

Successful Well Cement Standardisation Needs Research Underpinning

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SUMMARY

Well cement standardisation is being developed globally and there are already five international standards operative, which are applied globally but used locally. Their development has benefited from background research, which gives greater confidence in confirming existing limits or in assisting new developments. The trend is to give more impetus to operational requirements, as has happened to date with cements for deepwater well cementing and atmospheric foam cement compositions. Emphasis is increasingly being placed upon having better test methods for operational requirements and for technical report type standards (like cement slurry rheology) to be produced pending further experimentation.

1. INTRODUCTION

Currently there are five ISO standards available globally under the generic title 'Well Cements and Materials for Well Cementing' and another standard is nearing completion (Table 1).

Table 1: Petroleum and Natural Gas Industries – Well Cements and Materials for Well Cementing:

Part	ISO Number	Title
1	10426-1	Specification
2	10426-2	Testing of Well Cements
3	10426-3	Testing of Deepwater Well Cement Formulations
4	10426-4	Preparation and Testing of Foamed Cement Slurries at Atmospheric Pressure
5	10426-5	Determination of Shrinkage and Expansion of Well Cement Formulations at Atmospheric Pressure
6	10426-6	Methods for Determining Static Gel Strength of Well Cement Formulations (<i>in preparation</i>)

For these standards background research underpinning for verification of the test procedures is highlighted in various areas.

2. ISO 10426-1, Part 1: Specification

In this well cement specification background research has been beneficial for addressing limits for thickening (setting) time, compressive strength and free fluid. Early hydration of HSR Class G cement was investigated at water/cement ratio 0.44 alone, with 0.2% wt calcium lignosulphonate retarder, and then with 0.2% wt sugar-lignin proprietary product retarder, all at up to 5 hours at 25°C. The ettringite formed was essentially amorphous at first and thereafter became more crystalline. Retardation produced relatively more ettringite and less C-S-H, plus an increased dispersion and hindered crystal growth. With retarder present, there was more heat evolved in the presence of water. The sugar-lignin derivative gave more ettringite than the cement without water, but less ettringite than with the lignosulphonate retarder [1]. The prime cause of thickening was deposition of some C-S-H, with ettringite at best playing a minor support role [1]. This situation was comparable to that of final setting with a Portland cement investigated earlier [2] with around 3-4% wt C-S-H being present and with this phase having the main influence upon thickening.

Compressive strength was carried out at atmospheric pressure or at pressures up to 20.7 MPa (3000 psi). It was only in more recent years that the 20.7 MPa (3000 psi) pressure ceiling for well cement testing was generally found to be inaccurate at higher temperatures (normally above 100°C). Pressure alone has a very significant effect (although not quite as high as temperature does) upon thickening time [3]. This is why well cement slurries for field use needed to be based upon reliable pressure and temperature data, with the ISO compressive strength specification limits being simply a basic yardstick for conformance and not a realistic indicator of downhole compressive strength growth with time. For more critical wells, computer simulations of pressure and temperature gradients need to be evaluated before finalising the well cementing formulations.

The 30 minutes leeway in the ISO Schedule 5 thickening time test [4], which requires thickening time to be in the range 90-120 minutes, is certainly useful for minimising batch-to-batch inconsistency under downhole conditions of Class G cement from the same source under the same manufacturing conditions. This test is undertaken for achieving suitable additive responses from retarders, fluid loss controllers, dispersants and defoamers and any other desirable additive for securing a good seal in the downhole annulus in the field [5].

The old free fluid test (free water test) using a measuring cylinder was replaced by the Erlenmeyer flask method, which uses a larger vessel and thus gives a more reliable measurement, with a maximum free fluid of 5.9%. This test is important for ensuring that free fluid is sufficiently low in order to prevent segregation during thickening and hardening of the cement slurry. Such segregation would be likely to give rise to unwanted events (such as gas migration and influx of unwanted formation fluids) that would impede zonal isolation and thus be detrimental for long term well durability.

3. ISO 10426-2, Part 2: Testing of well cements

This is a large document due to numerous tests having been included over the years in the former API RP 10B from which ISO 10426-2 was developed, with the result that they are not classified tidily. The ISO standard is being revised and is likely to 'tidy up' the contents into subject areas for convenience of usage in the laboratory. Such possible subject areas could include the following:

- General testing of well cements
- Additional thickening time testing
- Rheological and related testing
- Pozzolans in well cementing.

Another area that is covered in the National Annex within the British version (BS EN ISO 10426-2) is free lime [6], where the global situation is not overtly straightforward for international standardisation purposes. It is well known that high free lime containing well cements can produce unacceptably high rheological characteristics like plastic viscosity and yield value, high downhole fluid loss and interference with cement slurry retardation [7]. Interestingly, in Brazil their national standard for MSR (medium sulphate resistant) and HSR (high sulphate resistant) Class G well cement has a maximum limit of 2.0% [8].

In the British version [6], the free lime requirements were set out thus after numerous experiments had been carried out on a wide range of cements from different countries:

Free lime (CaO) in cements is measured either by the ethylene glycol method or by X-ray diffraction.

Simple mandatory limits for free lime are not to date ascribed on a worldwide basis, because of the many interactive effects from other cement constituents which influence overall cementitious reactivity. High levels of free lime can affect:

- a) additive (especially retarder) responses*
- b) rheological characteristics of well cement slurries (like plastic viscosity and yield point)*
- c) fluid loss results (high).*

Optimisation of free lime levels in well cements is achieved on a plant-by-plant basis during manufacture. In most circumstances a useful "rule of thumb" guide for free lime limits applies as follows:

- a) If the magnesium oxide (MgO) content of the cement is 1.5% mass or less, free lime is limited to 1.0% mass or below.*
- b) If the MgO content lies above 1.5% mass, the free lime is limited to 0.5% mass or below.*

There are some individual exceptions to this “rule of thumb”, for example where higher contents of free lime give adequate retardation with appropriate retarder concentrations.

This information given for free lime limits is, in standardisation terms, purely informative (non-mandatory) and not normative (compulsory), because it is part of a useful, but individual, National Annex to an International Standard.

The apparent discrepancies in desirable free lime limits can be explained thus. In the United States, for example, well cements like Class G and H normally contain much higher magnesia (MgO) levels than in Western Europe, because of the common use of high magnesian limestones as a raw material for cement production. As a result the US cements contain high (relatively speaking) MgO in comparison with the Western European well cements. Although up to around 1.5% mass of the MgO content is normally contained in solid solution in the clinker phases, most of the rest is present as free magnesia (periclase, MgO). Free magnesia reacts slower with water than free lime, but the general effect is to augment the undesirable properties given to cement slurries by free lime. Thus only low levels of free lime can be tolerated, hence the desirability of a free lime limit of 0.5% mass (or at most 0.6% mass) for high MgO-containing cements. In Western Europe, where cement MgO levels in well cements are normally below 1.5% mass, there is generally little free magnesia and free lime values up to ca. 1.0% mass can usually be tolerated [9].

Most well cement producers of Class G and H cements in particular normally check the amounts of free lime present, so that the well cements perform satisfactorily in the field. Such international standardisation would need to be addressed globally before mandatory limits could be set for free lime contents of well cements. None of the rheological tests set any limits for plastic viscosity, yield point or gel strength development. The Brazilian national standard for MSR and HSR Class G cement has set limits for rheological properties at 27°C and 52°C as given in Table 2, which are determined by rotational viscometry [10]:

Table 2: Rheological Properties for Class G Well Cement

Rheological Properties	27°C	52°C
Initial gel strength (10 seconds) at 3 rpm, Pa (max.)	12	12
Final gel strength (10 minutes) at 3 rpm, Pa (max.)	16.8	16.8
Consistency after 1 minute at 3 rpm, Pa (max.)	9.6	9.6
Consistency after 5 minutes at 3 rpm, Pa (max.)	9.6	9.6
Plastic viscosity, Pa.s (max.)	0.055	0.055
Yield point, Pa	14.4-33.5	14.4-38.3

Maximum increment of final gel strength with temperature rise from 27°C to 52°C is 4.8 Pa at 27°C rising to 10.0 Pa at 52°C

Recommended maximum increment of yield point with temperature rise from 27°C to 52°C is 9.6 Pa

The limits for these rheological tests are appropriate for Class G cements made in Brazil for producing suitably pumpable well cement slurries downhole. However, whilst the cements conforming to these limits also work satisfactorily for European Class G cements, the aforementioned limits are not appropriate for Class G or H cements made from high magnesian limestones, as commonly experienced in the United States, for instance. This is because of the generally higher gel strengths and yield points normally found for the latter Class G or H cements. These increased rheological characteristics appear to arise through the hydration of periclase augmenting that from free lime, but the cement slurries can still be pumped satisfactorily downhole into the annular spaces of the wells during the well cementing process. If full international standardisation were required for rheological properties then the various limits would need to be changed, so as to accommodate the Class G and H cements derived from high magnesian limestones.

4. ISO 10426-3, Part 3: Testing of deepwater well cementing formulations

This standard was the first of a number of new well cementing standards that are being developed through ISO on a performance-related basis. Deepwater is usually regarded as water of depths exceeding 400-500 m with ultra-deepwater being water more than 1500 m deep [5].

There are numerous complexities involved in deepwater well cementing involving a number of variables impacting the thermal history of a cement formulation during placement and curing, plus the interdependence of many of those variables. As a result, the user is directed to employ numerical heat-transfer simulation or actual field measurement to determine the test temperature and the temperature/pressure schedule required. In this way, the testing of the cement formulation can reflect as closely as possible the actual temperature profile found during field cementing operations. Numerical modelling may need to be used for determining the relative magnitude of the input variables so that 'most likely' and 'least likely' scenarios of temperature history can be reliably assessed. These procedures serve not only for the testing of well cements under deepwater well conditions, but may also be used in those circumstances where low seafloor temperatures are found at shallow water depths [11].

Well cements that can be used in deepwater well cementing [11] can include those of ISO Classes A, C, G or H, high alumina cement, appropriate foamed cements, various types of suitable ductile cement compositions [12] etc. In each deepwater well cementing operation, the cement chosen needs to be fit for purpose [11]. Such cementations are normally critical and extensive pre-planning and pre-testing are essential for enabling the successful cementing of these critical wells.

5. ISO 10426-4, Part 4: Preparation and testing of foamed cement slurries at atmospheric pressure

This is another performance-related standard developed by ISO, which is closely related to ISO 10426-3 in that foamed cementing compositions are often utilised in deepwater well cementing operations. These two standards can often complement each other during well cementing activities. Foamed cement slurries have been described elsewhere in the overall context of ductile well cementing formulations that can give rise to good zonal isolation downhole with critical well cementing jobs [5,12].

Cements or cement blends used for foamed cement slurry preparation at atmospheric pressure should be fit for purpose. Such cements could include well cements of ISO Classes, high alumina cement, or other speciality cements. The cements and blending materials should conform to appropriate standards. Where ISO standards do not exist, conformance with other appropriate standards should be made [13]. The test procedures employed to characterise the foamed cement slurries produced are often similar to those used for deepwater cement slurries [11,13].

6. ISO 10426-5, Part 5: Determination of shrinkage and expansion of well cement formulations at atmospheric pressure

ISO 10426-5 [14] has been partially developed from the API Technical Report 10TR2 [15] as a base-line standard for determining shrinkage and expansion of well cement formulations at atmospheric pressure. Two methods have been described for use at atmospheric pressure [14]:

- The annular ring test under conditions of free water access
 - The membrane test under impermeable condition.
- a) The annular expansion mould is a device for measuring only the linear bulk shrinkage or expansion properties of a cement formulation. The magnitude of the expansion depends on the amount of expansion agent, cement powder, slurry design and curing condition (pressure, temperature, time, fluid access). It should be noted that expansion is strongly affected by boundary conditions. The chemical process of mineral growth is strongly controlled by the state of stress and mineral growth will tend to occur when the stress value is the lowest, i.e. in pore space or empty spaces. Therefore, the degree of cement shrinkage and expansion is dependent on a number of conditions, not all of which can be uniquely defined. The test does not represent fully the annulus of a well.
- b) However, the purpose of the membrane test method is to measure the bulk expansion or shrinkage when the cement is unable to imbibe water or gas. This is commonly the case when the cement is placed within impermeable boundaries within a well. An impermeable flexible membrane is used to

measure shrinkage or expansion under appropriate impermeable conditions. The membrane is sealed by tying a knot at the top in the experiments. The material of the membrane shall not react in a high pH environment and shall be capable of containing at least 150 ml +/- 30 ml of slurry.

Shrinkage can lead to unwanted wellbore phenomena such as a microannulus that leads to a bad bond, interzonal communication, resulting in costly remedial operations and lack of a hydraulic seal when utilising cement inflatable packers. Shrinkage and expansion in cement can result from the formation of hydration products having a density different from the compounded density of the reaction components. This can result in changes in pore volume, pore pressure, sample dimensions and internal stress [14].

ISO 10426-5 is likely to be the first of a number of future standards on the importance of shrinkage/expansion and is basically a yardstick standard for testing at ambient temperature and atmospheric pressure. Standards still to be worked on are likely to involve various high temperature-high pressure (HTHP) scenarios, where the effects of increases in temperature and pressure downhole can be better appreciated in the field than at present. Much laboratory work needs to be undertaken in this area, which is important for the successful cementing of ductile cement compositions [12].

7. ISO 10426-6, Part 6: Methods for determining static gel strength of cement formulations (in preparation)

A Technical Report type of standard is currently being prepared, which discusses various different methods for determining static gel strength of well cementing formulations in order to disseminate current available information. There is insufficient information available at present for more definitive standardisation at this particular stage in time. This should form a future basis for adopting either a suitable specification or a 'recommended practice' type of standard in the future, when more data becomes available. ISO 10426-6 is expected to be published by early 2008.

Note should be taken of the Brazilian Standard NBR 9831 [8] mentioned already in this paper in Table 2, which utilises normative limits for rheological properties of MSR or HSR Class G cement determined by rotational viscometry using procedures described in the Standard NBR 9830 [10]. This could act as a basis for starting to develop normative requirements in this particular area of viscometry on a global basis.

8. Conclusions

This paper has shown how research underpinning for international standards for oilwell cements has been very useful for producing good quality standards that are relevant to the industries (oil and construction) that need to make use of these documents. All future international standards and revisions of the existing ones, when the needs arise, require the input of modern scientific research.

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