# Optimising Silica Additions in a Durable Geothermal Cementing Formulation to Improve Rheological Properties

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## ABSTRACT

Following extensive research, we have recommended the addition of Microsilica 600 (MS600) at 20% addition by weight of binder to a Portland based oil well cement as the best option for providing carbonation resistance in geothermal well cementing. MS600 is a fine amorphous silica mined locally that reacts quickly with $Ca(OH)_2$ formed from the hydration of cement and inhibits crystallisation of any hydrothermally formed calcium silicate hydrates. This reaction with $Ca(OH)_2$ also prevents the phenomenon known as strength retrogression, caused by the crystallisation and growth of a phase known as $\alpha$-$C_2SH$, from occurring. Its use also stops the rapid carbonation of some cement formulations arising from the crystallisation of tobermorite ($C_5S_6H_5$) which forms when silica flour is used.

One of the drawbacks of using MS600 is its very fine particle size, which creates a high water demand which results in a cement slurry that is thick and more difficult to pump and place than regular cementing formulations when silica flour is used. Chemical admixture additions can be used to control and improve rheology but an increased use of these chemicals can be costly.

We have investigated a range of cement-silica blends containing MS600 to try to improve the rheological properties of the blend. By using silica containing materials in conjunction with MS600, lower water demand formulations and reduced levels of chemical admixtures can be obtained, while still maintaining the carbonation resistant properties of the amorphous binder associated with the use of MS600.

## 1. INTRODUCTION

### 1.1 Well cementing

In cementing wells, one of the primary roles of cement is to anchor the well casing to the formation. The hardened cement also plays critical roles in providing a seal between the casing and production fluid, ensuring all steam is delivered to the surface through the casing, and providing corrosion protection for the steel casing.

Cements used in geothermal wells have traditionally been based on oil well cements, specified by the American Petroleum Institute (API). Research by Kalousek (1951) showed curing cements at elevated temperatures (above 60°C) leads to the phenomenon known as strength retrogression, where the calcium silicate hydrate (C-S-H[i]) of the cement crystallised into a more impermeable and dense, but weak product known as alpha dicalcium silicate hydrate ($\alpha$-$C_2SH$, $Ca_2(SiO_4)H_2O$). This effect was able to be avoided by the addition of ~28% fine quartz (silica flour) by weight of binder (~40% by weight of cement), shown later by Kalousek and Adams (1954, 1955), to result in the formation of the product tobermorite ($C_5S_6H_5$), a higher strength, less dense and more permeable crystalline phase.

### 1.2 Issues with cementing geothermal wells

The conditions of oil wells, however, are different than those of geothermal wells, which are generally water laden with high levels of $CO_2$, reaching temperatures in excess of 300°C. In the presence of high levels of $CO_2$, many of the crystalline calcium silicate hydrates, formed from cement hydration, can carbonate via a 'through solution' mechanism, described by Milestone et al. (1986), where $Ca^{2+}$ ions migrate from the calcium silicate binder and, on encountering $CO_2$, precipitate as $CaCO_3$. This process happens extremely rapidly for tobermorite (and xonotlite at temperatures > 200°C) as shown by Milestone et al. (1987).

The carbonation of cement is not normally a problem in most common cement applications. The carbonation of most high Ca/Si ratio calcium silicate hydrates and $Ca(OH)_2$ is expansive and provides a carbonated cement sheath which is less porous and less permeable than the binder phase itself, stopping further carbonation. In geothermal environments, however, the high $CO_2$ concentration fluids lead to the corrosion of the cement through the dissolution of the $CaCO_3$, described by Bruckdorfer (1986). The $CaCO_3$ forms the soluble $Ca(HCO_3)_2$ which is lost in the circulating fluids, given in Equation 1.

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(Eq. 1)}$$

### 1.3 The use of Microsilica 600

Our research, (Milestone et al. (2012)), has shown the addition of ~20% Microsilica 600 (MS600) by weight of binder (BWOB) removes $Ca(OH)_2$ and stops the crystallisation of tobermorite, while also avoiding the formation of $\alpha$-$C_2SH$. MS600 is a fine, hydrothermally altered, amorphous silica, mined in New Zealand. It reacts rapidly with cement and does not crystallise so readily. The lower addition rate (compared to 28% silica flour) means the ratio of calcium to silica is too high to form tobermorite at elevated temperatures. Instead, the product formed is largely an amorphous calcium silicate hydrate, which does not carbonate nearly as rapidly as tobermorite, so corrosion is mitigated.

Using MS600, however, has one major drawback. Its very fine particle size creates a high water demand, which results in a cement slurry that is thick and more difficult to mix and pump than regular cementing formulations when silica flour or fly ash are used. At 20% BWOB, MS600 is at the limit

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[i] Cement nomenclature: C = CaO, S = $SiO_2$, H = $H_2O$

of being mixable with cement, as all the water is either taken up by the cement or adsorbed on the surface of the MS600.

Typical methods employed to avoid this issue where MS600 is used in geothermal cementing operations are:

- Use additional water
- Use less MS600
- Use additional chemical admixture e.g. dispersants

All three alternatives have significant disadvantages, with the first two having a detrimental effect on the cement durability. Adding extra water in the cement slurry, generally above a 0.45 water to binder (W:B) ratio, results in a weaker cement with a higher permeability, allowing $CO_2$ to permeate further into the cement body, increasing carbonation rates. Also, additional water often requires the use of additional fluid loss control chemicals.

Using less MS600 results in a significant drop in strength, as the pozzolanic reaction that occurs between the silica and $Ca(OH)_2$ formed in the cement hydration will be heavily reduced. Additionally, more of the weaker $\alpha$-$C_2SH$ binder phase will form with reduced silica, leading to greater strength retrogression.

The use of additional chemical admixtures is generally a preferable option to manage the thickness of the cement-MS600 blends. Most cementing operations already use a variety of chemical admixtures to control different cement properties, such as set retarders, dispersants, fluid loss controllers and defoaming agents, which aid in the placement of the cement correctly in extreme environments. They do not have the same detrimental effect on the hardened cement as reduced MS600 or additional water, but will still improve the rheological properties dramatically. The downside of using additional chemical admixtures is primarily cost. Cement chemical admixtures are generally proprietary materials supplied by the service companies, where their use is determined by the service company themselves.

### 1.4 The rheology of cement

The rheology of cement is determined by two primary properties obtained using the Bingham plastic model, the yield point (YP), sometimes called yield stress, and plastic viscosity (PV). The YP is the pressure which needs to be applied for the cement to flow as a Newtonian liquid with uniform flow (Fig. 1). A high YP means high pressures are required to overcome the plastic property of static cement. The PV of cement refers to the internal friction resisting uniform flow, which only becomes apparent when the cement is flowing, so a cement with a high PV will also require high pressures to maintain uniform flow.

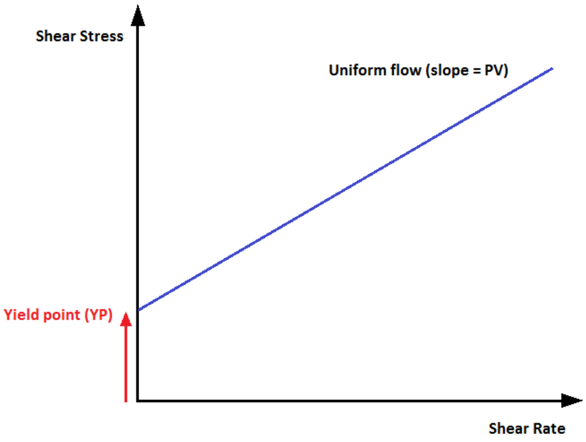

**Figure 1: Bingham plastic model**

Current well cementing operations using 20% MS600 use a combination of additional water (more than a W:B ratio of 0.45) and chemical admixtures to control the thickness, more specifically, the viscosity and yield point. This research investigated a range of cement-silica blends containing a large proportion of MS600, to try to improve the rheological properties of the blend to reduce the requirement of high levels of chemical admixtures, while still maintaining the carbonation resistant properties of the amorphous binder associated with the use of MS600.

## 2. EXPERIMENTAL METHOD

When cement is used in the field, the ideal YP and PV will vary between operations due to different equipment, pumping and placement method, environmental conditions, and materials. A guideline specification which has been used in cementing operations is a YP of less than 30 Pa, and a PV of less than 150 cP. This research used these values as the target points, where the rheology of alternative cement blends were tested then refined with chemical admixture to meet these values. A comparison of the amount of chemical admixtures required was then made against 20% MS600.

To ensure that any new designs did not lose the original benefits of 20% MS600, 50 x 50 x 50 mm cube samples were cast and wet-cured for 28 days in an autoclave at 150°C, pressurised with 6.5 bar $CO_2$, to simulated geothermal exposure. The extent of carbonation and the crystalline products in the cement designs were determined by powder X-ray diffraction (XRD) using a Philips PW1700 diffractometer with cobalt K-alpha radiation.

Cement designs were mixed to API standard 10B using a constant speed mixer. The cement and silica powders were pre-blended, and then added to the pre-mixed water in which the chemical dispersant (if used) was added. Rheology testing was conducted and analysed in accordance with API standard 10B using a standard cement rheometer. The plastic viscosities and yield points were measured at an ambient temperature of 22°C.

### 2.1 Cement design

The base cement design was made with an API Class G cement from Holcim (New Zealand) and Microsilica 600 from Golden Bay (New Zealand). The variations on this design were made by substituting proportions of MS600 with quartz silica flour from Unimin Ltd. (Victoria, Australia), and fly ash from Gladstone coal plant

(Queensland, Australia). These silica containing materials were chosen for their lower water demand and commercial viability. The addition of total silica containing powders was 20% BWOB for all mix designs and compared with 20% BWOB of MS600. Table 1 details the tested cement designs.

Cement slurries were made using a 0.4 W:B ratio. Slurries using a 0.5 W:B ratio, without chemical admixture, were also made to observe the effect on rheology and carbonation with additional water use.

**Table 1: Cement slurry designs tested**

| | % BWOB addition | | | |
|---|---|---|---|---|
| **Cement design** | **G cement** | **MS600 (MS)** | **Silica flour (SF)** | **Fly ash (FA)** |
| **MS20** | 80% | 20% | | |
| **MS15/SF5** | 80% | 15% | 5% | |
| **MS10/SF10** | 80% | 10% | 10% | |
| **MS15/FA5** | 80% | 15% | | 5% |
| **MS10/FA10** | 80% | 10% | | 10% |
| **MS5/FA15** | 80% | 5% | | 15% |

### 2.2 Chemical dispersant

A sodium polynapthalene sulfonate (NaPNS) water reducing dispersant was used as the chemical admixture to control rheology. NaPNS is a common dispersant used in the cement and concrete industry to control water demand, allowing thick cement slurries to be made pumpable or placeable. It is sold in both powder and liquid forms, commonly under tradenames such as CD31, D065, CFR-2, and P-D88 (with an additional L designating the liquid form). NaPNS acts as a dispersant by neutralising the attractive electrostatic charge forces of the cement and silica particles, allowing the particles to flow freely without resistance. As viscosities and yield stresses were the focus of this research, NaPNS was the only chemical admixture used.

## 3. RESULTS AND DISCUSSION

### 3.1 Reduction in required dispersant

Figure 2 shows the amount of NaPNS dispersant required to bring each of the cement designs in Table 1 within specification, < 30 Pa and < 150 cP, with the percentage reductions of MS20 shown in Table 2.

The reduction in NaPNS required is substantial, ranging from 25-75% of the amount required for the MS20 design. This highlights the large water demand of MS600, as the designs with less MS600 have the lowest requirement of NaPNS.

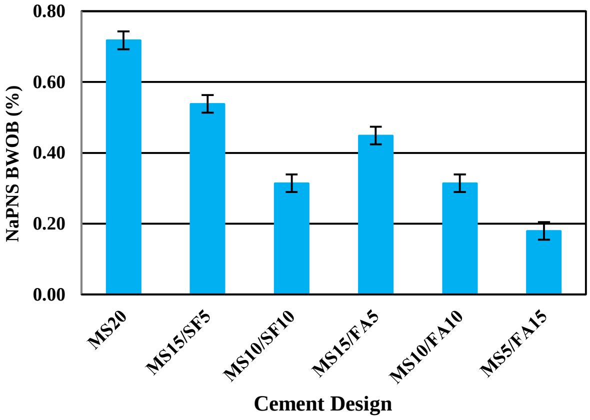

**Figure 2: Required amount of NaPNS (% BWOB) to meet design specification with each cement slurry formulation**

**Table 2: Percentage reduction in NaPNS used**

| Cement design | Reduction in NaPNS (%) |
|---|---|
| **MS15/SF5** | 25.0 |
| **MS10/SF10** | 56.3 |
| **MS15/FA5** | 37.5 |
| **MS10/FA10** | 56.3 |
| **MS5/FA15** | 75.0 |

### 3.2 XRD analysis

Powder XRD scans of the cement designs after being exposed to the simulated geothermal condidtions are shown in Figure 3, with a summary in Table 3.

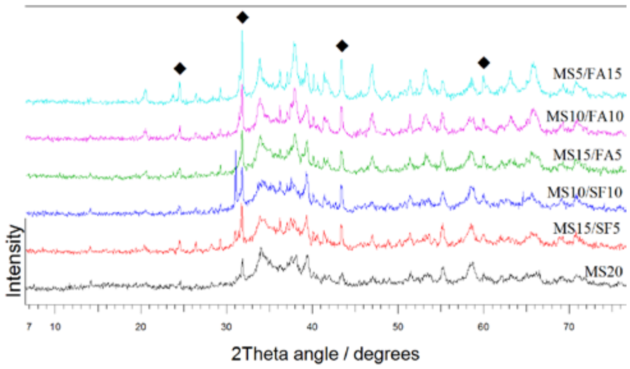

**Figure 3: XRD scans of cement designs. ◆ - α-$C_2SH$ ($Ca_2(SiO_4)H_2O$)**

The XRD scans show the structures of all samples are all quite amorphous, with only small peaks defining crystalline phases. Tobermorite was not detected in any samples, nor was there any carbonation in the interior of the samples. The exposed surface of each sample, including MS600, carbonates from the surface 1-2 mm inwards before the ingress of $CO_2$ stops. Distinguishable in the XRD scan of the interior of all samples are traces of unhydrated cement, quartz where silica flour was used, and small amounts of α-$C_2SH$. The presence of α-$C_2SH$ is not considered detrimental as it is not well crystallised, particularly in MS20, but the intensity of the α-$C_2SH$ 2ϴ peaks do increase with reduced amounts of MS600, particularly visible at 31.7° and 43.4° in Figure 3. While this small amount of crystallisation is not considered detrimental, longer exposure to the simulated geothermal conditions is needed to determine if this is the extent of α-$C_2SH$ crystallisation in these alternative designs.

**Table 3 –Summary of phases detected by XRD from slurry formulations. X - Not detected, Trace - small amounts detected, ✓ - Detected**

| Cement Design | Tobermorite | α-$C_2SH$ | Calcium carbonate |
|---|---|---|---|
| MS20 | X | Trace | X |
| MS15/SF5 | X | Trace | X |
| MS10/SF10 | X | Trace | X |
| MS15/FA5 | X | Trace | X |
| MS10/FA10 | X | Trace | X |
| MS5/FA15 | X | ✓ | X |

### 3.3 Effects of using additional water

To highlight effects of using additional water, Figure 4 shows the rheology results from using a 0.5 W:B ratio with no NaPNS dispersant.

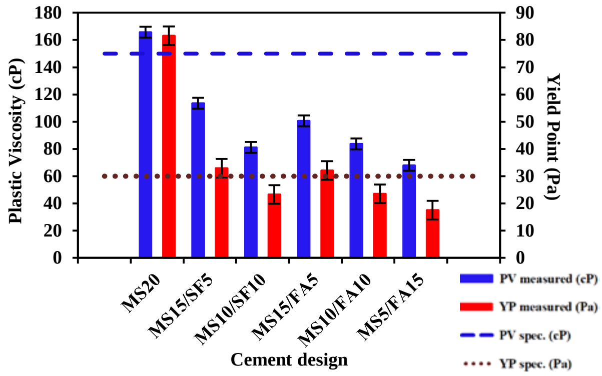

**Figure 4: Plastic viscosities and yield points of cement designs using 0.5 W:B ratio without NaPNS additions**

As shown in Figure 4, when the PV and YP measurements are compared against the target specification when a 0.5 W:B ratio was used, almost all cement designs fall within specification. Trying to obtain rheology data using only a 0.4 W:B ratio was not possible as the PV and YP values were too high to be measured.

When the samples are analysed after simulated geothermal exposure however, a negative effect is clear. Figure 5 shows the cross sections from cylindrical samples of MS20, using a W:B ratio of 0.5 (top) and 0.4 (bottom). Visible in the 0.5 W:B ratio sample is the increased depth of carbonation, seen by the brown discolouration along the edge, penetrating deeper into the grey cement body. This is due to the increased porosity of the cement, allowing for a higher permeability of the geothermal fluids, leading to more extensive carbonation.

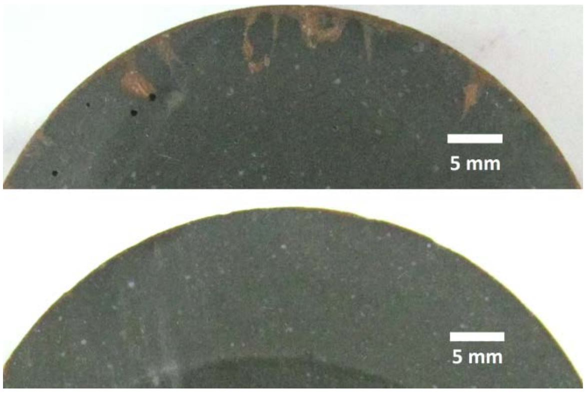

**Figure 5 – Cross sections of MS20 design after geothermal exposure, 0.5 W:B ratio (top) and 0.4 W:B (bottom)**

### 3.4 Use of other chemicals

In field cementing applications, other chemical admixtures, such as retarders and fluid loss controllers would also be used. Many of these have dual functions so it could be possible to also reduce their addition rates. For example, many retarders are chelating agents binding calcium ions to slow or stop hydration. As a result they often act as dispersants due to the availability of additional water. If reduced water is needed to ensure workability there could also be reduced use of fluid loss controllers.

## 4. CONCLUSION

The substitution of some of MS600 with alternative silicas did not produce any detrimental crystalline phases, and appeared very similar to the use of Microsilica 600. A slight increase in the amount of α-$C_2SH$ can be considered negligible. However, curing times in the geothermal fluid exposure time would need to be extended to 6-12 months to determine if this is the extent of crystallisation.

The reduction in the amount of NaPNS dispersant required to bring the alternative cement slurry designs within the workability specification, and achieve pumpable slurries is very positive. It demonstrates the potential of simply substituting or combining existing raw materials with similar alternatives to provide benefits that reduce the dependence on proprietary chemical admixtures.

Using a W:B ratio above 0.45 as a means of controlling rheology is not recommended. As shown in this research, its effect on durability of the hardened cement is severe, giving rise to increasing porosity which allows carbonic acid fluids to permeate and carbonate the cement body. Wherever possible, a W:B ratio of less than 0.45 should be used.

The use of chemical admixtures will always need to be a part of any well cementing operation to produce the required properties needed for a usable cement slurry in the extreme conditions of well cementing. However, their dosage can often be reduced in ways that do not reduce the beneficial properties of the cement, which could ultimately result in overall cost benefits for cementing operations.

## ACKNOWLEDGEMENTS

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## REFERENCES

API RP 10B Section 5 Preparation of Slurry, “Recommended Practice for Testing Well Cements”, 22nd edition, American Petroleum Institute (1997)

API RP 10B Section 12 Determination of Rheological Properties, “Recommended Practice for Testing Well Cements”, 22nd edition, American Petroleum Institute (1997)

Bruckdorfer R.A., “Carbon dioxide corrosion in oil well cements”, SPE 15176, (1986)

Kalousek, G.L. and Adams, M., “Hydration Products formed in cement pastes at 25 to 175°C”, J Amer. Concr. Inst. 23 77-90 (1951)

Kalousek, G.L. and Adams, M., “Studies on cementitious phases of autoclaved concrete products made from different raw materials”, J Amer. Concr. Inst. 25 365-378 (1954)

Kalousek, G.L. and Adams, M., “Tobermorite and related phases in the system CaO-$SiO_2$-$H_2O$”, J Amer. Concr. Inst. 26 989-1011 (1954)

Milestone, N.B., St John, D.A., Abbott, J.H., Aldridge, L. P., “$CO_2$ corrosion of geothermal grouts”, Proc. 8th Internat. Cong. Chem. Cements, Rio de Janeiro, V141-144 (1986)

Milestone, N.B., Sugama, T., Kukacka, L.E. and Carciello, N., “Carbonation of Geothermal Grouts - Part 1: $CO_2$ Attack at 150°C”. Cement Concr, Res. 17 295-306 (1987)

Milestone, N.B., Bigley, C.H., Durant, A.T., Sharp, M.D.W., da Silva, J.R.M.C., “Chemical Reactions in Geothermal Cements”, Proc. New Zealand Geothermal Workshop 2012, Auckland, (2012)