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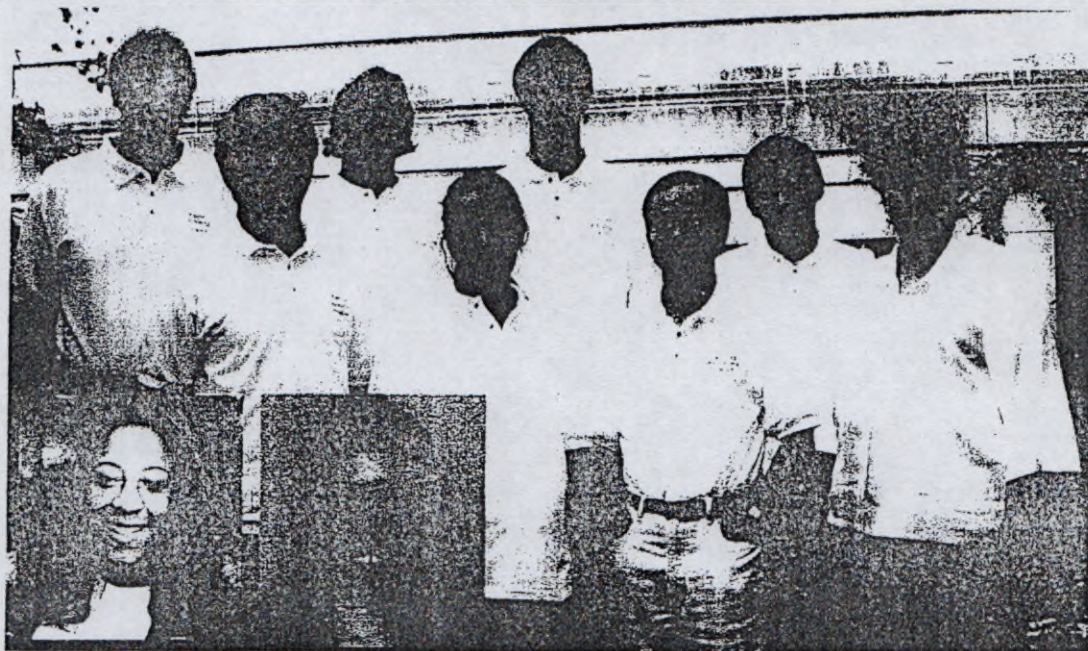
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The Effect of Expanding Additives to Improve Cement Isolation Strength to 250°C and 2000 psi Conditions

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Keywords: Expanding Additive, Shear Bond Strength, Compressive Strength, High Pressure-High Temperature, Curing Time

ABSTRACT

Cementing is a very important part in oil-well drilling, the recent technologies development in oil-well drilling has led to a more problematic case in cementing. High temperature cementing is one of those problem, high temperature cementing consists of steam recovery wells, geothermal wells and ultra deep wells.

The use of expanding cements for improving the sealing efficacy of Annulus cementing has been considered for a long time as a possible solution to existing problems. CaO and MgO had been proposed as two of the most effective additives to create good expanding cement.

The purposes of this study are to find the effect of burnt pure CaO and MgO addition on the value of compressive strength and shear bond strength of API class G in high pressure and high temperature condition. The method applied on this research was by evaluating the data taken from simulator which was simulate with 100-250°C temperature and 2000 psi pressure.

The conclusions taken according to the results are: The addition of CaO and MgO will increase the shear bond strength and the compressive strength on specific condition up to 200°C temperature. The addition will be ineffective for the 250°C condition. The cement strength behavior will be also affected by the length of curing time.

This expanding cement needs some further research for other composition, temperature and curing time condition. The compatibility when mixed with other additives beside silica flour hasn't been figured out yet.

1. INTRODUCTION

Environmentally compatible, safe, and economical production from gas, oil, and geothermal wells is an essential manner on flawless cementation of the installed casing strings, whose function is the prevention of fluid and gas flow through the annuli, among other items. The requirements on annulus cementing can be satisfied only if the cement ensures an impermeable bond between the casing string and the surrounding rock and exhibits sufficient compressive and shear bond strength until the ultimate plugging of the well.

Migration from the pay zone to higher zones of lower pressure can result in production losses without noticeable pressure build-up at the wellhead. In practice, definite effects of leakage can occur in comparatively short liner cementation in gas wells. In combination with insufficient sealing of the liner hanger, the gas often can easily penetrate into the production casing string.

The fact that volumetric shrinkage of the cement during hydration likewise contributes substantially to the existing problems has become generally known and recognized first in recent decades. Consequences include an increase in the porosity and permeability of the hardened cement slurry or the formation of microannuli by contraction of the external dimensions of the cement or both. The resulting flow channels may offer decided mobilization possibilities within the annulus, especially for gas.

The oil and gas industry has recognized the benefits of expanding cement that could generate a better bond between casing-cement and cement formation. Expanding cements, which exhibit a real expansion in external dimensions as of the instant where a stable spatial matrix is formed, offer a possible solution to the problems encountered. With appropriate expansion coefficient, the formation of microannuli is prevented, and existing cavities are filled. The build up of contract stresses at the interfaces with the rock and with the casing results in the possibility of compressing filter cake and drilling residues, and thus in a decided improvement of shear bond strength.

However, these advantages can be achieved and utilized only if effective and permanent expansion can be ensured even under the exposed conditions in deep wells (pressure, temperature, and electrolytes) with simultaneous realization of all other required operational properties of cement slurry and hardened cement paste (rheology, thickening time, permeability, and strength values).

2. STATE OF THE ART

Standard cement slurry consists of powdered cement, additives, and water, will harden, become a rigid solid with high compressive strength after hydrated process. Hydrating is not hydrates linked by clinker or dried process or reducing excess water from cement slurry, but it is reactions between water and cement components. Hydration forms setting, hardened and make up compressive strength in cement slurry, in surface or sub-surface condition.

2.1. Volumetric Shrinkage of Hardening Cement

In the case of cement hydration, the chemical and physical processes are of special importance for the occurrence of leaks. Immediately after the contact between the cement and make-up water, the hydration of the cement clinker phases begins. The reactions which thereby occur are both chemical and physical in nature and result in hardening of the cement by forming a spatially stable matrix. The hydration kinetics is strongly dependent on the environmental conditions. High temperature and pressure result in acceleration and intensification of the reactions.

The make-up water is of vital importance for the volume balances the starting materials and final products of cement hydration. In a simplified manner, two essentials processes can thereby be distinguished⁴:

An exothermic chemical reaction proceeds between the water and clinker phases to yield hydrate phases with gel structure. As a result of this conversion from free water, the volume component and degree of dispersion of the solid phase increase, whereas the volume component of the liquid phase decreases. Especially the CSH gel, which forms during the conversion of silicate phases, is the fundamental solidifying agent of the hardened cement.

Gel water is physically attached in the form of four to five water dipole layers to the negatively charged surfaces of the newly formed gel structures or hydrate phases.

In a closed system, both processes result in a reduction of the total volume (absolute formulation volume) of the cement, which is defined as the sum of the volumes for all participating components (water, cement clinker, minerals, and hydration products). In contrast to free water, which occurs in statistically disordered form, the ordered structures of both the chemically occluded water and the physically attached gel water occupy only 75 percent of the original volume. In the first case, therefore, a chemical or molecular shrinkage is involved, and a physical shrinkage occurs in the second case. As a matter of principle, two limiting cases are distinguished as possible consequences for bodies of cement, as shown in Figure 1:

- An increase in cement porosity;
- A decrease in the exterior dimensions of the cement body, the so-called matrix or bulk volume, comprising the volumes of the cement components and of the water-or gas filled pores.

2.2. High Temperature Cementing

At high temperature condition, the physical and chemical behavior of well cements changes significantly. Basically high temperature cementing encompasses three types of wells: ultra deep wells, geothermal wells, and thermal recovery wells.

Cement is essentially a calcium silicate material, the most abundant components being tricalcium silicate (C_3S) and dicalcium silicate (C_2S). Upon the addition of water, both hydrates will form a gel called C-S-H gel, which is responsible for the strength and dimensional stability of the set cement at ordinary temperatures. At well temperatures that exceed 230°F, C-S-H Gel is subject to metamorphosis, which usually results in decreased compressive strength. This phenomenon is what we know as "Strength Retrogression", which is the main obstacle faced in high temperature cementing. This problem can be prevented by reducing the bulk lime-to-silica ratio (C/S ratio) in the cement. To accomplish this, the cement is partially replaced by silica. Previous research has been done by Nelson and Eilers (1985) that concluded the optimum value of silica added is 35-40% BWOC.

2.3. The mechanisms of expansion for Expanding Cements

Expanding of cements means that expanding of cement relative volume due to cement bulk expansion (Danjuschewskij, 1983). It is caused by ²:

- Chemical contraction that formed another hydrated product on liquid phase condition, i.e. crystallizing of dissolved salt at high temperature.
- The presence of expanding materials in cement slurry before hardened condition, i.e. CaO, MgO, CaSO₄, etc.

- The presence of electrolyte around the cement bulk after the hardened condition.

The (b) part is merit condition that might bring to increase the shear bond strength, and also the expansion effect could be controlled by arranging the burning temperature and surface area of the expanding materials.

During the interim, a number of expanding additives have become available from the service industry; most of these are patented and therefore unknown composition and efficacy.

Under borehole conditions, many of the known additives, such as powdered aluminium or ettringite-forming products, present problems with respect to affectivity or controllability, or both, because of the expansion mechanism involved. Even under atmospheric conditions, several cements do not exhibit any expansion at all, but merely a decrease in volumetric shrinkage.

Danjuschewskij in 1983 proposed CaO and MgO as expanding additives to create expanding cement. He found the expansion effect more than 1% and up to 25% in specific condition. Several other investigations also had been conducted on the effectivity of expanding cements based on these calcium and magnesium oxide additives. Both materials are characterized by the capability of influencing the reactivity and thus the swelling behavior by way of the manufacturing process.

Industrially, CaO and MgO are usually manufactured by calcining of calcium and magnesium carbonates (liberation of CO₂, deacidification). In contrast to other expanding additives, CaO and MgO provide two possibilities of influencing the reactivity (hydration activity) by means of the manufacturing process ²:

Decreasing the reactivity by increasing the calcining temperature during manufacture of the swelling additive, as well as

Increasing the reactivity by augmenting the specific surface area of fineness during grinding of the swelling additive.

The other preliminary research was done by Rudi Rubiandini which investigates the characteristics of CaO and MgO cement expansion and the strength profile. Rubiandini found that the shear bond strength increased around 250% to 1000% by mixing CaO and MgO that were burnt up to 1600°C with certain fineness. These results were found when running with temperature condition up to 150°C.

3. SIMULATOR DESIGN AND LABORATORY TESTING

3.1. Simulator Design

To fulfill the specification, it was designed a physical simulator model as a modification of pressure curing chamber that could be operated under 350°C operating temperature and 3000 psi operating pressure.

The advantages of the simulator, besides could handle large amount of sample (30 samples), it was designed that could be operated using formation water both from oil-gas field or geothermal field. It was also equipped with CO₂ and H₂S injection appliance. Figure 7 shows the modified pressure curing chamber and the schematic drawing pressure is shown in figure 8.

The main parts of simulator are listed below:

- Simulator tubes were equipped with heater and thermocouple.
- Maximator pump, pressure source that could supply hydraulic pressure up to 6500 psi.
- Safety valves and rupture disc.
- Formation fluid injector.
- Automatic thermo controller.
- Gas injection flow meter.
- Outlet exchanger and reservoir chamber.
- Manometer and in/out simulator liquid gas regulator valves.

The test required 3 types of specimen molds as cement slurry chamber that should be treated during hardening. The specimen molds describe as referred to below:

Cubic type, with dimensions 2" x 2" x 2", to determine the tensile and compressive strength of the cement, see figure 6.

Cylindrical type, with 1" diameter and 2" height (figure 6) to determine the shear bond strength between cement-casing and also to measure cement casing-permeability. The specimen mold needs chamber caps when it is placed into simulator.

Cylindrical type, with 1" diameter and 2.5" height. This specimen mold contains 6 cement chambers. The cement specimens are used to determine both cement permeability and the compressive strength. (figure 6)

All those specimen molds are designed that could be run simultaneously in the simulator at given well condition.

Besides of the main apparatus, the other test equipments that are needed to perform the tests are:

Fann VG Viscometer for determining the rheological properties of cement slurry.

Hydraulic press for determining both the compressive strength and shear bond strength of cement.

The equipment that could not be enumerated, which were used in this research.

3.2. Sample Tested

Sample testing schedule schematic is shown at figure 3. Samples were tested using Portland cement class G HSR type, by adding silica flour (SiO₂) 0% and 35% BWOC (By weight of cement) respectively. Expanding additive were added around 0% to 10% and using aquadest as media in curing chamber. Treating temperature are ranging between 100-250°C under remaining 2000 psi treating pressure. The duration of treating time was starting from 24 hours (1 day).

Expanding Additives

The additives used in this experiment were CaO and MgO with 1400°C burnt temperature. From research conducted by Rudi Rubiandini, Published on Jurnal Teknologi Mineral - IATMI (Society of Indonesian Petroleum Engineers), in 1995 this additives show the largest expanding effect on the

cement compared to CaO and MgO with lower burnt temperature. Moreover, these additives had been investigated less effective than additives with 1200°C burnt temperature for curing temperature 100°C and better if the curing temperature reach 150°C. The fineness of grains was ranging between 2800-3000 cm²/gram.

Compressive Strength Testing

Cement cores after treating in certain time were taken out from specimen mold and putted on hydraulic press apparatus. Then cement cores were applied uniaxial loads until rupture. The compressive strength value is a load when the cement core rupture at the first time or the maximum point that manometer pointed. It was done at rate 20-80 seconds.

Compressive strength value is calculated with the following formula:

$$CS=k.P.(A1/A2) \dots\dots\dots(1)$$

where,

CS : compressive strength, psi

P : maximum load, psi

A1 : hydraulic mortar's bearing block cross section area, in²

A2 : cement core's cross section area, in²

k : correction constant, function of height (t) and diameter (d) ratio.

Shear Bond Strength Measurement

Shear bond strength was tested to determine bonding strength between casing to cement and cement to formation (wellbore).

Casing to cement shear bond strength was tested with if along casing wall was clean. The appliance is the same with when measured the compressive strength, but it was equipped with displacement thorax and chamber hold support. The shear bond strength is defined as the maximum load at the first movement.

Shear bond strength is calculated using the following formula:

$$SBS=P.(A1/\pi.D.h) \dots\dots\dots(2)$$

where,

SBS : shear bond strength, psi

P : strain maximum load, psi

H : cement core's cross section area, in²

D : cement core's height, in

4. RESULTS

Test Results. The results of investigation are briefly shown by figure 9, 10, 11, 12, 13, 14, 15, 16, and 17. Figure 12 shows a phenomenon known as cement strength retrogression. Figure 14, 15, 16, 17, shows the trends of compressive strength and shear bond strength of cements according to the number of added additives for certain burning temperature with different conditioning time and temperature, and correlation between amount of expanding

additives and compressive strength and shear bond strength of cements at certain conditioning temperature for different curing time.

Matrix Expansion. The matrix expansion of this cement is already investigated by Rubiandini and Ghofrani. The result is shown in figure 9.

Density. The value of density as shown in figure 10 is relatively high. From the test result it is shown that the number is ranging between 15.3 up to 16.55. It is recommended for the next research to combine this additive with *extender* to investigate the compatibility.

Viscosity. The value of viscosity as shown in figure 11 is still below the tolerance value given by API which is 200 cp.

Temperature Effects. The investigation used two kinds of temperature, namely burning temperature and conditioning temperature (curing temperature). Burning temperature is the temperature which the pure-MgO and pure-CaO were burnt. On the other hand, conditioning temperature is the temperature that was set for approaching the condition similar to wellbore in the field.

From figure 14, it is shown that the increase on temperature will cause the compressive and shear bond strength of CaO and MgO cement without silica tend to decrease. The strength retrogression effect is still occurred in this cement system. The addition of CaO itself is giving the improvement of strength compared to basic cement without any additives at all. This strength retrogression is disappeared when silica added to the cement system as shown in the figure 16. The same thing phenomenon is also happening in the MgO cement system as shown in the figure 15 and 17. The effectiveness of these 1400°C burnt CaO and MgO addition is only up to temperature about 200°C. We can see in the results that for conditioning temperature 250°C, basic cement with silica is giving the better result than cement with CaO and MgO addition. By merging with Rubiandini results which declared that for conditioning temperature up to 150°C the most effective burnt temperature for additives are CaO and MgO is 1200°C, we may take the conclusion that the additives on this paper is recommended for temperature between 150°C and 200°C. The work should be continued to investigate the most effective burnt temperature for conditioning temperature higher than 250°C. The conclusion of best additive for certain temperature is shown in table 2.

Curing Time Effects. Since the hydration of cement is always occurring along with time, the strength of cement will always change as well. From figure 14, 15, 16, and 17, we can see that the addition of time from 24 hour to 72 hour will cause the cement strength tend to decrease for conditioning temperature higher than 200°C, but increase for temperature below than 200°C. This is because the conditioning temperature will affect the velocity of cement hydration. For temperature below 200°C, the hydration process is not as fast as temperature higher than 250°C. The addition of curing time from 24 hours to 72 hours for conditioning temperature below 200°C will improve the cement strength because the hydration process is still occurring. Cement with conditioning temperature higher than 200°C, the hydration process is taking shorter time less than 72 hours and addition of curing time will caused the cement strength start to decrease.

5. CONCLUSIONS

The usage of silica is not effective for temperature below than 150°C.

Basic cement without expanding additives will be more effective for conditioning temperature below than 100°C. For temperature higher than that, the addition of these additives will give better results.

The addition of additives mentioned on this paper is effective for conditioning temperature up to 200°C.

Combination of silica with the expanding cement system will give the best result for temperature between 150°C and 200°C.

The optimum concentration of expanding additives is ranging from 3% to 5%.

The effectiveness of these additives is only ranging from 150°C to 200°C.

Curing time addition will cause cement strength to tend to decrease for temperature higher than 200°C, and conversely will cause the strength increase for lower temperature.

RECOMMENDATIONS

The research may be continued for different fluid condition from oil and gas field or geothermal field.

The compatibility with *extender* should be investigated in order to create expanding cement with low density.

The research may be continued with curing time longer than 72 hours.

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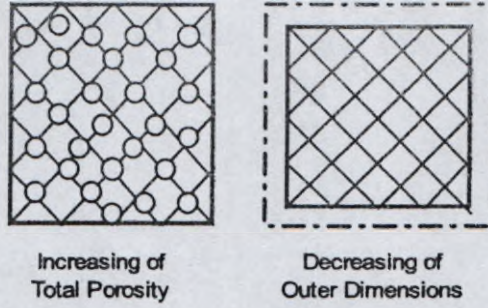


Figure 1 – Possible consequences of hydration volume reduction (boundary cases).⁴

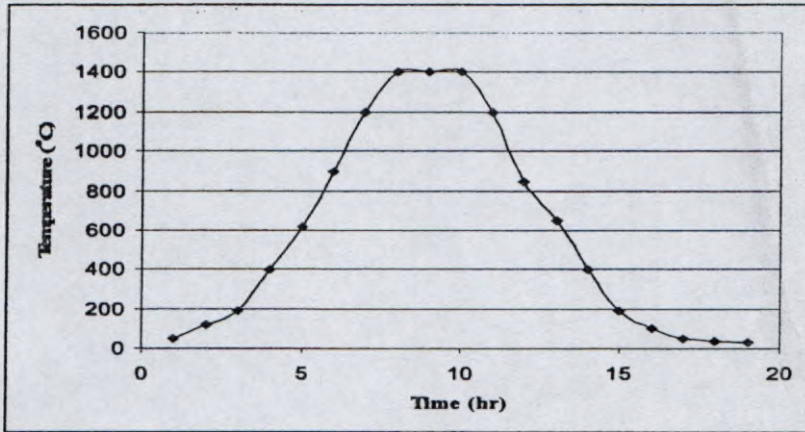


Figure 2 – CaO and MgO burning process.

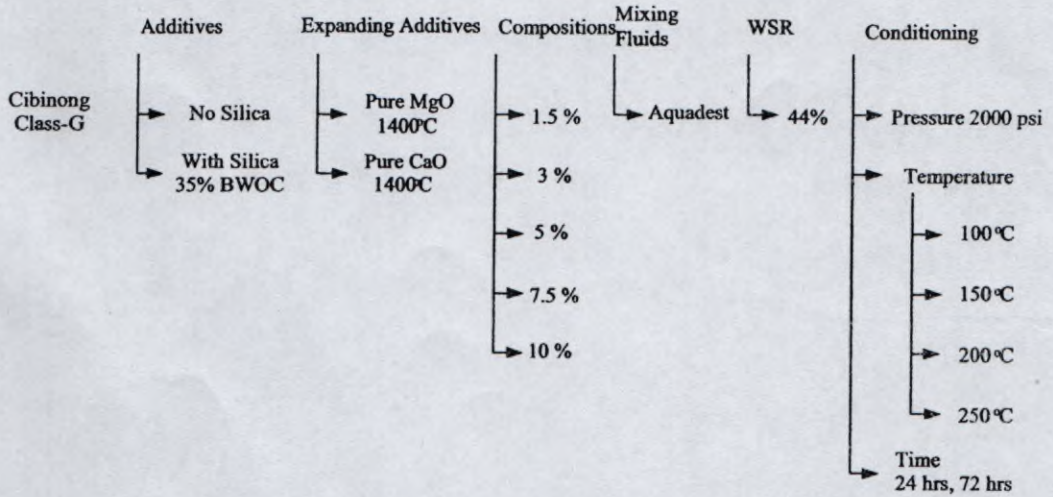


Figure 3 – Schematic diagram of research.



Figure 4 - The Specimens Molds (Cubic and Cylindrical Type).

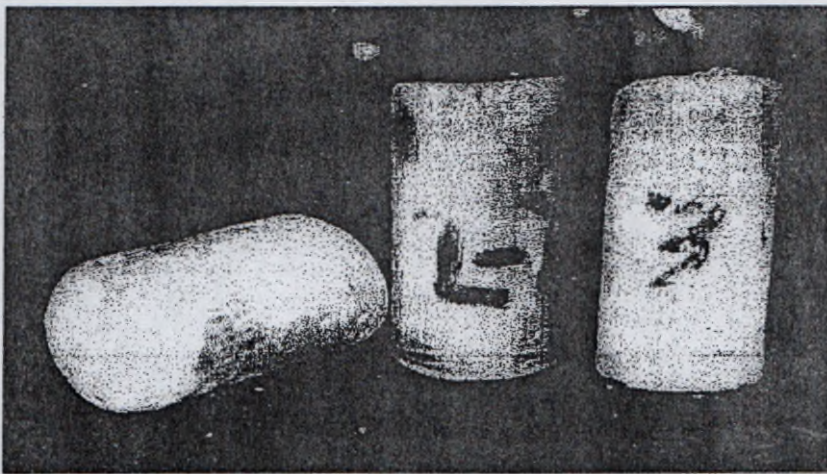


Figure 5 - Cement Specimens

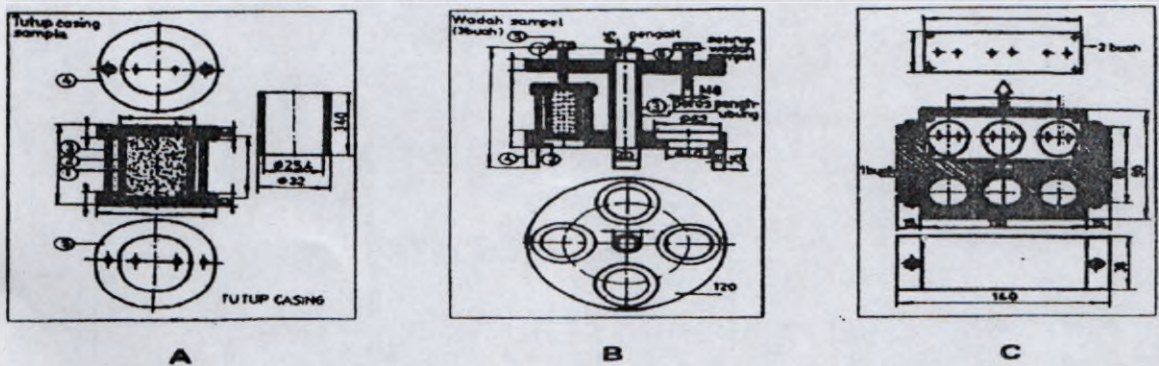


Figure 6 - Schematic Diagram of the Specimen Molds. (A) Cylindrical Type Molds for Shear Bond Strength, (B) Chamber Caps, (C) Cylindrical Molds for Compressive Strength.¹⁴



Figure 7 - Modified HPHT Curing Chamber

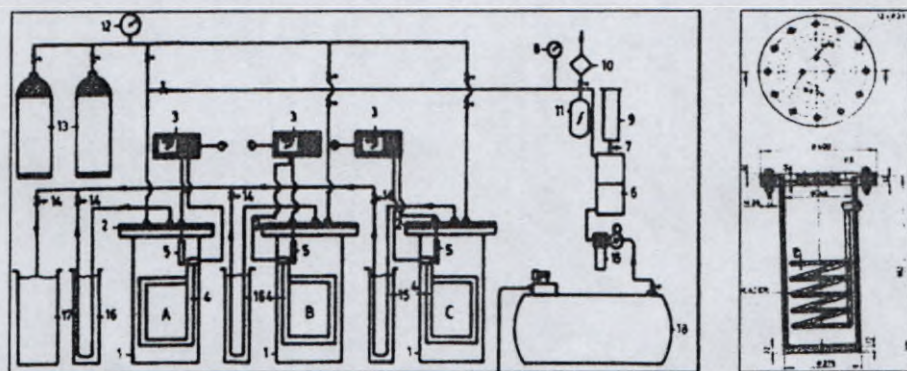


Figure 8 - Schematic Diagram of Modified Pressure Curing Chamber.

Table 1 – List of Tested Cements Composition.

No.	Composition	Base Cement (gr)	CaO (gr)	MgO (gr)	Silica (gr)	Cement (gr)
1.	Base Cement (BC)	250	-	-	-	568.18
2.	Silica Cement(SC)	250	-	-	198	369.32
3.	BC + CaO 1.5% BWOC	250	8.40	-	-	559.79
4.	BC + CaO 3% BWOC	250	16.55	-	-	551.63
5.	BC + CaO 5% BWOC	250	27.06	-	-	541.13
6.	BC + CaO 7.5% BWOC	250	39.64	-	-	528.54
7.	BC + CaO 10% BWOC	250	51.65	-	-	516.53
8.	SC + CaO 1.5% BWOC	250	8.40	-	195.92	363.86
9.	SC + CaO 3% BWOC	250	16.55	-	193.07	358.56
10.	SC + CaO 5% BWOC	250	27.06	-	189.39	351.73
11.	SC + CaO 7.5% BWOC	250	39.64	-	184.99	343.55
12.	SC + CaO 10% BWOC	250	51.65	-	180.79	335.74
13.	BC + MgO 1.5% BWOC	250	-	8.40	-	559.79
14.	BC + MgO 3% BWOC	250	-	16.55	-	551.63
15.	BC + MgO 5% BWOC	250	-	27.06	-	541.13
16.	BC + MgO 7.5% BWOC	250	-	39.64	-	528.54
17.	BC + MgO 10% BWOC	250	-	51.65	-	516.53
18.	SC + MgO 1.5% BWOC	250	-	8.40	195.92	363.86
19.	SC + MgO 3% BWOC	250	-	16.55	193.07	358.86
20.	SC + MgO 5% BWOC	250	-	27.06	189.39	351.73
21.	SC + MgO 7.5% BWOC	250	-	39.64	184.99	343.55
22.	SC + MgO 10% BWOC	250	-	51.65	180.79	335.74

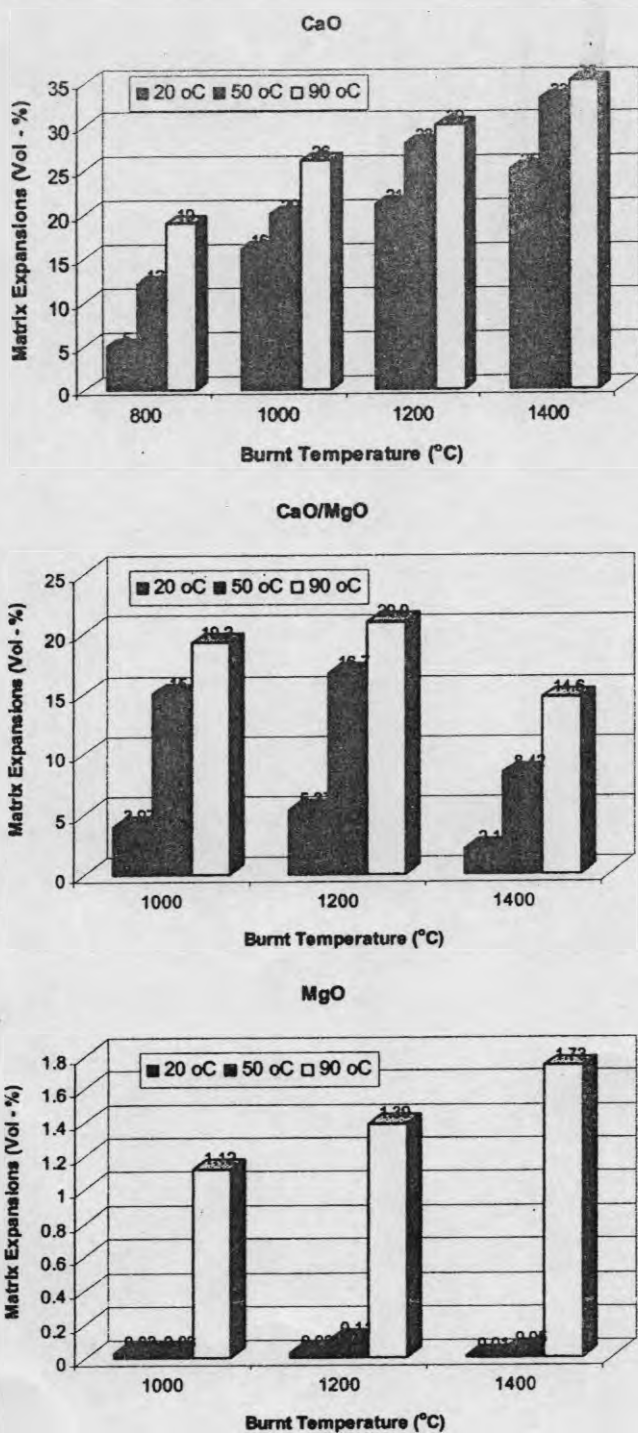


Figure 9 – Total matrix expansion, on 20, 50 and 90°C cell temperature; Expanding additives CaO, MgO, and CaO/MgO with 1400°C burnt Temperature.¹⁴

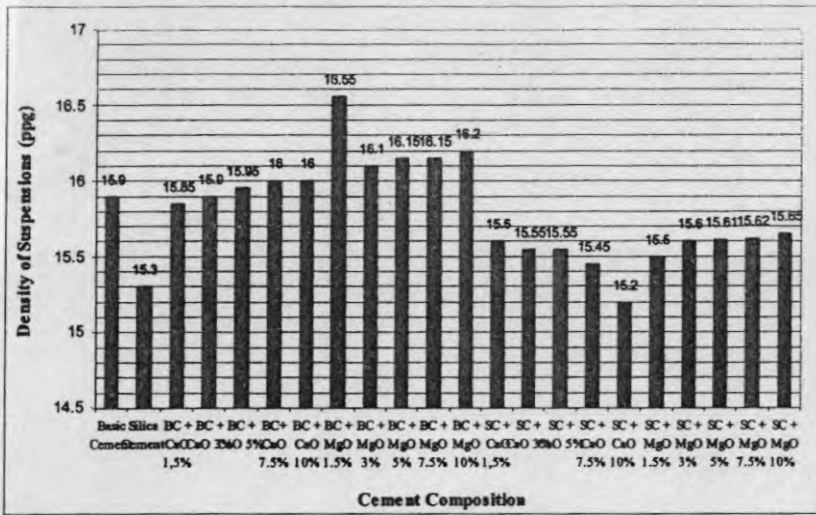


Figure 10 – Density of cement suspension.

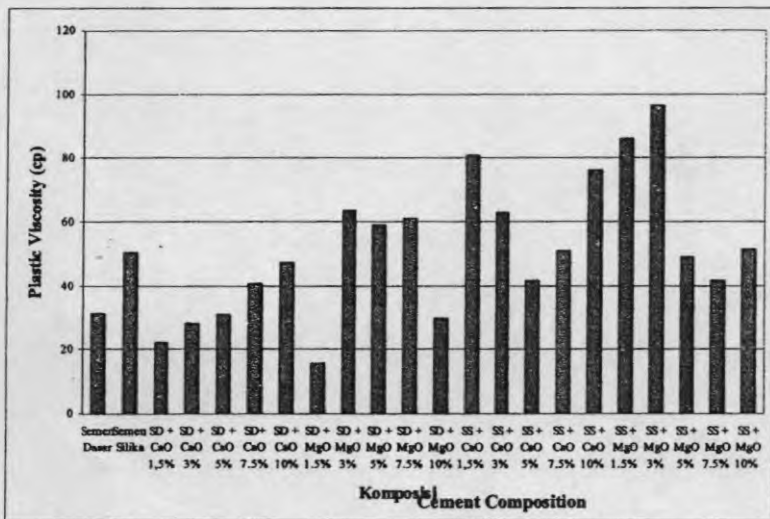


Figure 11 – Plastic viscosity of cement suspensions.

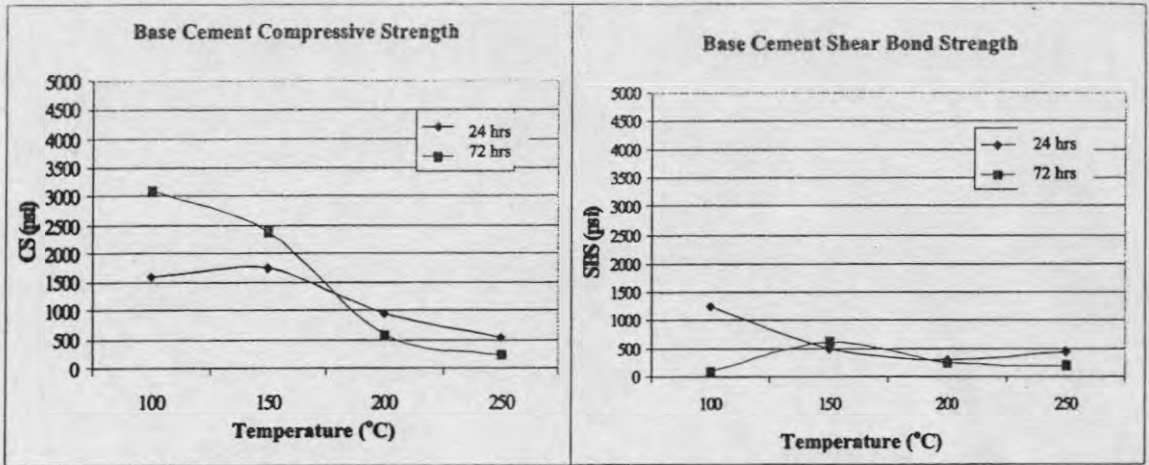


Figure 12 – The effect of temperature and curing time on strength of base cement.

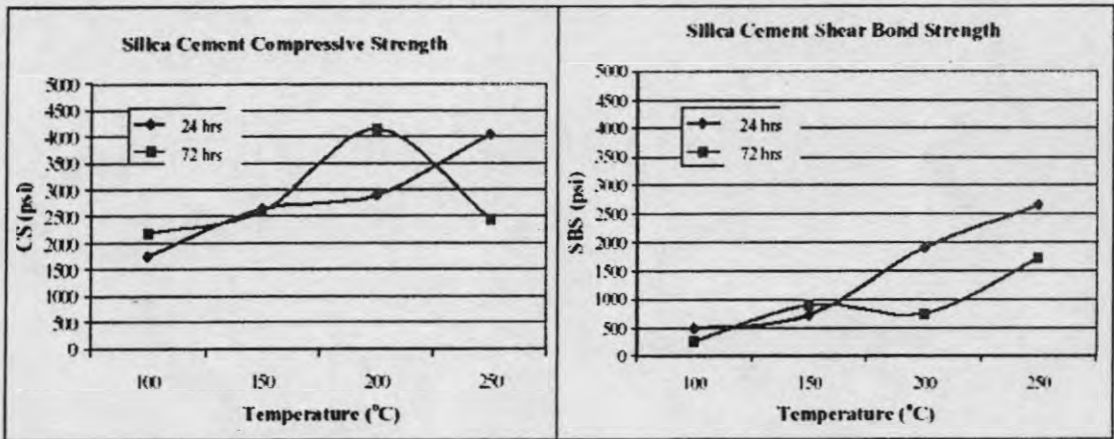


Figure 13 – The effect of temperature and curing time on strength of silica cement.

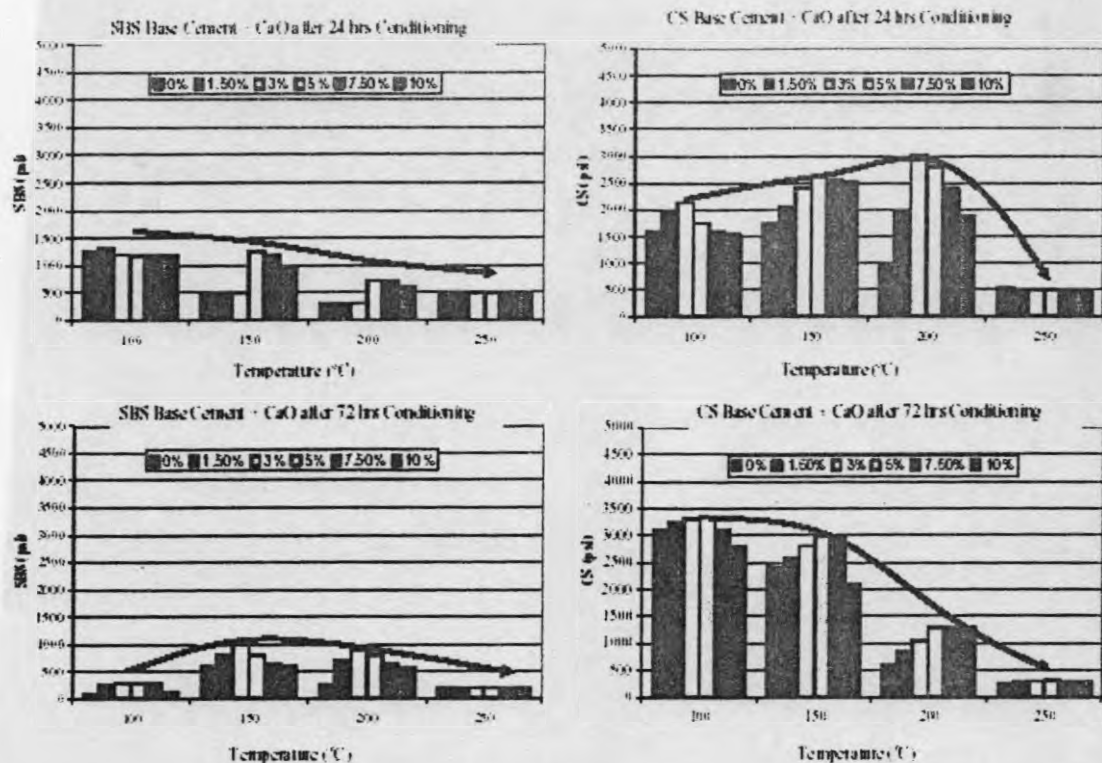


Figure 14 – The Effect of CaO addition on Base Cement.

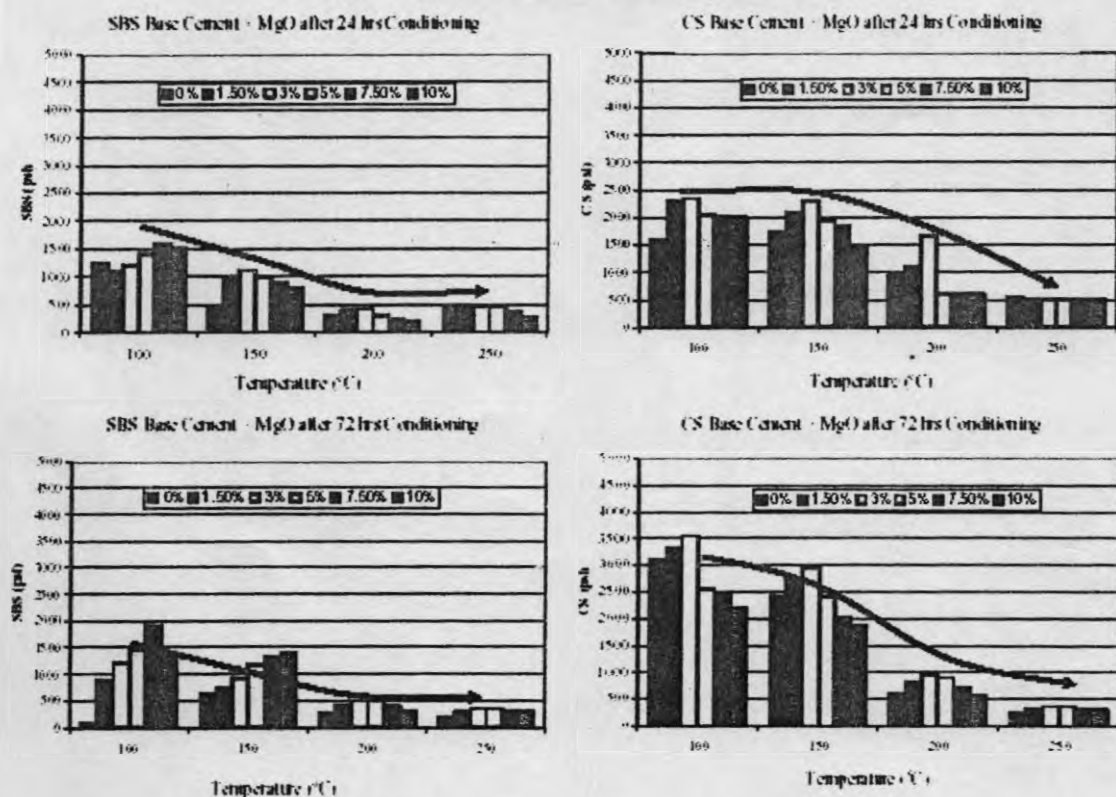


Figure 15 – The Effect of MgO addition on Base Cement.

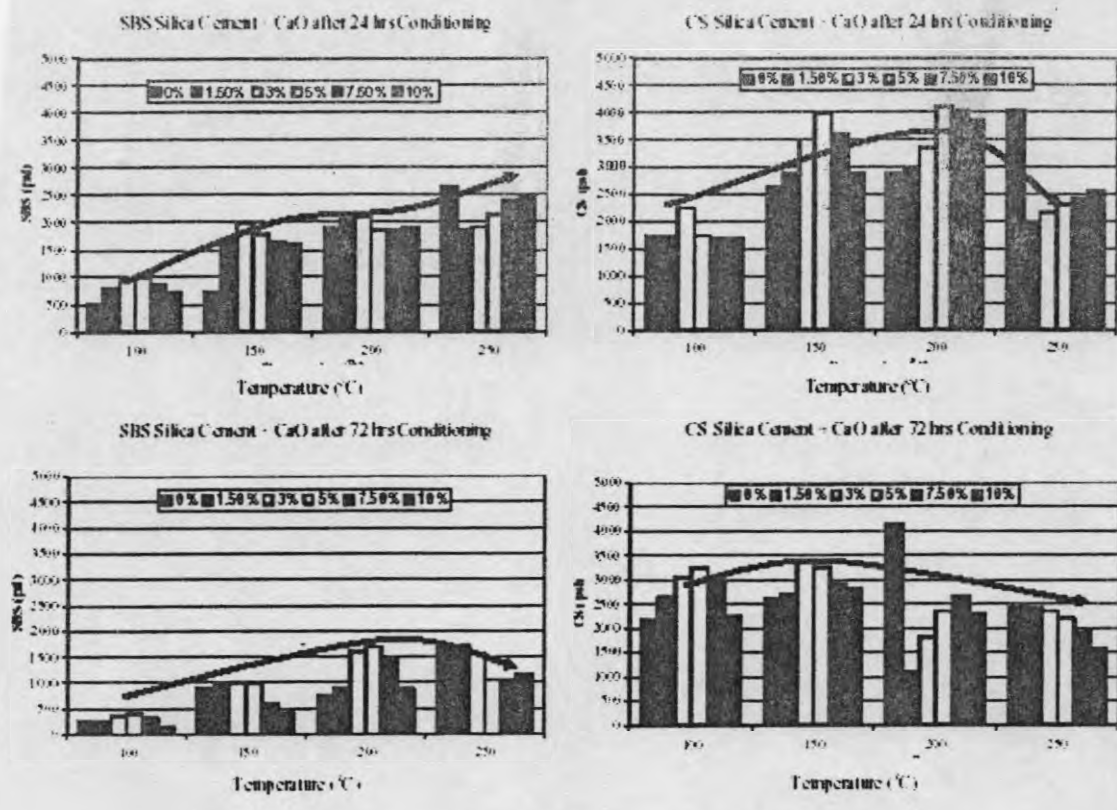


Figure 16 – The Effect of CaO addition on Silica Cement.

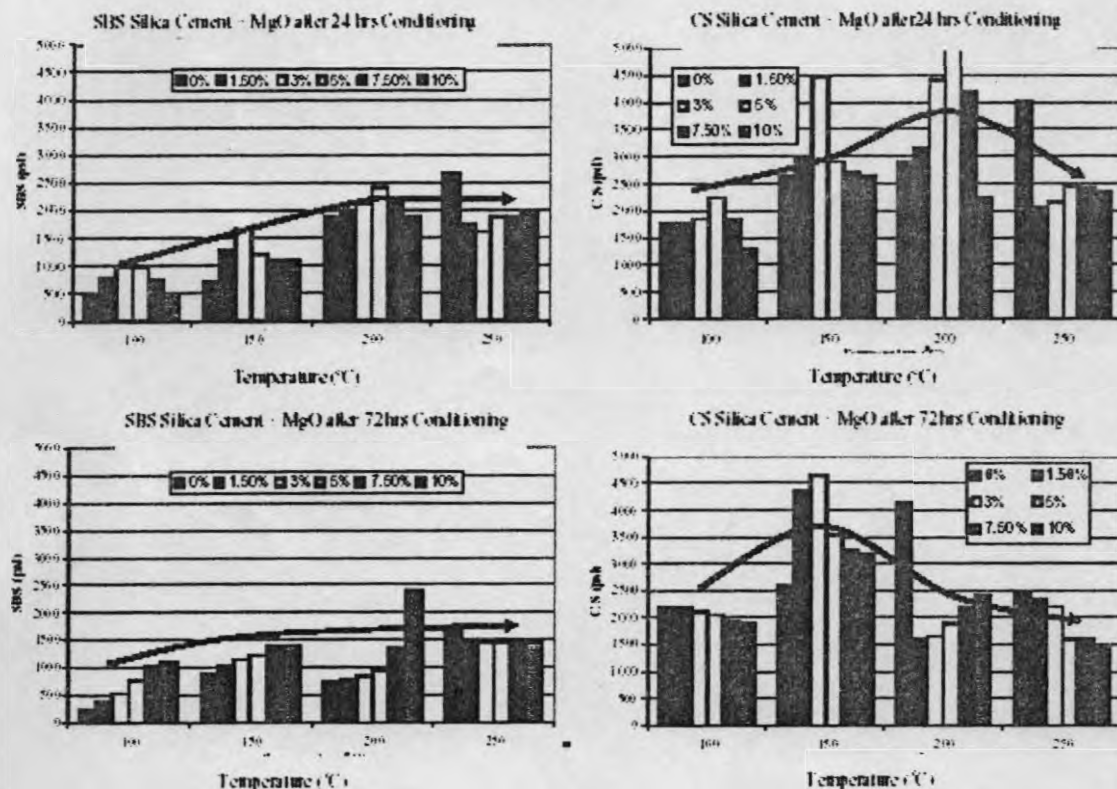


Figure 17 – The Effect of MgO addition on Silica Cement.

Table 2 – The best additive for certain temperatures (highlighted).

Cement System	1 day Conditioning				3 days Conditioning			
	100°C	150°C	200°C	250°C	100°C	150°C	200°C	250°C
Base Cement	***	-	-	-	-	-	-	-
Silica Cement	*	*	***	*****	*	*	**	*****
BS + CaO	****	***	**	**	**	**	***	*
SC + CaO	**	*****	****	****	***	***	****	****
BS + MgO	*****	**	*	*	*****	****	*	**
SC + MgO	***	****	*****	***	****	*****	*****	***