shows the coefficients of models of three and seven days compressive strength respectively:

Table (4) Linear regression coefficients for models of 3-days and 7-days compressive strength.

Factor	3-days compressive strength			7-days compressive strength		
	Blaine.et.al 1968	Alexand 1972	Egorove. 1975	Blaine.et. 1968	Alexand 1972	Egorove.et 1975
constant	-20.355	-10.19	21.07	-97.504	-8.591	29.596
C ₃ S	0.286	0.17	2.215	0.388	0.284	3.979
SO ₃	2.98			2.609		
K ₂ O	2.258			2.71		
L.O.I	-1.724			-0.474		
Ss	0.005	0.033		0.074	0.0024	
AIR	-0.342			-0.414		
C ₃ A	0.152	0.2789	1.46	0.624	0.544	2.019
C ₄ AF			1.45			1.666
C ₃ S*C ₄ AF			0.911			
C ₃ A*C ₄ AF			0.588			-1.401
MgO				-0.271		

4. Building of a statistical model.

Based on the gained information from the literature survey, the following factors are selected to be included in these models as explanatory variables: C_3A , C_4AF , C_2S , C_3S , $F.CaO$, SO_3 , $I.R.$ and fineness. Although literatures indicates that Alkalis content has a significant effect on strength of cement mortars, it is intended to exclude Alkalis contents from the independent variables used to build the model. This is because sulphate resistant cement produced in Kerbala plant is low Alkalis cement.

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 (574) observations of low 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. Chauvenet 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 [6]. Table (5) displays the refined data of (494) cases, used in building the statistical model.

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

	C_3A	C_4AF	C_2S	C_3S	$F.CaO$	SO_3	$I.R$	Fineness	Strength 3days(Mpa)	Strength 7-days(Mpa)
Min	.49	14.65	17.6	41.5	0.54	1.90	0.35	2813	18	27.7
Max	2.53	18.35	33.89	58.06	1.96	2.50	1.06	3392	24.3	33.4
Av	0.88	16.55	25.67	49.20	1.60	2.21	0.67	3093	21	30.3
St. Dev.	0.68	0.75	3.46	3.50	0.62	0.15	0.16	126	1.4	1.23
(Min- av)/St.dev	1.97	2.53	2.33	2.20	1.70	2.07	2	2.22	2.14	2.11
(Max- av)/St.dev	2.43	2.40	2.37	2.53	0.60	1.93	2.43	2.37	2.35	2.52

5. Proposed statistical model

By using the group of (494) observations as mentioned previously, the models obtained with and without intercept as following respectively:

With the aid of computer software SPSS version 13, stepwise method is used to develop this model. The factors: C_3S , C_2S , C_3A , C_4AF , I.R, SO_3 , F.CaO and Fineness are included in the regression analysis. Two models are developed one with intercept and other without intercept. The model with intercept is:

The model without intercept is:

$$\text{Comp Strength 3-days} = 0.333(C_3S) + 1.575(SO_3) + 0.098(C_2S) - 2.731(I.R) + 0.375(C_3A)$$

$$R = 0.999$$

$$R^2 \text{ adj} = 0.997$$

$$F = 33382$$

$$SEE = 1.12$$

$$P\text{-VALUE} = 0$$

It is clear that the standard error of estimate (SEE) and p-value are the same for both models, but the coefficients of determination ($R^2 \text{ adj}$) are different.

However, $R^2 \text{ adj}$ of the model without intercept is higher than that of the model with intercept, therein the model without intercept is the best one. Figure (1) shows the distribution of residuals, from this figure it is obvious that the residuals are normally distributed. Figure (2) displays the relationship between the observed and predicted of 3-days strength according to the developed model. It is clear that the points are clustered well around the line of equality. This indication gives the impression that the model could be used with relatively high significance level.

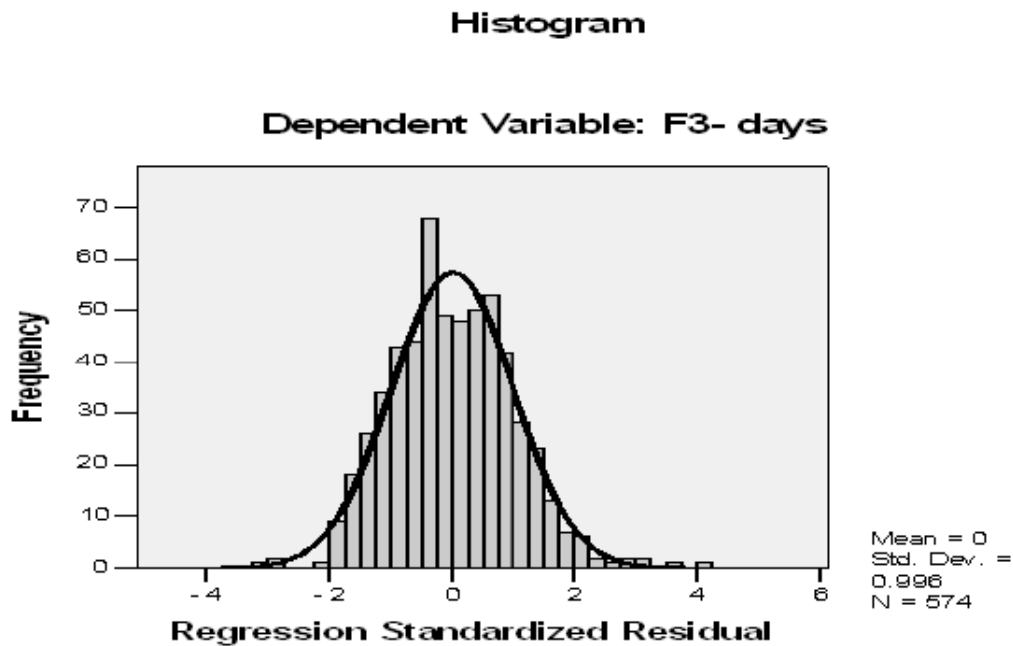


Figure (1) residuals distribution of 3-days strength.

Normal P- P Plot of Regression Standardized Residual

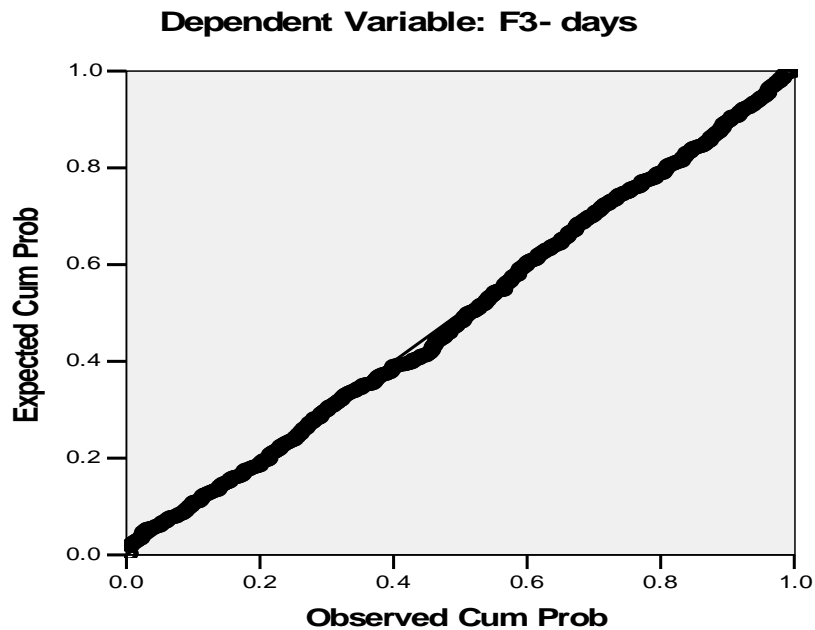


Figure (2) observed versus predicted values of 3-days strength.

In Figure (3) the residuals are plotted against predicted values. It is clear that the residuals gathered around zero concentrically as a horizontal band, and that confirms assumptions of linear regression model.

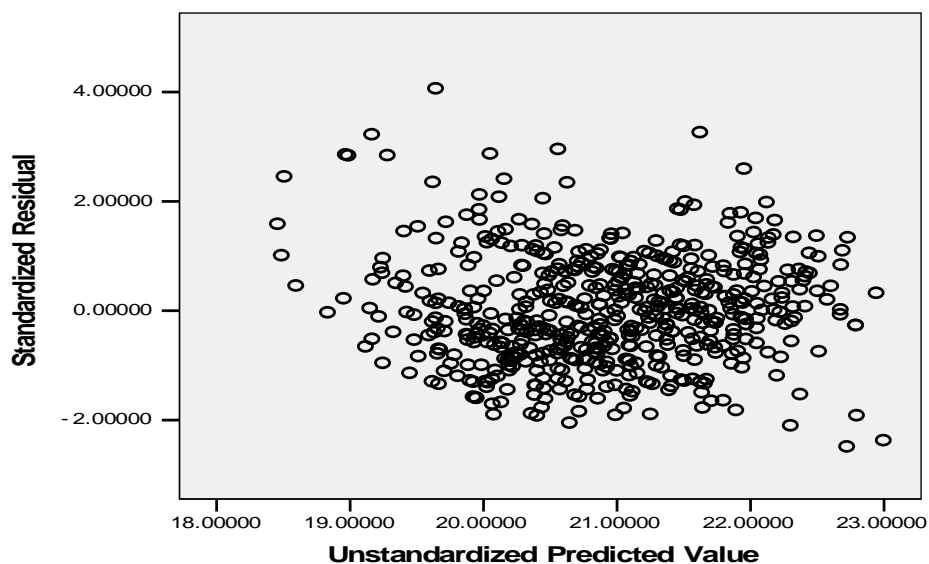


Figure (3) predicted values against residuals of 3-days strength.

This model includes the most important factors in a properly way according to the literatures, that C_3S , C_2S , C_3A and SO_3 have a positive effect on compressive strength, while I.R has a negative effect alone.

It is obvious that the influence of C_3S is more than three times the effect of C_2S . This is due to the high rate of hydration of C_3S respect to the hydration rate of C_2S especially at the early ages, and thereby it seems that the C_3S has essential role in this respect, while the C_2S seems to be of minor effect.

A simple comparison between this developed model and the other models which developed by different researches in table (2-4) leads up to that there is partial similar with Blaine's model (Blaine et. al. 1968), where C_3S , SO_3 and I.R have the same effect in both models.

Moreover, the positive effect of C_3A and C_3S as found by this study confirms Alexander (1972) and Egorove (1975) results, who finds that both C_3A and C_3S affect positively early compressive strength. There is an agreement with Kiattikomol et. al.(2000) about the negative effect of insoluble residue on compressive strength.

On the other hand, the following developed model for 7-days compressive strength without intercept is the best one because the R^2_{adj} is higher in this model than the other, while the other statistics is almost the same in both models:

$$\text{Strength (7days)} = 0.446(C_3S) + 0.238(C_2S) - 2.326(I.R) + 0.353(C_3A) + 1.578(SO_3)$$

$$R = 0.999$$

$$R^2_{adj} = 0.999$$

$$SEE = 1.046$$

$$F = 96377$$

$$P\text{-VALUE} = 0$$

The Figures below are plotted according to the developed model. From Figure (4) it is clear that the residuals are distributed normally.

According to Figure (4), it can be seen that all the points are gathered completely around the equality line. This refers that the model could be used with high level of significance. Generally, this model in line with the cement technology, it includes the most important factors, which affect cement paste strength.

From this model, it seems that the C_3S has a major role in strength development at early ages, while the C_2S and C_3A have a minor effect. This fact as found from this study is completely in line with the research results of many researchers like: Blaine et. al.(1968), Wood (1932) and Bogue and Lerch (1934).

Additionally, they report that C_3S exhibits the fastest strength development followed by C_2S which grows significantly slower than C_3S , Whereas, C_3A has a very low strength even after a long period of time.

Also the negative effect of I.R on the compressive strength is confirmed by Soroka (1979) and Kiattikomel (2000), who educe that the insoluble residue reduces the strength of cement mortar.

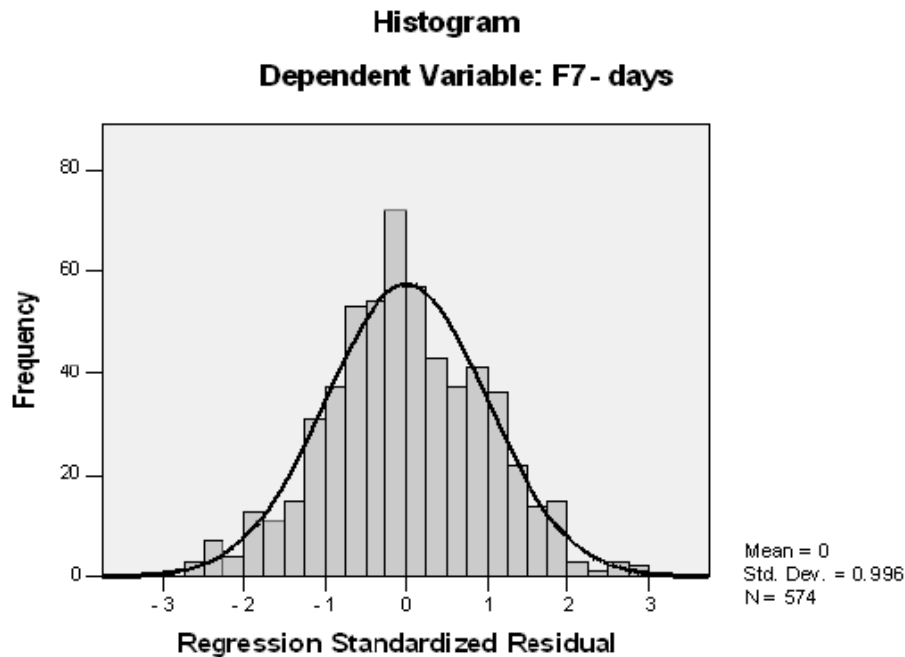


Figure (4) residuals distribution of 7-days strength.

Normal P-P Plot of Regression Standardized Residual

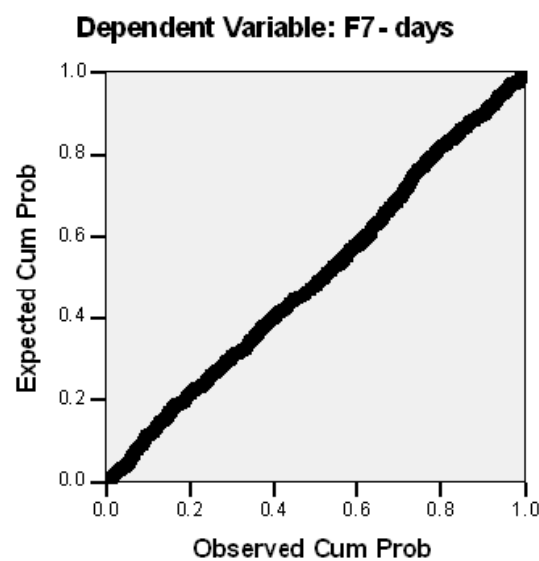


Figure (5) observed against expected values of 7-days strength.

In Figure (6) the residuals are plotted against predicted values, it is obvious that the residuals clustered well around zero. This indicates no abnormality and our regression analysis would not appear to be invalidated (Draper, et. al., 1966).

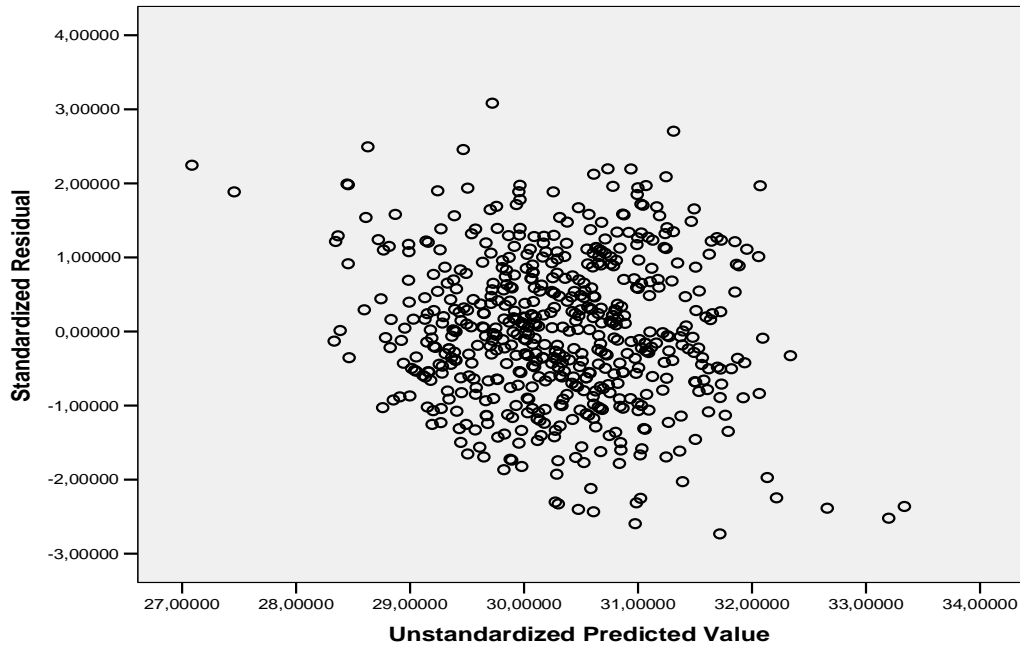


Figure (6) predicted values against residuals of 7-days strength.

The positive effect of SO_3 on strength as found in this model agrees with the research works of Lea (1970) and Menetrier (1980) who mentions that the gypsum accelerates the hydration of calcium silicate. However, there is somewhat similarity with the model of Blaine et. al. (1968) that they both consist of the same variables: C_3S , C_3A , SO_3 . This is also compatible with the research results of Soroka (1979) and AL-Aaraji (2003). The positive effect of C_3S and C_3A is confirmed by Alexander (1972) and Egorove (1975), who finds that C_3S and C_3A contribute positively on compressive strength.

6. Validation of Developed models

It is necessary to evaluate the developed model through the following statistics:

1- Coefficient of determination (R^2):

It is used to measure the proportion of total variation about mean Y explained by the regression (Draper et. al. , 1966).

The value of R^2 is ranging between zero and one. The greater the value of R^2 is the better the model. Many researchers prefer to work with the adjusted R^2 , therefore, adjusted R^2 will be considered in this study.

2- Analysis of variance (ANOVA):

In order to decide that the model is properly fitting the data, it is useful to compute F-value which must be greater than tabulated F value, the later is taken from special tables (Al-Khathi et. al. , 1986).

3- P-Value test:

The significance level or p-value is the probability of obtaining results as extreme as the one observed. If the significance level is very small, less than 0.05, then the correlation is significant and the two variables are linearly related. If the significance level is relatively large, for example equal to 0.05 and more, then the correlation is not significant and the two variables are not linearly related (Al-Jumeily, 2001).

4- Standard Error of Estimation (SEE):

Sometimes, no decision could be reached about the best model according to the above statistics if they are the same. Therefore, the assessment is made by examining the standard error of estimate.

The standard error of estimate is calculated directly by the SPSS software. The smaller the SEE value is the better and more precise will be the predictions (Al-Attar, 2001).

5- Residuals Analysis:

Residual is the amount which the regression equation has not been able to explain. If the developed model is correct, the residuals should exhibit tendencies that confirm some assumptions (Drapper and Smidth, 1981) :

- i. The residuals are independent.
- ii. They have a zero mean and a constant variance.
- iii. They follow normal distribution.

The examination of residuals may be graphical such as plotting the residuals against the predicted value and plotting the residuals in a histogram.

6- Plotting observed versus predicted value:

This plot is very useful to see whether or not the expected value, according to the developed model, near from the observed value. The predicted values must be as near as possible to the observed values.

7. Conclusions

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

1. The number of the independent variables used in this study is (8). The value of adjusted determination coefficients are: ($R^2_{adj}=0.997$) in the model of 3-days compressive strength, and ($R^2_{adj}=0.999$) in the model of 7-days compressive strength
2. Test of these models refers that the models are adequate for prediction.
3. The regression coefficients are determined through these proposed models are generally in line with these of the models presented previously by other researchers.
4. Multivariable linear regression without intercept (which passes through the origin) proves to yield better predicted results than that with a given intercept.
5. The positive effect of C_3S on cement strength is clearer at the early ages.
6. There is a little effect of C_2S at the early ages and becomes pronounced positive effect at the later ages.
7. The positive effect of C_3A on the compressive strength is most pronounced at the age of 3-days.
8. From the values of regression coefficients obtained in this work, it is found that each variable had a certain extent of effect on the cement paste forces, this effect may increase or decrease with the age of cement mortar.
9. The effect of C_3S on compressive strength is twice the effect of C_2S at early ages.

8. Recommendations

This research may be followed by further efforts and works in this field in the future, therefore we will present the following recommendations:

1. Improving these proposed models to be suitable to apply in other sulphate resisting Portland cement in addition to the products of karbala cement plant.
2. Studying the possibility of using these models for the prediction of other types of cement.
3. Improving the accuracy of the present models.
4. Improving the proposed models to predicted the compressive strength of cement paste to include other different ages than 3 and 7-days.

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