Analysis of anhydrite gypsum effects on quality of cement

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Abstract - *The main aim of this report is the comparison of two clinker samples with respect to anhydrite($CaSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$) in different percentages. The result of this research has indicated that compare with gypsum, samples which have been prepared with anhydrite have high water demand, short setting time, and low flowability after 30 and 60 minutes and compressive strength of 7 and 28 day.*

Key Words: anhydrite, gypsum, clinker, cement

1.INTRODUCTION

As it is well known, the workability property of cement solutions depends on reaction rate of C_3A with water and to justify this, retarder raw materials are used. In cement industry, natural gypsum ($CaSO_4 \cdot 2H_2O$) is the most effective raw material for this purpose. In the natural gypsum sources, anhydrite gypsum can often be encountered, so its effect on cement's quality parameters must be focused on [1-3].

Furthermore, in the many different literatures, the usage of industry wastes which contain $CaSO_4$ on cement production is likely to be seen. Application of phosphogypsum can be given as an example for this case. Phosphogypsum is a raw material which is produced from orthophosphote as a byproduct and contains $CaSO_4$ as a dust form. Remainder of phosphor and fluoride can be completely separated by washing and chemical ways. However, the gypsum in the phosphogypsum converts to anhydrite and remainder of phosphor and fluoride become inert when it is heated by high temperatures. Result of conducted researches displayed that on the base of phosphogypsum, cement with anhydrite has lower energy supply than conventional construction materials [4-6].

This research from the laboratory of NORM cement plant is dedicated to anhydrite which can be found in pure form in gypsum resources of Azerbaijan.

2. EXPERIMENTALS

The experiments and their results are carried out and prepared in the quality assurance and quality control laboratory of NORM cement plant. The chemical content of raw materials which are used in the experiment are outlined in the Table 1.

Clinker sample is taken from the clinker production process of NORM cement plant and gypsum and anhydrate are taken from the natural sources.

Cement samples are prepared by method which is displayed below.

Raw materials (clinker, gypsum and anhydrite) sieved (1.18 mm) individually by crusher. After this, in the lab mill, the cement samples is the mixture of various ratio of clinker, and gypsum and anhydrite and have 3650±50 cm^2/g fineness. During the grinding process, chemical grinding aid is used.

Table 1. Chemical composition of raw materials' samples

Parameter name	Unit	Clinker	Gypsum $CaSO_4 \cdot H_2O$	Anhydrite $CaSO_4$
Loss On Ignition	%	0.31	20.45	3.58
SiO_2	%	21.29	3.42	0.35
Al_2O_3	%	4.79	0.97	0.18
Fe_2O_3	%	3.27	0.22	0.01
CaO	%	64.68	32.74	40.9
MgO	%	1.20	1.28	0.14
SO_3	%	0.61	39.45	53.19
Na_2O	%	0.58	0.11	0.01
K_2O	%	0.56	0.27	0.03
Water Crystals	%	Not specified	19.09	1.47
LSF		95.80	Not specified	Not specified
SM		2.64	Not specified	Not specified
AlM		1.46	Not specified	Not specified
C_3S	%	57.87	Not specified	Not specified
C_2S	%	17.38	Not specified	Not specified
C_3A	%	7.16	Not specified	Not specified
C_4AF	%	9.95	Not specified	Not specified
Free CaO	%	1.24	Not specified	Not specified

3. RESULTS AND DISCUSSION

With respect to learn effects of gypsum and anhydrite on cement parameters, the physical and mechanical parameters of cement samples which is mixture of clinker-gypsum and clinker-anhydrite with 4.0, 4.5, 5.0, 5.5 and 6.0% are investigated.

3.1. Fineness and grinding time of cement samples

The Sieve residue (40 µm) and specific surface (Blaine) results of samples were prepared based on by EN 196-6 standard and determined by Air jet screen SLS 200 device (Siebtechnic company from Germany) and Automatic blaine analyzer (Testing company from Germany).
In the Table 2, the outcomes of grinding process and chemical analyses of samples are exhibited.
As seen from the Table 2, in the gypsum mixtures, when percentage of gypsum increased from 4% to 6%, grinding time that are needed to get 3650±50 cm2/g fineness decreased from 50 minutes to 45 minutes. Furthermore, sieve residue of 40 µm rose from 1.8% to 2.9%. On the other hand, when percentage of anhydrite developed from 4% to 6%, grinding time that are needed to get 3650±50 cm^2/g fineness was witnessed an extension by 2 minutes.
As a result, the amount of sieve residue of 40 µm was varied between 1.1 and 1.2% and this is not likely to be considered as significant alteration. Therefore, looking at the findings of experiment, it can be stated that in order to acquire 3650±50 cm^2/g fineness, grinding time of anhydrite samples should be longer than gypsum samples'.
The difference of grinding time of gypsum and anhydrite can explained as follows:
As is known, comparing with clinker gypsum has tendency to be grinded easily and quickly. For this reason, as the amount of gypsum increases, fineness target (3650±50 cm^2/g) is obtained thanks to gypsum grindability. This results in reduction in clinker grindability and sieve residue of 40 µm growths. As far as anhydrite is concerned, its grindability approximately same as clinker's, so their grinding process goes on identical rate and fineness target (3650±50 cm^2/g) is obtained thanks to both clinker's and anhydrite's grindability. Thus, unlike gypsum, during the grinding process of anhydrite, sieve residue of 40 µm nearly remains steady.
In this report, quality parameters gypsum and anhydrite cement samples are also investigated.

Table 2. The Results of grinding process of lab Mill and chemical analyses of samples

	Unit	Gypsum ($CaSO_4 \cdot 2H_2O$)					Anhydrite ($CaSO_4$)				
Clinker	%	96.0	95.5	95.0	94.5	94.0	96.0	95.5	95.0	94.5	94.0
Gypsum	%	4.0	4.5	5.0	5.5	6.0	-	-	-	-	-
Anhydrite	%	-	-	-	-	-	4.0	4.5	5.0	5.5	6.0
Grinding time	min.	50	50	47	45	45	50	51	51	52	52
Dosage of grinding aid	g/kg cem.	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sieve residue (40 µm)	%	1.8	1.9	1.9	2.1	2.9	1.2	0.9	0.9	1.1	1.1
Blaine	cm^2/g	3615	3674	3678	3622	3645	3674	3686	3678	3641	3667
Loss on ignition	%	1.13	1.23	1.33	1.43	1.53	0.45	0.47	0.50	0.51	0.53
SiO_2	%	20.78	20.69	20.60	20.51	20.42	20.66	20.55	20.45	20.34	20.23
Al_2O_3	%	4.68	4.66	4.64	4.63	4.61	4.65	4.63	4.61	4.58	4.56
Fe_2O_3	%	3.18	3.16	3.15	3.13	3.12	3.17	3.15	3.14	3.12	3.11
CaO	%	64.04	63.88	63.71	63.55	63.39	64.37	64.25	64.13	64.01	63.89
MgO	%	1.22	1.22	1.22	1.22	1.22	1.17	1.16	1.16	1.15	1.15
SO_3	%	2.19	2.38	2.58	2.77	2.97	2.74	3.01	3.27	3.54	3.80
Na_2O	%	0.57	0.56	0.56	0.56	0.56	0.56	0.56	0.56	0.55	0.55
K_2O	%	0.55	0.55	0.55	0.55	0.55	0.54	0.54	0.54	0.54	0.53

3.2. The water demand and setting time analyses of cement samples

The water demand and setting time results of samples were prepared based on by EN 196-3 standard and determined by Manuel Vicat device (Toni Technic company from Germany) and Automatic Vicat B26660 device (Form Test company from Germany).

In the Figure 1, the cement samples that are produced from various ratios of gypsum and anhydrite are also demonstrated in the graphic form.

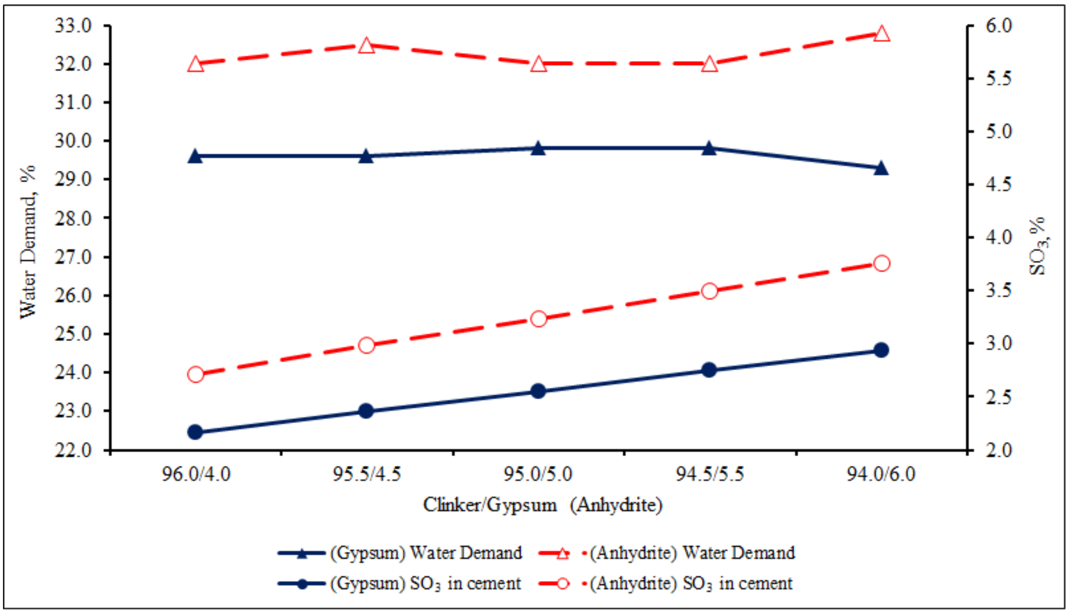

Figure 1. Result of Water demand of Cement samples

As seen from the figure, when there was an increase in amount of gypsum in cement samples from 4% to 5.5%, the water demand saw a rise by 0.2%, and increase to 6% result in 0.5% decrease.

When it comes to anhydrite, the water demand witnessed some significant changes whereas ratios of anhydrite increase from 4% to 5.5%. In addition of this, studies showed that the water demand of anhydrite samples are 2% higher than the water demand of gypsum samples which has same ratio.

The setting times of gypsum and anhydrite samples are indicated in the Figure 2.

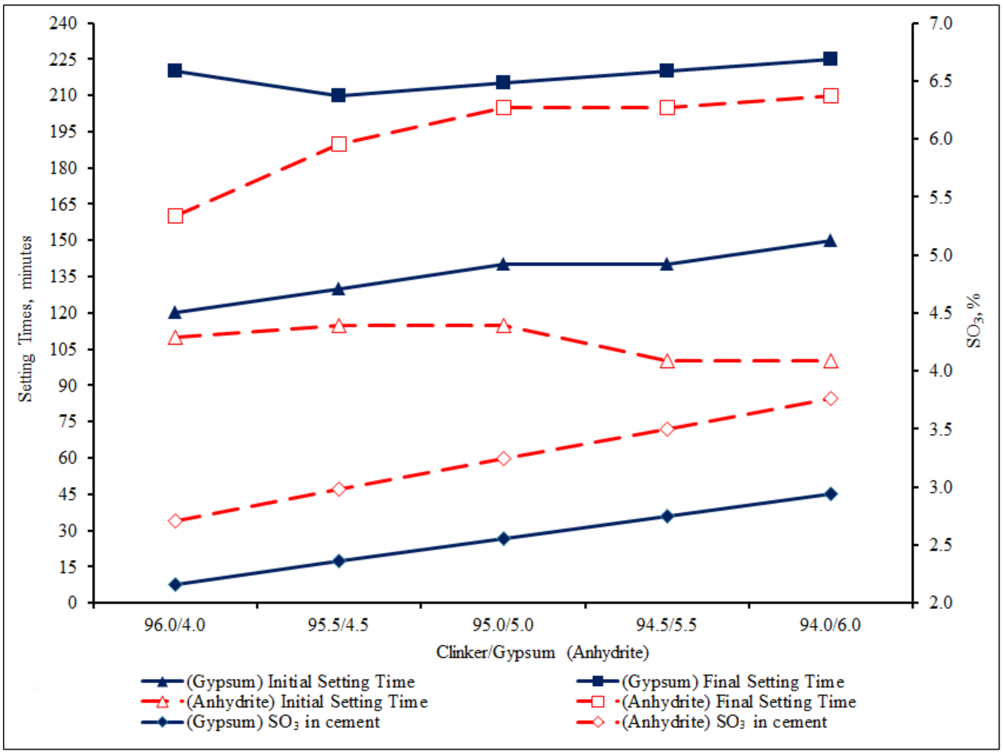

Figure 2. The Setting Times results of cement samples

In Figure 2, when quantity of gypsum in the sample increased from 4% to 6%, the initial setting time observed

30 minutes extension while the final setting time did not demonstrate any notable alteration.

In spite of this, when quantity of anhydrite in the sample rose from 4% to 5%, there was not noteworthy change in initial setting time whereas the final setting time was extended by nearly 110-115 minutes. Above the 5% in quantity of anhydrite, the initial setting time lessened by 15 minutes while the final setting time changes can be considered negligible.

The difference of water demand and setting times of gypsum and anhydrite samples can be explained as follow:

Theories that are related with hydration of cement state that when contact with water, the materials which contain $CaSO_4$ are solved in the water and produced sulphate anions which can react with C_3A particles and convert into (1) ettringite [1,7,8]. The ettringite crystals produce thin coating and with this, it delays C_3A by preventing its reaction with water. Hence, with this the hardening process is adjusted.

$$3CaO{\cdot}Al_2O_3 + 3CaSO_4{\cdot}\ 2H_2O + nH_2O \rightarrow 3CaO{\cdot}\ Al_2O_3{\cdot}\ 3CaSO_4{\cdot}\ 32H_2O \quad (1)$$

It can be understood from these theories that the solubility of materials which contain $CaSO_4$ and the rate of ettringite production are likely to affect hardening rate of cement. As it is known, solubility of both gypsum and anhydrite in the water are approximately same and solubility rate of gypsum a little more than solubility rate of anhydrite [9, 10]. During the hydration of anhydrite cement with water, because of low rate of anhydrite's solubility, conversion of ettringite is slow and it is not able to prevent the reaction of C_3A with water. For this reason, false setting occurs in the solution; however it can be adjusted by adding more water. As the amount of water increases in the solution, the solubility of anhydrite also rises slightly and ettringite is produced. Thus, anhydrite cement samples have high water demand and short initial setting times.

Comparing with anhydrite, due to high solubility of gypsum, by increasing its amount, it can give more sulphate ions to solution and lead to resistant ettringite formation. For this reason, when gypsum percentage rises, the setting times are also extended.

3.3. The flowability analyses of cement samples

During flowability analyses, cement pastes were prepared based on by EN 196-1 standard and their diameters were determined by Flow table device (Form Test company from Germany).

Preparation of cement samples is performed as follow.

On the condition to hold water : cement ratio as 0.5, 400 g cement, 200 g water, 1350 g standard sand and 1 % concrete aid are put into mixer for mixing. Then the diameter of solution is determined at 0, 30 and 60 minutes by the device.

The results are shown in Figure 3.

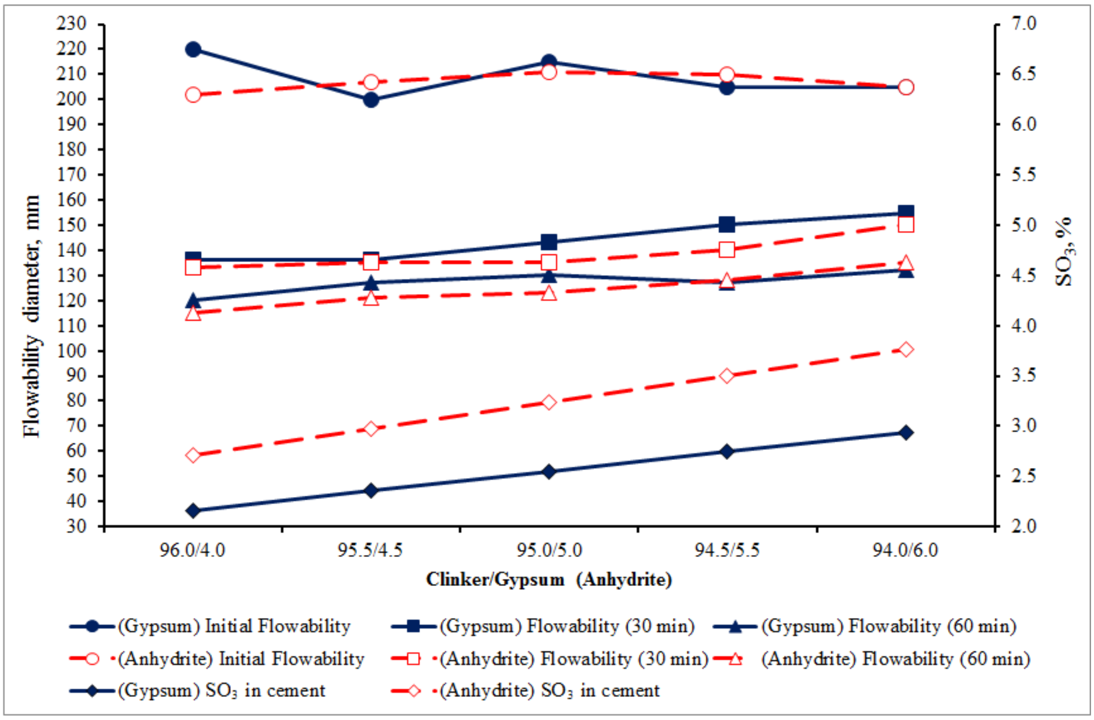

Figure 3. Flowability Results of Cement Samples

In the Figure 3, although the percentage of gypsum increases, the changes in initial flowability results are not observed. However, after 30 minutes, there is some rise which is that the diameter of 4% gypsum and 6% gypsum became 136 mm and 155 mm respectively. After 60 minutes, there are some alterations that increase in 5% gypsum (130 mm), decrease 5.5% gypsum (127 mm), and increase in 6% gypsum (132 mm).

As far as anhydrite is concerned, relation between flowability test results can be seen.

From the results, it can be stated that when the percentage of anhydrite increased from 4% to 5%, the initial flowability diameter also increased from 202 mm to 211 mm. In addition to this, while initial flowability diameter of 5.5% anhydrite remained constant (210 mm), in 6% anhydrite there was a slight decrease in flowability diameter (205 mm). As increasing anhydrite percent from 4% to 6%, both 30 minutes 60 minutes results were witnessed a rise from 133 mm to 150 mm and from 115 mm to 135 mm respectively.

It can be concluded that compare to anhydrite, gypsum has better results in 30 and 60 minutes.

3.4. Compressive strength tests of cement samples

The compressive strength results of samples were prepared based on by EN 196-1 standard and determined by Compression and Bending Testing device (Machine type MEGA 100-300-20 DM1-S) which is produced from Form Test company in Germany.

In Figure 4 compressive strength tests are shown:

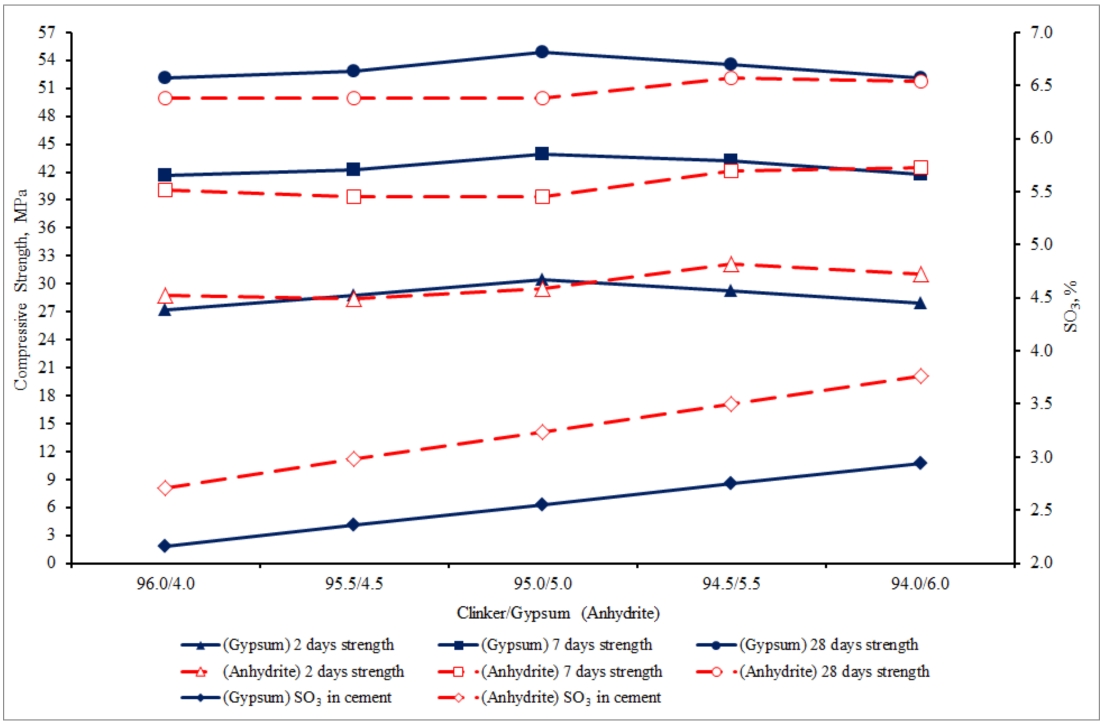

Figure 4. Compressive Strength results of Cement Samples

As seen from the Figure 4, by increasing amount of gypsum in samples (from 4% to 5%), the compressive strength of samples in 2, 7 and 28 days increased by nearly 2-3 MPa. However, for 6% gypsum cement samples, there was a decrease in 2, 7 and 28 days increased by roughly 2-3 MPa.

In the 6% gypsum sample, there are two reason why it is dropped. One of this is that when the percentage of gypsum increased, the percentage of the clinker decreased. The another reason is that according to Table 2, when the percentage of the gypsum increases, it prevents partially grinding process of the clinker and therefore, it changes reaction rate of clinker with water and affects compressive strength of samples.

However, for anhydrite, the results were different. Based on the Figure 4, there were not any noticeable changes in 2, 7 and 28 days of compressive strength when the percentage of the anhydrite increased from 4% to 5%. However, when it increased from 5% to 6%, the compressive strength go up by approximately 2 MPa.

Moreover, comparing to the compressive strength of second day, anhydrite samples results were than gypsum's (1-2 MPa). The main reason of this case is that anhydrite is harder than gypsum and this forms better environment for the grinding of clinker. The finer particle it has, the faster hydration reaction occurs. Hence, due to reason above, anhydrite samples had high compressive strength in 2 days.

Nevertheless, in 7 and 28 days results, gypsum had higher compressive strength and it can be concluded that anhydrite samples had more water demand than gypsum samples.

4. Conclusion

According to study carried out, it can be stated that comparing to anhydrite gypsum samples have

- lower water demand
- more setting times
- longer flowability diameters
- lower compressive strengths in 2 days
- and higher compressive strengths in 7 and 28 days

By considering these results, compare to anhydrite, it can be manufactured better concrete from gypsum samples with regard to workability and compressive strength.

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