

The Effect of CaO and MgO as Expanding Additives to Improve Cement Isolation Strength under HPHT Exposure

by Nur Suhascaryo

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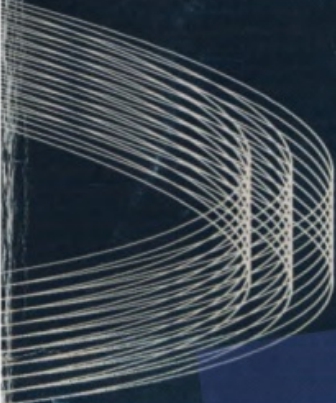
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The Effect of CaO and MgO as Expanding Additives to Improve Cement Isolation Strength under HPHT Exposure

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Abstract. Cementing is one of the most important parts in oil-well drilling. Recent development in oil-well drilling technology has led to a more problematic case in cementing. High temperature cementing is one of the problems. High temperature cementing may cover steam recovery wells, geothermal wells and ultra deep wells.

The use of expanding cements as an effort to improve the sealing efficacy of annulus cementing has been considered for a long time as a promising solution to the existing problems. CaO and MgO have been proposed as two of the most effective additives to create excellent expanding cement.

The purpose of this study is to find the effect of adding up burnt pure CaO and MgO to the value of compressive strength and shear bond strength of API class G cement in high pressure and high temperature condition. The method that we used within this research is an evaluation of the data taken from a simulator that simulated within temperature range of 100 – 250°C and pressure of 2000 psi.

The conclusion is taken according to the results which saying that the addition of burnt pure CaO and MgO would increase the shear bond strength and the compressive strength on specific condition up to 200°C temperature. The addition won't be effective for the condition of 250°C temperature. The behavior of cement strength was also influenced by the length of curing time.

Further more, research on expanding cement needs to be developed and extended whether to vary its compositions, temperatures, or curing time conditions. The compatibility when mixed with other additives together with silica flour has not yet been figured out.

Keywords: *Cementing; high temperature cementing; expanding cements; shear bond strength; compressive strength; curing time; simulator.*

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 to prevent fluids and gases to flow through the annuli, among other items. The requirements for 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.

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Migration of fluids or gases from the pay zone to the higher zones of lower pressures would give 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 the occurring of volumetric shrinkage of the cement during hydration giving contribution 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 cement powder, additives, and water. It will harden and becomes a rigid solid with a high compressive strength after hydration process. Hydration is not hydrates linked by clinker or dried process or reducing excess water from cement slurry, but a reaction 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 cracks. 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 reaction.

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

1. 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.
2. 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.

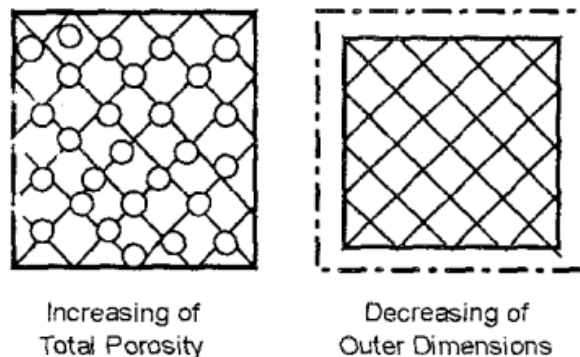


Figure 2.1 Possible consequences of hydration volume reduction (boundary cases).⁴

In a closed system, both processes result in a reduction of 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% 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 2.1:

1. An increase in cement porosity;
2. 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.

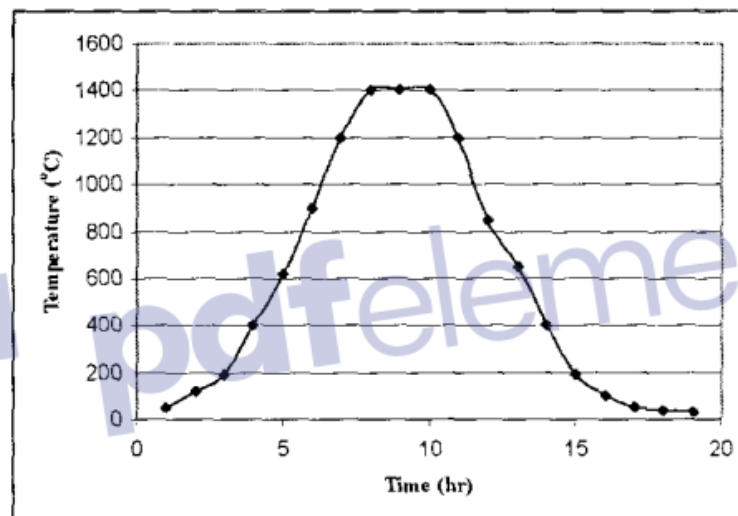


Figure 2.2 CaO and MgO burning process.

2.2 High Temperature Cementing

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

Cement essentially consists of calcium silicate materials. The most abundant components that built a sack of cement are 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 responsible for the strength and dimensional stability of the set cement at atmospheric temperatures. At well temperatures exceeding 230°F, C-S-H Gel is subjected to metamorphosis, which usually results in decreasing of compressive strength. This phenomenon is known as "Strength Retrogression", which is the main obstacle 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 conducted 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 expansion of cement relative volume (an external part of cement visually becomes bigger) due to cement bulk expansion (Danjuschewskij, 1983). This occurrence is caused by ⁹:

- a. Chemical contraction that formed another hydrated products on liquid phase condition, i.e. crystallizing of dissolved salt at high temperature.
- b. The presence of expanding materials in cement slurry before hardened condition, i.e. CaO, MgO, CaSO₄, etc.
- c. 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 aluminum or ettringite-forming products, are showing 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 that the expansion effect is more than 1% and up to 25% in a specific condition. Several other investigations had also been conducted on the effectiveness of the work of expanding cements based on these calcium and magnesium oxide additives. Both materials are characterized by their capabilities 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 process⁹:

- 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 investigated the characteristics of CaO and MgO cement expansion and the strength profile. It was found that the shear bond strength increased around 50% to 1000% by mixing CaO and MgO that were burnt up to 1500°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, the physical simulator model, pressure curing chamber, was designed to modifying and adjusting temperature and pressure which is expected to operate under temperature of 350°C and pressure of 3000 psi.



Figure 3.1 Modified HPHT Curing Chamber.

The advantage of the simulator is that it can be operated using formation water either from oil-gas fields or geothermal fields. In addition to that it also can handle a large amount of samples (e.g. 30 samples altogether at the same time). The simulator is also equipped with CO₂ and H₂S injection apparatus.

From Figure 3.1, we can see the picture of a modified pressure curing chamber and from Figure 3.2, we can see the schematic drawing of a modified pressure curing chamber.

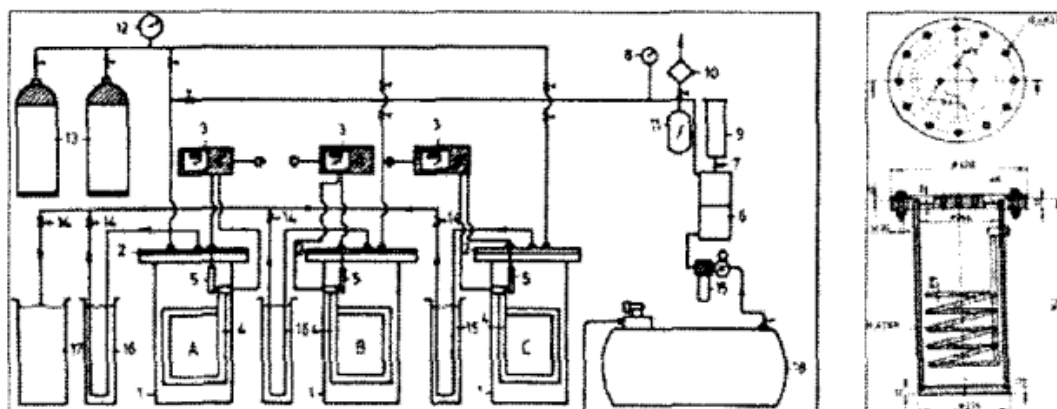


Figure 3.2 Schematic Diagram of Modified Pressure Curing Chamber.

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 are described in the following:

- Cubic type, with dimensions 2" x 2" x 2", to determine the tensile and compressive strength of the cement, see Figure 3.3.
- Cylindrical type, with 1" diameter and 2" height (Figure 3.3) to determine the shear bond strength between cement-casing and also to measure cement casing-permeability. The specimen mold needs chamber caps (Figure 3.4b) when it is placed into simulator.
- Cylindrical type, with 1" diameter and 2.5" height. This specimen mold (Figure 3.4a) contains 6 cement chambers. The cement specimens are used to determine both cement permeability and the compressive strength. (Figure 3.3).

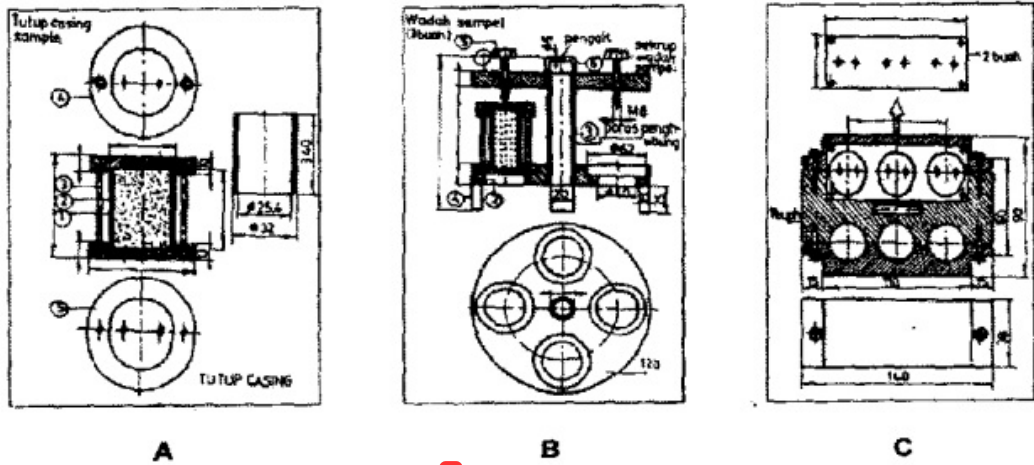


Figure 3.3 Schematic Diagrams of the Specimen Molds: (A) Cylindrical Type Molds for Shear Bond Strength, (B) Chamber Caps, (C) Cylindrical Molds for Compressive Strength.¹⁴



Figure 3.4 (a) the Specimens Molds (Cubic and Cylindrical Type). (b) The Chamber Caps.

All those specimen molds are designed to be able to operate 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 (Figure 3.5) for determining both the compressive strength and shear bond strength of cement.
- The equipments that could not be enumerated that were used in this research.



Figure 3.5 Hydraulic Press.

3.2 Sample Tested

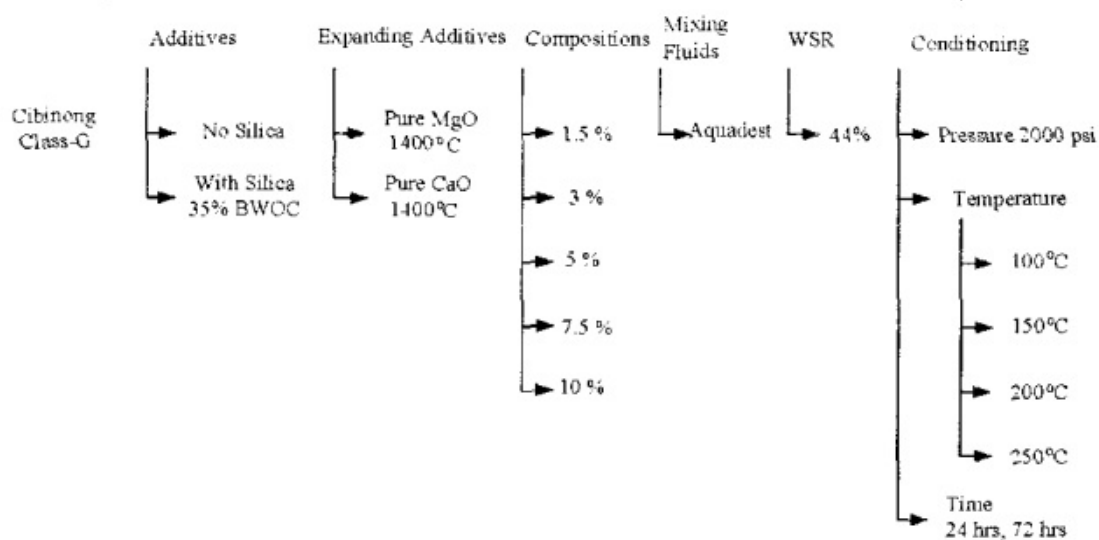


Figure 3.6 Schematic diagram of research.

The sample testing schedule schematic is shown at Figure 3.6. Samples were tested using Portland cement class G HSR type, by adding silica flour (SiO_2) 0% and 35% BWOC (By weight of cement) respectively. Expanding additive were added around 0% to 10% and using aquadest (fresh water) 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).

Table 3.1 List of Tested Cements Composition.

No.	Composition	Aquadest (mL)	CaO (gr)	MgO (gr)	Silica Flour (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	8.4	-	-	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	8.4	-	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	-	8.4	-	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	-	8.4	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

3.3 Expanding Additives

The additives used in this experiment were CaO and MgO with 1400°C burnt temperature. These additives showed¹³ greater expanding effect on the cement compared to the same additives (CaO and MgO) with lower burnt temperature. Moreover, these additives were investigated having effectiveness lower than those with 1200°C burnt temperature for curing temperature 100°C and greater

if the curing temperature set to reach 150°C. The fineness of grains was ranging between 2800-3000 cm²/gram.

3.4 Compressive Strength Testing

Cement cores after treating for certain time were taken out from the specimen and put on hydraulic press apparatus. Then cement cores were exposed to uniaxial loads until they became rupture. The compressive strength value is loaded when the cement core became rupture at the first time or at the maximum point that manometer pointed. It was given at rate 20-80 seconds.

Compressive strength value is calculated with the following formula:

$$CS = k.P.\left(\frac{A1}{A2}\right) \quad (1)$$

Whereas,

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.

3.5 Shear Bond Strength Measurement

Shear bond strength is tested to determine bonding strength between casing to cement and cement to formation (well bore).

Casing to cement shear bond strength is tested if the condition along the casing walls is clean. The same thing will be similar to the measurement of the compressive strength, but it is equipped with displacement thorax and chamber hold supporter. The shear bond strength is defined as the maximum load at the first movement.

Shear bond strength is calculated by using the following formula:

$$SBS = P.\left(\frac{A1}{\pi.D.h}\right) \quad (2)$$

Whereas,

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

4.1 Test Results

The results of investigation are briefly shown by Figure 4.1, 4.2, 4.3, 4.4, 4.5, 4.6, 4.7, 4.8, and 4.9. Figure 4.1 shows a phenomenon known as cement strength retrogression. Figure 4.6, 4.7, 4.8, 4.9 show the trends of compressive strength and shear bond strength of cements according to the number of added additives in 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.

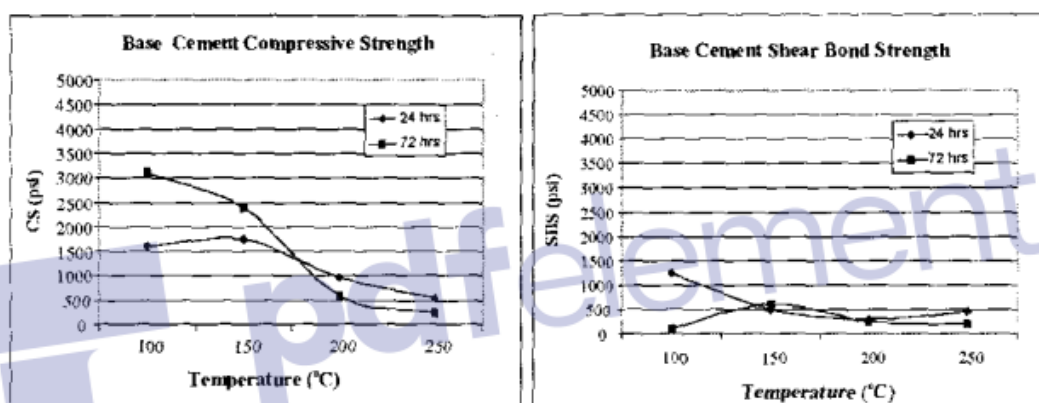


Figure 4.1 The effect of temperature and curing time on strength of base cement.

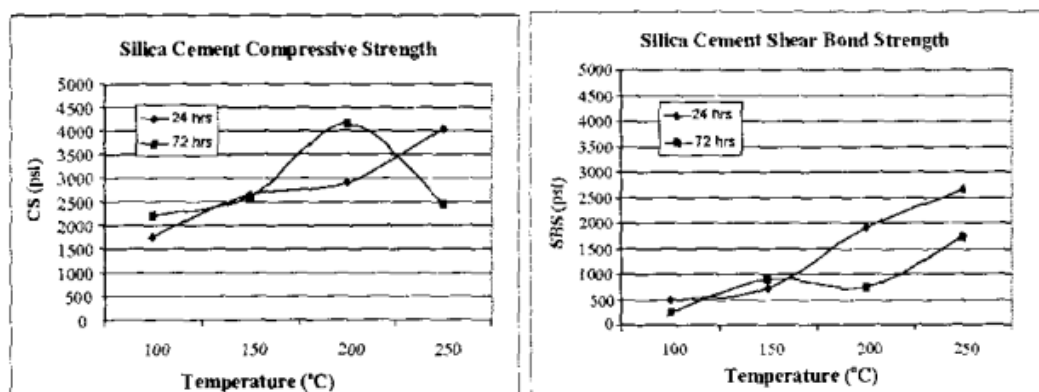


Figure 4.2 The effect of temperature and curing time on strength of silica cement.

4.2 Matrix Expansion

The matrix expansion of this cement is already investigated^{4,14}. The result is shown in Figure 4.3.

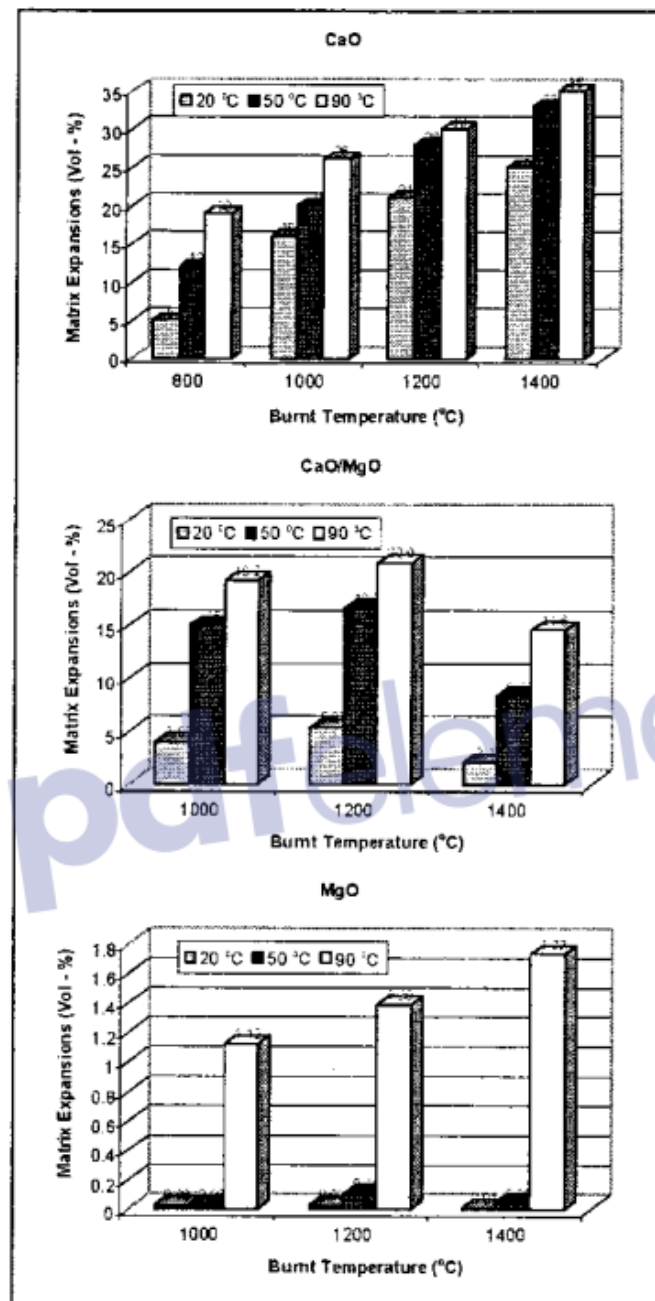


Figure 4.3 Total matrix expansion, on 20, 50, and 90°C cell temperature; Expanding additives CaO, MgO, and CaO/MgO with 1400°C burnt Temperature.¹⁴

4.3 Density

The value of density as shown in Figure 4.4 is relatively high. From the test result it is shown that the number is ranging between 15.3 up to 16.55 ppg. It is recommended for the next research to combine this additive with extender to investigate their compatibility.

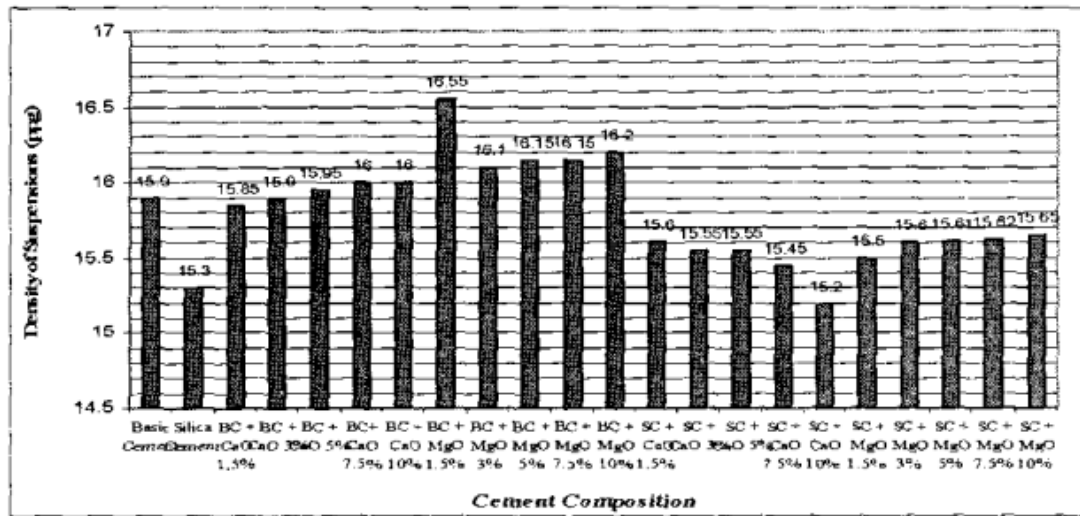


Figure 4.4 Density of cement suspension.

4.4 Viscosity

The value of viscosity, as shown in Figure 4.5, is still below the tolerance value given by API which is 200 cp.

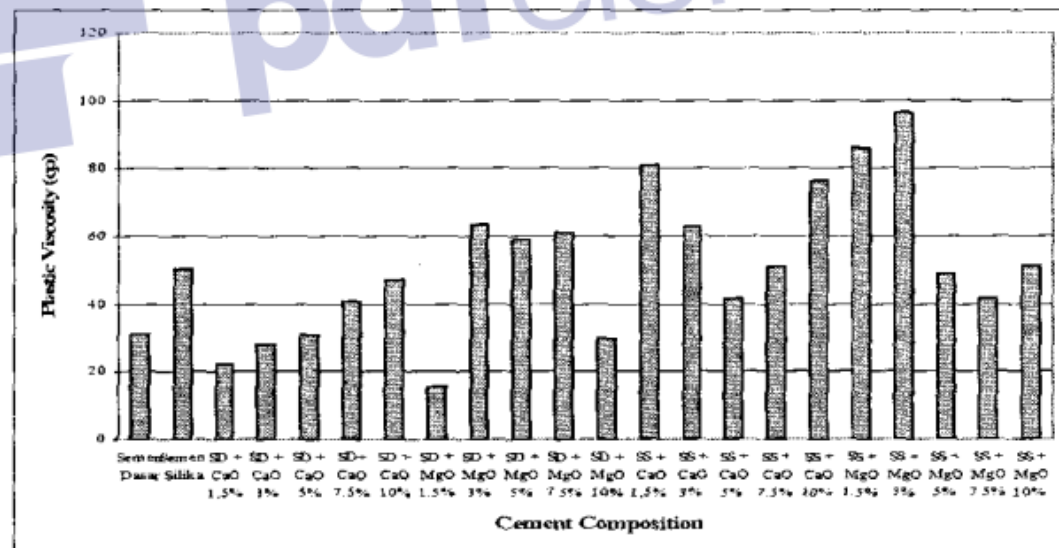


Figure 4.5 Plastic viscosity of cement suspensions.

4.5 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 well bore in the field.

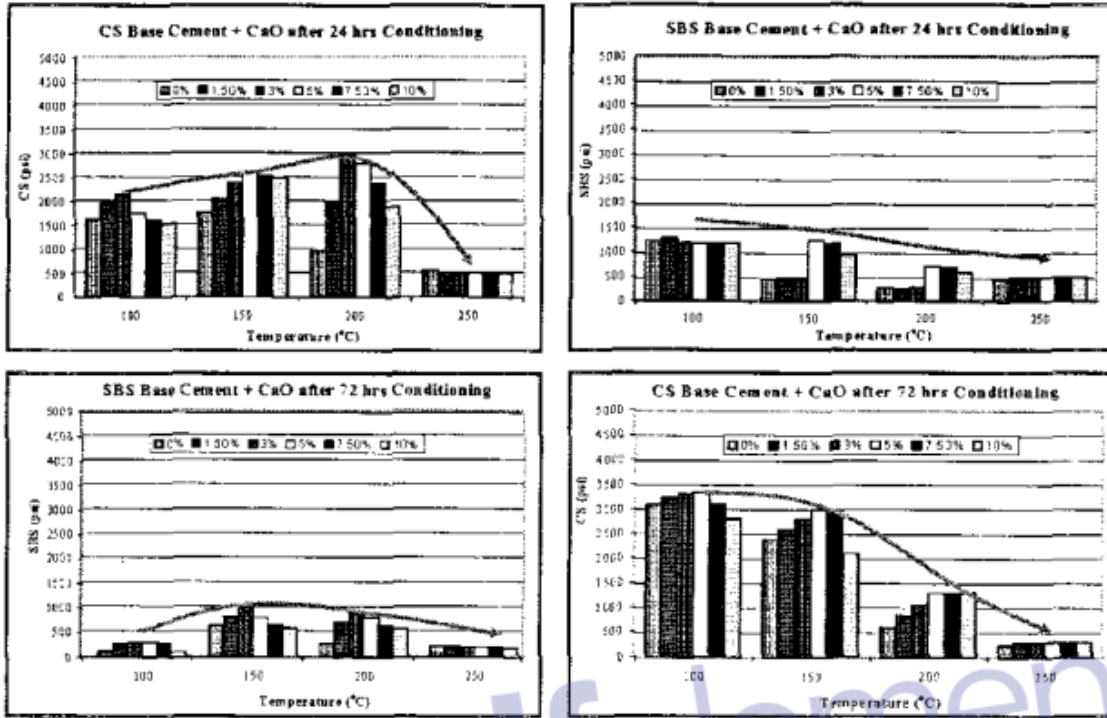


Figure 4.6 The Effect of CaO addition on Base Cement.

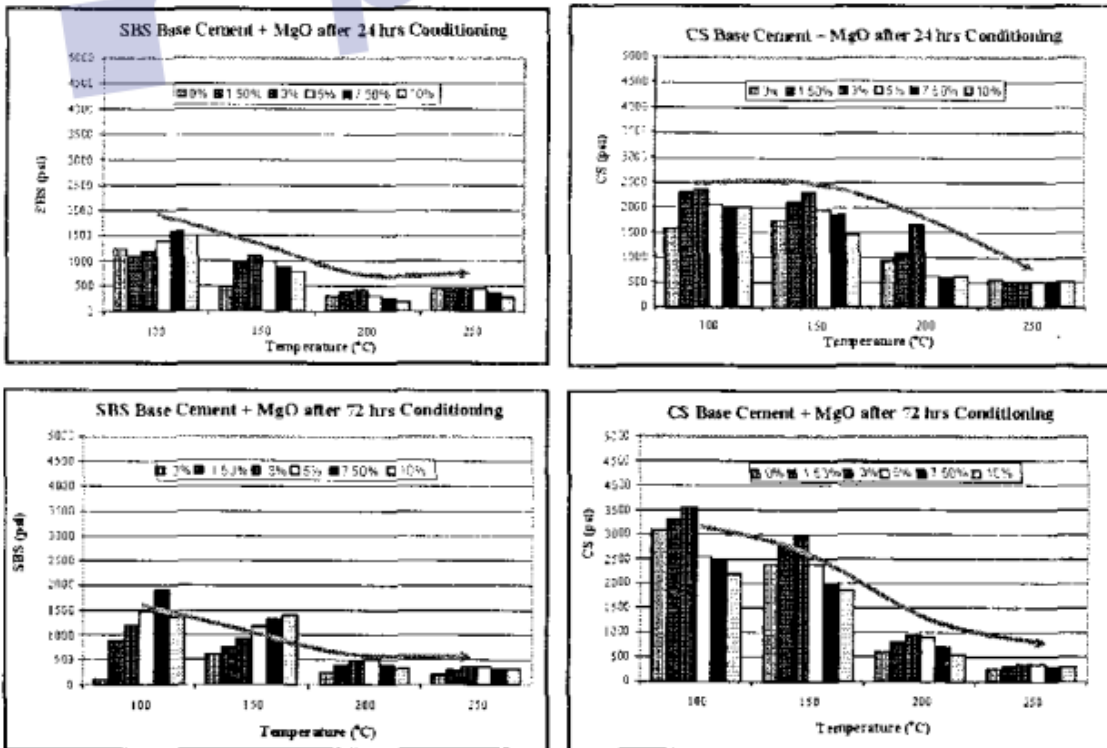


Figure 4.7 The Effect of MgO addition on Base Cement.

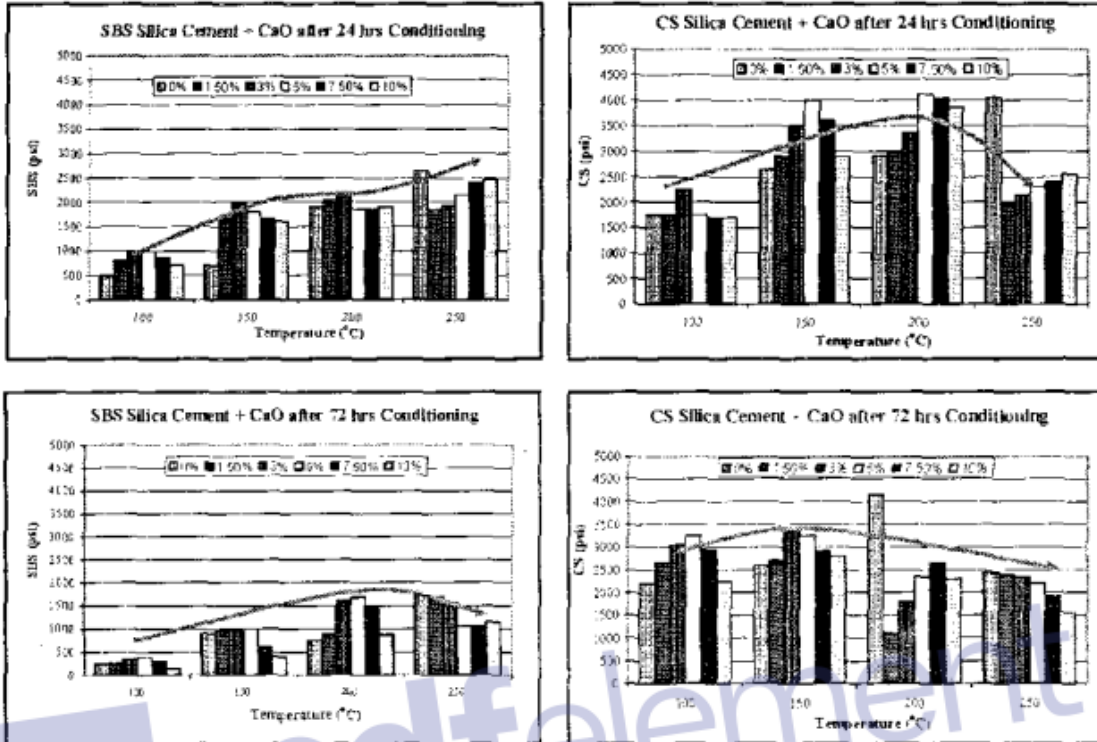


Figure 4.8 The Effect of CaO addition on Silica Cement.

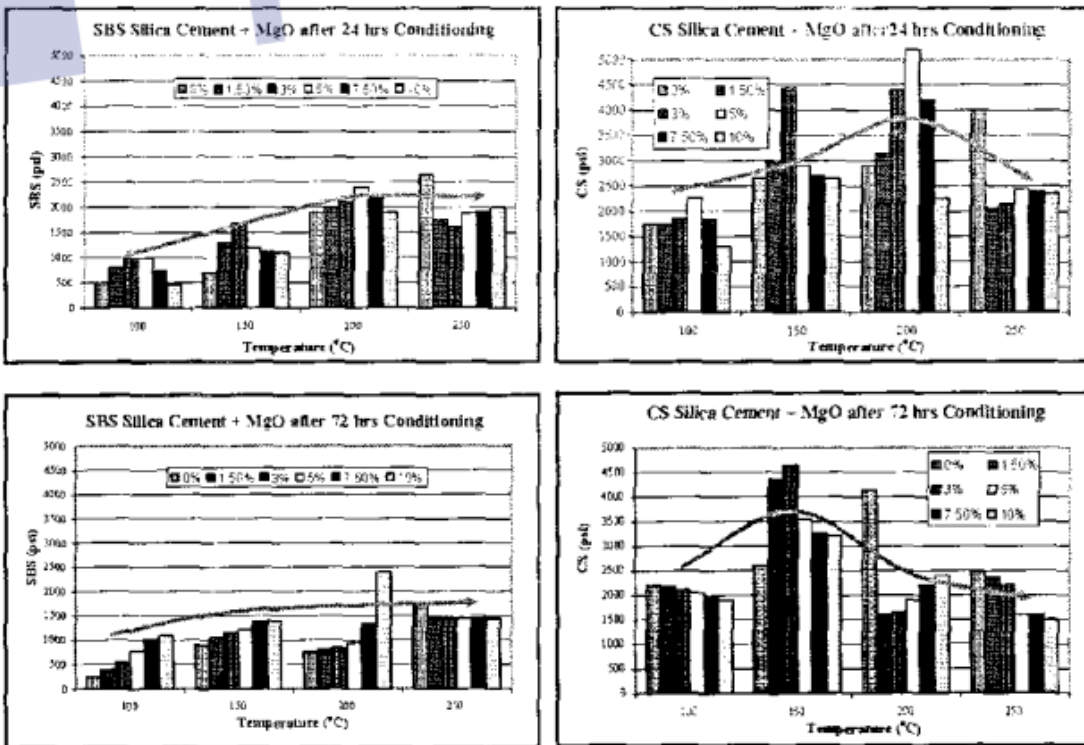


Figure 4.9 The Effect of MgO addition on Silica Cement.

From Figure 4.6, 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 decreasing when silica is added to the cement system as shown in the Figure 4.8. The same phenomenon is also occurring in the MgO cement system as shown in the Figure 4.7 and 4.9. 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 4.1.

Table 4.1 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	***	****	*****	***	****	*****	****	***

More* means better

4.6 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 4.6, 4.7, 4.8 and 4.9, we can see that the addition of time from 24 hour to 72 hour will cause the tendencies of cement strength to decrease for conditioning temperature higher than 200°C, but increasing for temperature lower than 200°C. This is because the conditioning temperature affects the rate of cement hydration. For temperature lower than 200°C, the hydration process is not as quicker as those with temperature higher than 250°C. The addition of curing time from 24 hours to 72 hours for conditioning temperature lower than 200°C will improve the cement strength because the hydration process is still occurring. Cement with conditioning temperature higher than 200°C, would cause the hydration process

to take shorter than 72 hours of time and addition of curing time would cause the cement strength start to decrease.

5 Conclusions

1. The use of silica flour is not effective for temperature lower than 150°C.
2. The use of basic cement without expanding additives will be more effective for conditioning temperature lower than 100°C. For temperature higher than that, adding of these additives will give better results.
3. The addition of additives mentioned on this paper is effective for conditioning temperature up to 200°C.
4. Combination of silica with the expanding cement system will give the best result for temperature between 150°C and 200°C.
5. The optimum concentration of expanding additives is ranging from 3% to 5%.
6. The effectiveness of these additives is only ranging from 150°C to 200°C.
7. Curing time addition will cause cement strength tend to decrease for temperature higher than 200°C, and vice versa will cause the strength increase for temperature lower than it.

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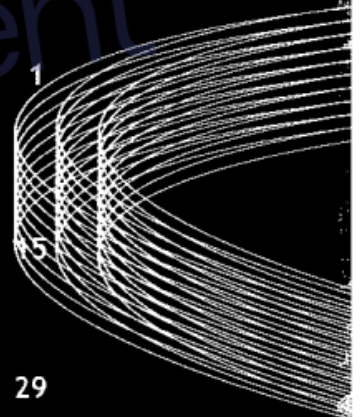


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