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THE EFFECT OF NEAT MAGNESIUM OXIDE (MgO) AS EXPANDING ADDITIVE ON CEMENT SHEAR BOND STRENGTH AT HIGH TEMPERATURE UP TO 2500C

Aris Buntoro, UPN "Veteran" Yogyakarta; Rudi Rubiandini R.S., Bandung Institute of Technology

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ABSTRACT

Good bonding between cement and casing and between cement and formation is essential for effective zone isolation. Poor bonding will create problems in production operations both for oil wells and geothermal wells. Expanding additives, such as magnesium oxide (MgO) are used for improving primary cementing.

Based on the results of previous research, there is a dangerous temperature transition at 150^0C, because the lowest compressive strength as well as shear bond strength of cement will be attained after 24 hours curing time. The presence of mud film on casing wall and mud cake on formation will decrease shear bond strength, and, for the composition without expanding additive, it may reach zero. However, by adding expanding additives, shear bond strength of cement will increase, because the improved bonding is the result of mechanical resistance or tightening of the cement against the casing and formation. There is no chemical bonding.

I. INTRODUCTION

Bonding between cement and casing is affected by temperature changes which cause the casing to expand and contract alternately. During the initial setting of the cement slurry, the casing is in an expanded state because of the heat generated from hydration in the cement. Subsequent internal temperature reduction, as the result of mud circulation, can cause the casing to contract and this may destroy the cement/pipe bond partially or wholly.

Expanding additives can alleviate this problem because they tend to expand after the initial set, resulting in the development of a stress condition in the cement that helps to maintain bonding during pressure and temperature changes. The overall result is greatly improved zone isolation. Because the bonding between cement and formation determines its bonding quality, the increased shear bond strength caused by an expanding additive becomes necessary.

In this research, neat magnesium oxide (MgO) with fineness 2000 - 3000 sqcm/gr. and burned up to 1400^0C was used as expanding additive[2,5)]. This additive was selected based on the result of previous research. Laboratory testing was performed in a modified pressure curing chamber simulator. It was designed to operate at a temperature up to 350^0C and pressure up to 3000 psi.

The objective of this research is to determine the concentration usage and the quality of neat magnesium oxide (MgO) as an expanding additive of cement for both oil and gas and geothermal wells.

This research was done by using API Class G Portland Cement HSR Type with silica flour (SiO_2) 35 % by weight of cement (BWOC) and neat magnesium oxide (MgO) with the concentrations varying from 0 to 20 % BWOC. Fresh water was used as the curing chamber medium. The temperatures in the test vary from 100 to 250^0C with the pressure constant (1500 psi). The duration of the tests varies from 24 hours (1 day) to 7 days (1 week).

II. LITERATURE REVIEW

Cementing is an integral, necessary aspect of drilling both oil and gas wells and geothermal wells. Cement is used to secure the casing string and to isolate zones for production purposes as well as to solve various hole problems, such as vibration, and to protect the casing from attack by corrosive fluids.

These compounds are formed in a kiln by a series of reactions at temperatures as high as 1500^0C between lime, silica, alumina and iron oxide. When hydrated, these compounds make a major contribution to the strength of the cement.

In the manufacturing process selected raw materials are ground to a fine powder, and proportioned in such a way that the resulting mixture has the desired chemical composition. The raw material consists of two types of materials which are needed to prepare a mixture, i.e. "calcareous" materials which contain lime, and "argillaceous" materials which contain alumina, silica and iron oxide. After blending, the raw material mixture is fed into the kiln and converted to cement clinker. The clinker is cooled, a small amount of gypsum (3% to 5%) is added, and the mixture is pulverized. The pulverized product is finished Portland cement.

The hydration of Portland cement is a sequence of overlapping chemical reactions between clinker components, calcium sulfate and water, leading to continuos cement slurry thickening and hardening. Although the hydration of C_3S is often used as a model for the hydration of Portland cement, it must be kept in mind that many additional parameters are involved. Portland cement is essentially a calcium silicate material, the most abundant components being tricalcium silicate (C_3S) and dicalcium silicate (C_2S). Upon addition of water, both hydrate to form gelatinous calcium silicate hydrate called "C-S-H gel", which is responsible for the strength and dimensional stability of the set cement at ordinary temperatures. In addition to C-S-H gel, a substantial amount of calcium hydroxide (CH) is liberated.

C-S-H gel is the early hydration product even at elevated temperature and pressure, and is an excellent binding material at well temperatures less than about 230^0F (110^0C). At higher temperature, C-S-H gel is subject to metamorphosis, which usually results in decreased permeability of the set cement. This phenomenon, known as "strength retrogression", was first reported by SWAYZE (1954)[7] in the petroleum literature because of the growing trend towards deep well completions.

C-S-H gel often converts to the phase called "alpha dicalcium silicate hydrate (α-C_2SH)". α-C_2SH is highly crystalline and much more dense than C-S-H gel. As a result, shrinkage occurs which is deleterious to the integrity of the set cement. Significant loss of compressive strength occurred within one month; however, the level to which strength falls is sufficient to support casing in a well (SUMAN and ELLIS, 1977)[4]. The real problem lies in the severe permeability increase. To prevent interzonal communication, the water permeability of well cements should be no more than 0.1 md. Within one month, the water permeabilities of the normal density Class G system (1,2) were 10 to 100 times higher than the recommended limit.

The strength retrogression problem can be prevented by reducing the bulk lime-to-silica ratio (C/S ratio) in the cement (MENZEL, 1935; KALOUSEK, 1952; CARTER and SMITH, 1958)[4]. To accomplish this, the Portland cement is partially replaced by ground quartz, usually as fine silica sand or silica flour. In some areas, special cements are available where quartz has been interground with Portland cement clinker (ITALCEMENTI, 1977; BERRA et al., 1988)[4]. C-S-H gel has a variable C/S ratio, averaging about 1.5. The conversion to α-C_2SH at 230^0F (110^0C) can be prevented by the addition of 35% to 40% silica (BWOC), reducing the C/S ratio to about 1.0. At this level, a mineral known as tobermorite ($C_5S_6H_5$) is formed; fortunately, high strength and low permeability are preserved. As the curing temperature increases to about 300^0F (150^0C), tobermorite normally converts to xonotlite (C_6S_6H) and smaller amounts of gyrolite ($C_6S_3H_2$) with minimal deterioration. Tobermorite sometimes persists to 482^0F (250^0C) in Portland cement systems because of aluminum substitution in the lattice structure (KALOUSEK and CHOW, 1976)[4].

At 480^0F (250^0C) the phase truscottite ($C_7S_{12}H_3$) begins to appear (LUKE and TAYLOR, 1984)[4]. As the curing temperature approaches 750^0F (400^0C), both xonolite and truscottite are near their maximum stable temperatures, and dehydration of the residual CH to C occurs. At higher temperatures the xonolite and truscottite dehydrate, resulting in the disintegration of the set cement.

In addition to the compounds cited above, other phases such as pectolite (NC_4S_6H), scawtite ($C_7S_6CH_2$), reyerite ($KC_{14}S_{24}H_5$), kilchoanite (C_3S_2H approximately), and calcio-chondrodite (C_5S_2H approximately) may appear in Portland cement system cured at elevated temperatures. These phases can affect the performance of set cement, even when present in small quantities.

Cements containing significant amounts of truscotite are usually characterized by low permeability (GALLUS et al., 1978)[4]. The formation of pectolite, a sodium calcium silicate hydrate, is accompanied by cement expansion (NELSON and EILERS, 1982)[4]; in addition, pectolite appears to render cements more resistant to corrosion by highly saline brines (NELSON and KALOUSEK, 1977; NELSON et al., 1981)[4]. Scawtite has been shown to enhance cement compressive strength when present in minor amounts (EILERS et al., 1983)[3]. In general, set cements which consist predominantly of calcium silicate hydrates with C/S ratios less than or equal to 1.0 tend to have higher compressive strengths and lower water permeabilities.

Previous research[2,5)] concerning shear bond strength, which is the adhesion strength between cement and casing and between cement and formation, concluded that the failure of cement was caused by poor bonding. Furthermore, they determined that the shear bond strength minimum was 100 psi after 24 hours curing time. That research was also done to understand the compressive strength phenomenon at elevated temperatures by adding silica flour (SiO_2) in varying concentrations, and shear bond strength phenomenon, which never increased at elevated temperatures by adding expanding additives cement, but they tend to expand after the initial set, resulting in the development of a stress condition that helps to maintain the bonding during pressure and temperatures changes.

DANJUSHEVSKY[5] stated that increasing cement volume means increasing the relative volume which is affected by the increasing size hardened cement. This increase in volume is caused by :

- ***Liquid condition*** Increase is caused by chemical contraction, the other hydrate products are formed such as the formation of salt dissolved crystal at elevated temperature.

- ***In curing time condition*** Increase is caused by expanding materials in cement matrix such as CaO, MgO and $CaSO_4$.
- ***After curing time condition*** Increase is caused by salt water in the formation, as the electrolyte charges.

In cementing operations, the second point above is an important condition in increasing cement shear bond strength.

DANJUSHEVSKY's research, which was done by adding CaO and MgO where those materials are burned before use as expanding additive at certain temperature, shows that the expansion is more than 1%, even up to 15% in particular conditions.

RUDI RUBIANDINI[5], in his research concerning shear bond strength phenomenon, stated that by adding CaO and MgO as expanding additives, with the burning temperatures up to 1600^{0}C and with certain fineness which was tested up to 150^{0}C, caused increased shear bond strength that varies from 250% to 1000%. He also stated that the silica flour concentration less than 30% BWOC did not improve compressive strength, because the C/S ratio was still more than 1.0.

III. LABORATORY TEST

3.1. Simulator Preparation

The apparatus for this research was a simulator with a modified pressure curing chamber which can be operated at temperature up to 350^{0}C with pressure up to 3000 psi. The main parts of the simulator for conditioning cement slurry are :

- *Cylindrical simulator, completed with heater and thermocouple in the inside.*
- *Maximator pump, used to increase pressure from the compressor up to 6500 psig.*
- *Safety valve or rupture disk*
- *Reservoir liquid injection reserve*
- *Temperature regulator*
- *Flowmeter for injection gas*
- *Cooling drum*
- *Manometer and valves to regulate flow distribution of liquid and gas.*

3.2. Curing Molds

For testing both compressive strength and shear bond strength, three types of curing molds were used to place cement slurry. These are :

- ***First mold***, a cubic form with the size 2x 2x 2in. This mold is used for standard API compressive strength test.
- ***Second mold***, a cylindrical form with inside diameter and height of 1 inch and 2 inches respectively. It is completed with caps both at the top and the bottom. This mold is used to test shear bond strength between cement and casing.
- ***Third mold***, a cylindrical core with the hole diameter 1 inch and height 1.5 inches. This mold consists of six holes to place the cement slurry. The specimens from this mold are used to test compressive strength, and cement permeability without casing .

These molds were designed to be placed into the simulator simultaneously before testing.

3.3. Specimens Test

This test was done by using API Class G Portland cement - HSR Type, with the following composition :

- Water Solids Ratio (WSR) = 44%
- Silica Flour (SiO_2) = 35% BWOC
- Neat Magnesium oxide (MgO) varies from 0 to 20% BWOC

The medium used in the curing chamber was fresh water. The duration of the tests varied from 24 hours (1 day) to 30 days (1 month).

3.3.1. Calculation of Compressive Strength

The specimens of cement are removed from the molds, then placed in a hydraulic press where increasing uniaxial pressure is exerted on each until failure. The compressive strength is then calculated from the pressure at which failure occurred referenced to the cross-sectional area of the specimen. The calculation of compressive strength can be calculated by using the equation below :

$$CS = kP\left[\frac{A1}{A2}\right] \tag{1}$$

where ;

CS = compressive strength, psi.
P = maximum load, psi.
A1 = block bearing cross section area at the hydraulics mortar, sqin.
A2 = specimen cross section area, sqin.
k = correction constant, is a function of the height/diameter (t/d) ratio.

3.3.2. Calculation of Shear Bond Strength

In this test, it is assumed that the casing is real clean. The shear bond strength test is done in the same manner as the compressive strength test, but with a driving stick and cylindrical holding. The pressure at which initial shear occurred is the maximum shear stress. Shear bond strength can be calculated by using the equation below :

$$SBS = P\left[\frac{A1}{pdh}\right] \qquad (2)$$

where ;

SBS = shear bond strength, psi.

P = maximum shear stress, psi.

A = block bearing area at the hydraulic mortar, sqin.

d = inside diameter of casing, in.

h = the height of specimen in cylindrical mold, in.

IV. RESULTS OF THE LABORATORY TESTS AND DISCUSSION

4.1. Results of The Laboratory Tests

The results of the laboratory tests can be seen in data plots for each specimen test. Thus, the concentration of neat magnesium oxide (MgO) which provides the best shear bond strength can be selected.

Figures-1, **2** and **3** depict the effect on shear bond strength of neat magnesium oxide (MgO) as an expanding additive at temperatures of 100^0C, 150^0C, 200^0C and 250^0C; at constant pressure (1500 psi); with durations of curing of 24 hours (1 day), 3 days and 7 days. **Figures-4, 5** and **6** depict the effect on compressive strength of magnesium oxide (MgO) as an expanding additive at temperatures of 100^0C, 150^0C, 200^0C and 250^0C; at constant pressure (1500 psi); with durations of curing of 24 hours (1 day), 3 days and 7 days.

4.2. Effect of Temperature

Figure-1 (24 hours curing time) shows that the shear bond strength significantly decreases to 150^0C, increases sharply at 200^0C, then at 250^0C increases slightly. However, for the 20% BWOC concentration of the neat magnesium oxide, its bonding decreases from 200^0C to 250^0C. **Figure-2** (3 days curing time) indicates the inverse trend to 24 hours curing time, with the shear bond strength increasing sharply at 150^0C, then increases slightly at temperature of 200^0C and 250^0C. However, for 3 and 20% BWOC concentration of the neat magnesium oxide, bonding decreases at temperatures of 150^0C and 200^0C, then at 250^0C increases slightly. **Figure-3** (7 days curing time) shows that the curve at 150^0C is similar to the curve in **Figure-2**. However, the shear bond strength from 100^0C to 150^0C increases slightly, and also from 150^0C to 200^0C and from 200^0C to 250^0C.

The effect of temperature on compressive strength for 24 hours curing time is illustrated in **Figure-4.** The compressive strength significantly decreases at 150^0C, increases sharply at 200^0C, but sharply decreases from 200^0C to 250^0C. However, for 3 - 5% BWOC concentration neat magnesium oxide, the strength increases significantly. The behavior of the curves in **Figure-5** (3 days curing time) is inverse to that in **Figure-4**, with the compressive strength significantly increasing at 150^0C to 200^0C, but decreasing at 250^0C. However, for 3 - 5% concentration neat magnesium oxide, values sharply increase at 150^0C, but sharply decrease at 200^0C, and slightly increase at 250^0C. **Figure-6** (7 days curing time) shows a trend that is similar to **Figure-4**, but at 150^0C the compressive strength decreases, and slightly increases at 200 to 250^0C. However, for 0% BWOC concentration MgO (by adding silica flour only), the compressive strength increases for temperatures of 100 to 200^0C, but decreases at 250^0C.

The trends in **Figures-1**, **2** , **3**, **4**, **5** and **6** indicate that the values of shear bond strength and compressive strength significantly change at 150^0C for all concentrations with 24 hours, 3 days, and 7 days curing time. Thus, the temperature of 150^0C is called a ***dangerous transition temperature***. It agrees with the results of RUDI RUBIANDINI.[5]

The trends in the curves of **Figures-1**, **2**, **3**, **4**, **5** and **6** can be evaluated to determine the best concentration of neat magnesium oxide as an expanding additive in well cementing, especially at high temperature up to 250^0C.

Figure-1 illustrates that after 24 hours curing time the 3 - 5% BWOC concentration of neat magnesium oxide as an expanding additive provides the highest value of shear bond strength, even though at 150^0C the shear bond strength decreases sharply, *but the minimum shear bond value is more than 100 psi*.[4] In this case, the minimum shear bond strength value at 150^0C is 628 psi. From **Figure-2** it is seen that after 3 days curing time the 3 - 5% BWOC concentration of neat magnesium oxide also provides the highest shear bond strength. **Figure-3** (after 7 days curing time) also shows the same trend. However, at the transition temperature (150^0C) the shear bond strength values are less than those for the 10 - 20% BWOC MgO concentration.

The addition of 3 - 5% BWOC concentration of neat magnesium oxide provides the highest value of compressive strength at 250^0C after 24 hours curing time, although at 150^0C its value is slightly lower, but this value is more than 1000 psi, i.e. 1153 psi, as seen in **Figure-4**. **Figure-5** also indicates that the 3 - 5% BWOC concentration of neat magnesium oxide provides the best value of compressive strength. From **Figure-6** it is seen that after 7 days curing time the 3 - 5 % BWOC neat magnesium oxide concentration gives fair compressive strength, although its value is less than for the 0 - 1.5% BWOC MgO concentration.

From these evaluations, it can be recommended that ***the 3 - 5% BWOC concentration of neat magnesium oxide*** as expanding additive which is burnt up to 1400^{0}C provides the best ***shear bond strength*** and fair compressive strength for geothermal and oil well cementing at high temperature of up to 250^{0}C.

4.3. Effect of Time

Figures-7 and **8** depict the effect of time on shear bond strength and compressive strength respectively. **Figure-7 and 8** show that for curing time up to 3 days, there is a significant effect of time on shear bond strength and compressive strength. After 7 days curing time there is a slightly lower rate of increase in shear bond strength and compressive strength .

Two days of curing will yield high shear bond strength and compressive strength, thus 2 days waiting on cement will improve safety on drilling forces for the next trajectory.

4.4. Effect of Neat Magnesium Oxide as Expanding Additive

Addition of neat magnesium oxide as an expanding additive will increase the CaO/SiO_2 (C/S) ratio more than 1.0. The C/S ratio value significantly effects the compressive strength at high temperature.

Figures-4 to **6** indicate that there is a decrease of compressive strength value with the addition of neat magnesium oxide as an expanding additive into cement slurry. In these figures it is seen that cement slurry without neat magnesium oxide (by adding silica flour only, 0% BWOC MgO) provides the highest compressive strength values. However, **Figure-1** to **3** illustrate the increase in shear bond strength with the addition of MgO as an expanding additive.

V. CONCLUSIONS

We have reached the following conclusions from this laboratory study on the effect of neat magnesium oxide (MgO) as an expanding additive on cement shear bond strength at high temperature of up to 250^{0}C :

1. The temperature of 150^{0}C is a dangerous transition temperature, because there is no specific composition able to increase both shear bond strength and compressive strength after 24 hours curing time.
2. The concentration of neat magnesium oxide as expanding (MgO) additive from 3 to 5% BWOC will provide excellent shear bond strength and fair compressive strength in geothermal and oil well cements at high temperature of up to 250^{0}C.
3. For a curing time of up to 3 days there is a significant effect on both shear bond strength and compressive strength, but after 7 days curing time, the increase in both shear bond strength and compressive strength is less.
4. Addition of neat magnesium oxide (MgO) to cement slurries will decrease compressive strength and increase shear bond strength.

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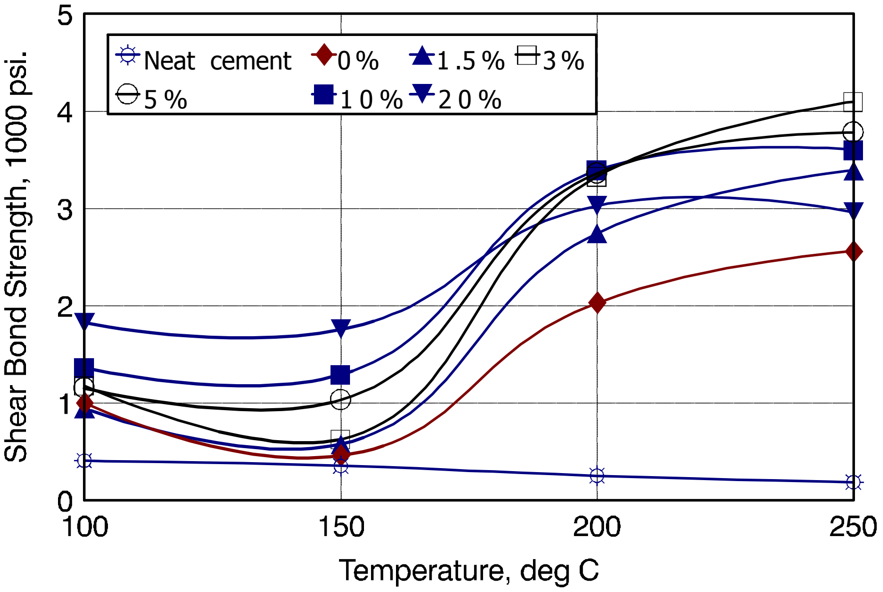

Figure-1
Effect of temperature on the shear bond strength of API Class G Portland cement containing silica flour (SiO2) 35 %BWOC and various amount of neat MgO (0 - 20%BWOC) after 24 hours curing time at 1500 psi

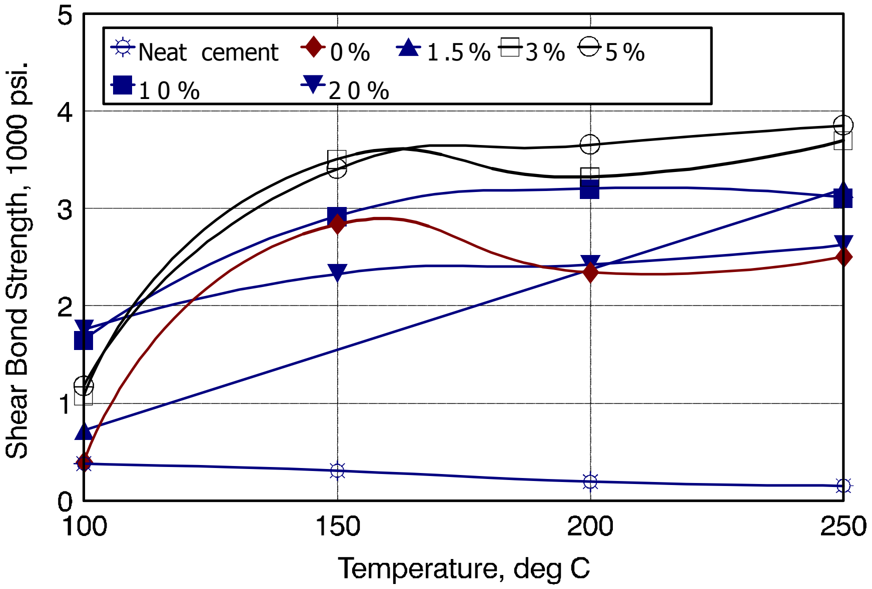

Figure-2
Effect of temperature on the shear bond strength of API Class G Portland cement containing silica flour (SiO2) 35 %BWOC and various amount of neat MgO (0 - 20%BWOC) after 3 days curing time at 1500 psi

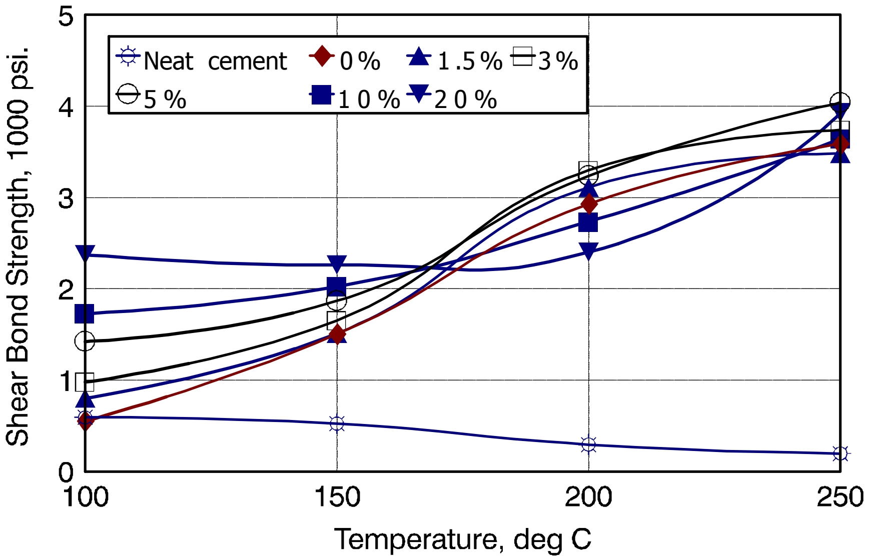

Figure-3
Effect of temperature on the shear bond strength of API Class G Portland cement containing silica flour (SiO_2) 35 %BWOC and various amount of neat MgO (0 - 20%BWOC) after 7 days curing time at 1500 psi

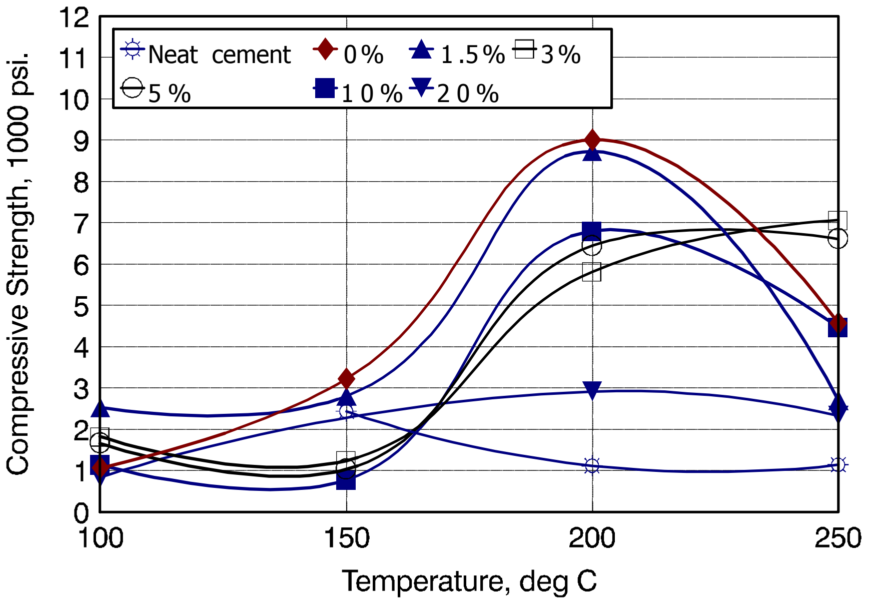

Figure-4
Effect of temperature on the compressive strength of API Class G Portland cement containing silica flour (SiO_2) 35 %BWOC and various amount of neat MgO (0 - 20%BWOC) after 24 hours curing time at 1500 psi

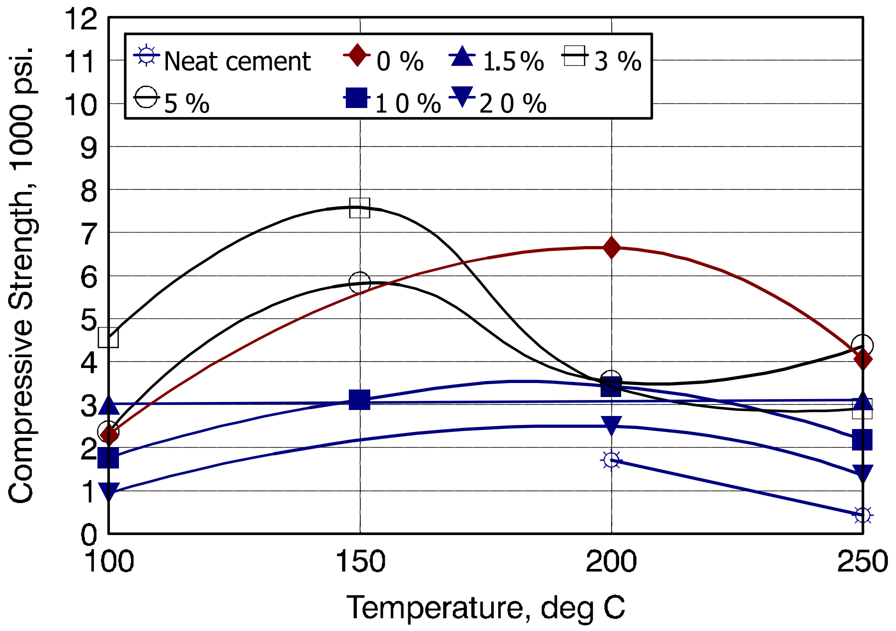

Figure-5
Effect of temperature on the compressive strength of API Class G Portland cement containing silica flour (SiO2) 35 %BWOC and various amount of neat MgO (0 - 20%BWOC) after 3 days curing time at 1500 psi

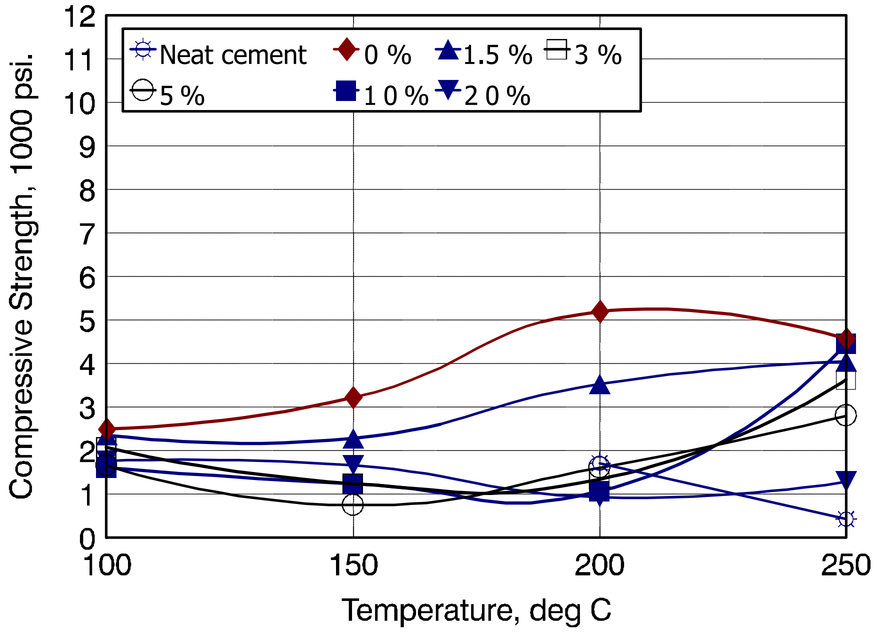

Figure-6
Effect of temperature on the compressive strength of API Class G Portland cement containing silica flour (SiO2) 35 %BWOC and various amount of neat MgO (0 - 20%BWOC) after 7 days curing time at 1500 psi

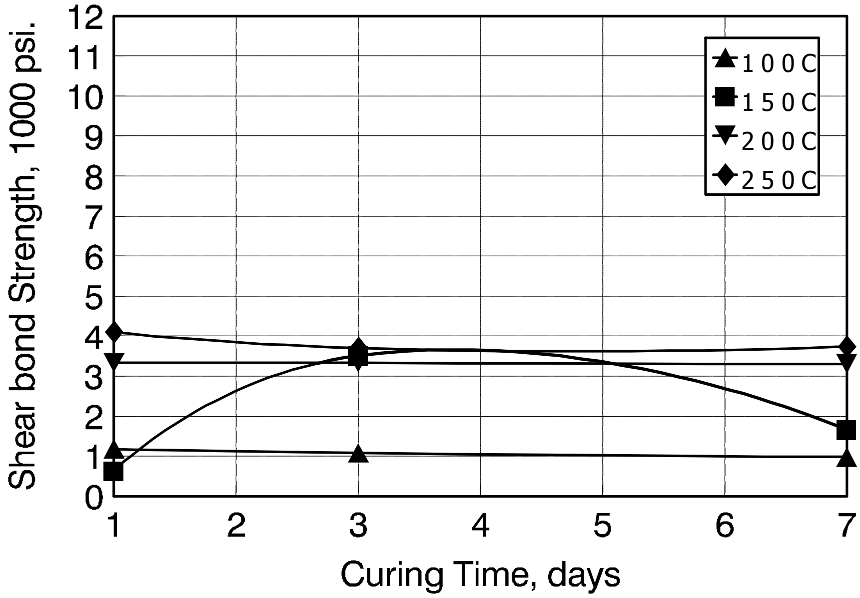

Figure-7
The effect of time on shear bond strength behavior of Portland cement system containing silica flour 35% and 3% BWOC of neat magnesite at various temperature

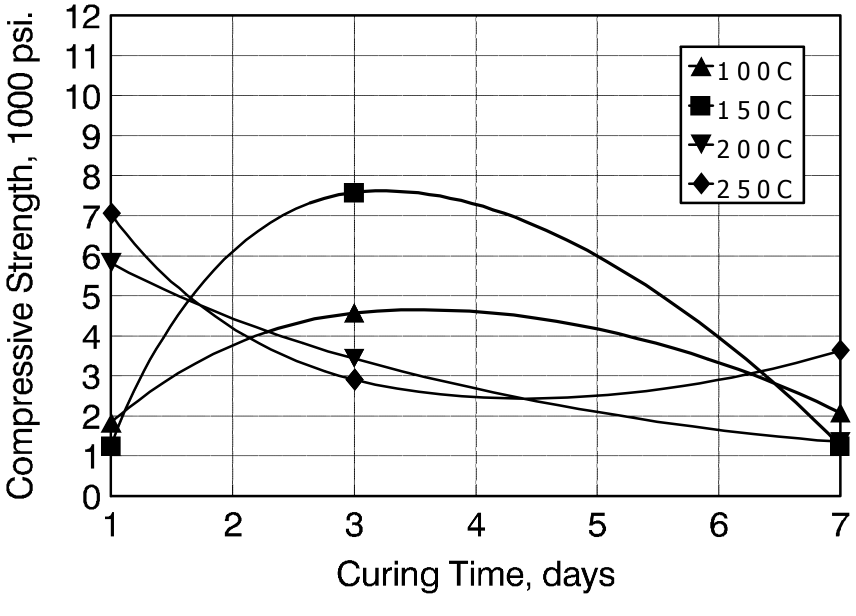

Figure-8
The effect of time on compressive strength behavior of Portland cement system containing silica flour 35% and 3% BWOC of neat magnesite at various temperature