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Evaluation of the Na-EDTMP/borax system as a non-dispersing, high temperature retarder for oil well cement

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ABSTRACT

For well cementing at temperatures above 120 °C, thermal thinning depicts a major problem, promoting particle sedimentation *via* decreasing slurry viscosities. This is partly caused by dispersing properties of common high temperature retarder systems and can lead to imperfect zonal isolation, endangering the stability of the wellbore. Counteracting additives tend to start losing their effectiveness at temperatures >140 °C. Other options are often not economically sufficient, increase system complexity or show negative interactions with other additives.

Hence, this work presents a comprehensive study on the sodium ethylenediamine tetra (methylene phosphonate) (Na-EDTMP)/borax retarder system, which was found to combine sufficient retardation with low thermal thinning, leading to an enhanced slurry stability at high temperatures. Thickening times (TT's) from 7 to 13 h (increasing with temperature) were achieved from atmospheric pressure and 50 °C up to high pressures and temperatures (HP/HT) of 19.0 kpsi and 200 °C bottom hole circulating temperature (BHCT). Furthermore, On/off-cycle HP/HT consistometer tests at 160 and 190 °C and rheological measurements were performed to examine stability of the slurry's viscosity. Experiments with fluid-loss additives show potential compatibility with other additives.

Total retarder dosages of 0.97–2.64 % bwoc (by weight of cement) were applied. Compared to prior literature, higher Na-EDTMP/borax ratios (0.29–0.34 vs. 0.055) were found to improve retarding performance probably by enhancing synergetic effects. The slurries featured a sufficient initial viscosity (<40 Bc) and a constant pumpability (10–25 Bc) during the tests followed by a swift setting and compressive strength (CS) development. Additionally, high slurry stability was shown and compatibility with common fluid-loss additives is probable. Main disadvantage was the relatively high sensitivity of the system, especially at moderate temperatures, requiring exact dosage.

Summarizing, the Na-EDTMP/borax retarder system might present a low-complexity opportunity for common high temperature retarders, avoiding thermal thinning while improving slurry stability.

1. Introduction

Despite huge efforts for switching from fossil energy carriers to renewable ones, the production of oil and gas will continue for decades. Whereas oil production will likely decrease, natural gas will gain importance due to its lower CO_2-footprint [1,2].

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Oil and gas are produced by drilling wells into reservoirs. Typical oil wells consist of an inner steel tubing protected by an outer cemented casing. The annular cement sheath is made by pumping a cement slurry through the tubing and letting it flow back on the outside to the surface. After hardening it is guaranteeing zonal isolation between environment and oil/gas. Nevertheless, poor mixing design of the slurry can lead to wellbore integrity failure [3,4]. With higher depth of drilling temperature and pressure increase, reaching bottom hole circulating temperatures (BHCT) of over 260 °C and pressures of 30,000 psi. Even more, future reservoirs often require deeper drilling increasing those challenging conditions [5–7]. Therefore, developing cement-based casing systems which can also face those harsher conditions are a point of interest. Crucial properties are (a) a low viscosity with defined rheology, enabling sufficient pumping down the well, (b) high (temperature-)stability so that no segregation of the cement particles and water appears thus containing zonal isolation, (c) high resistivity against acidic or basic environmental influences and (d) a strongly and controlled delay of hydration reaction followed by a swift compressive strength development to enable necessary pumping/working times and a high mechanical stability after completion.

To fulfill such requirements several additives like (a) dispersants, (b) fluid-loss/anti-settling agents, (c) special additives and (d) retarders are normally added to the cement slurry [8–11].

Typical retarders include sugars, polycarboxylates, lignosulfonates, phosphonates, borates, etc. which can delay the hydration reaction of the cement paste *via* four different mechanisms [12–16].

- Ca ion complexation: The retarder forms complexes with dissolved Ca ions of the cement, lowering the Ca^{2+} concentration of the pore solution and therefore hindering/lowering C-S-H formation.
- Surface adsorption: The retarder adsorbs on the cement particles surface, therefore reducing contact with water and lowering dissolution rate of Ca, Si, etc. into the pore solution.
- Nuclei poisoning: Adsorption of the retarder on freshly formed C-S-H crystals, disturbing further crystallization and therefore delaying setting/hardening.
- Precipitation of a semi permeable layer: Some retarders (sugars, some carboxylic acids, etc.) enhance early formation of calcium aluminate sulfates or other Ca compounds which precipitate on the cement grains, reducing water access to the clinker grains and/or hindering C-S-H growth.

One decisive issue while cementing oil wells is thermal thinning. It describes the decreasing viscosity of a cement slurry with increasing temperature which – at some point – leads to a segregation of the slurry [17]. Therefore, addition of e.g. anti-settling agents is required within limited dosage ranges to contain pumpability at surface near conditions [8,18]. However, most anti-settling agents start losing their effectiveness or decompose at temperatures above 120 °C. Therefore, utilization of special additives is necessary [19–21]. Still, such additives have disadvantages like higher costs, interactions with other additives and limited thermal stability above 140 °C [17].

Furthermore, synthetic polymer retarders made from various monomers, including carboxylate-based ones, often show disadvantageous properties above 120 °C too. For example, the aberrant thickening phenomena or thickening time reversal (TTR) can lead to flash setting or annular gas channeling [22–24]. Lignosulfonate-based ones exaggerate thermal thinning by their dispersing properties [25].

Several phosphonic acids and their salts are known to possess highly effective temperature and pressure stable retardation capabilities for oil well application. Patents from Nelson [26,27], Casabonne [28] and Barlet-Gouedard [29] and other authors [5,30,31] investigated various phosphonate acids and their salts as high-temperature oil well retarders. Additionally, it was found out that the combination of phosphonates with borax/boric salts results in a synergetic effect – which is not completely understood yet – greatly enhancing the retarders performance and applicability. The combination of the sodium salt of ethylenediamine tetra(methylene phosphonic acid) (Na-EDTMP) and borax with a ratio of 0.055 yielded most promising results with over 7 h of retardation at 232 °C [28,29].

Phosphonic acid and their salts retarding mechanisms are a result of the strong Ca ion chelating capabilities, forming Ca complexes. This leads to a decreased dissolution rate of clinker phases by surface adsorption onto clinker phases, a decreased Ca ion concentration in solution (Ca complexation) and – according to previous research showing the most decisive effect – an interrupted C-S-H phase formation due to nuclei poisoning [12–16].

Boric acid and its salts also decrease Ca dissolution, form Ca compounds or poison C-S-H nucleation. However, the main retardation mechanism is meant to be a reason of the formation of a Ca borate compound, its precipitation and formation of a more-or-less dense layer around the clinker grains, especially the freshly formed C-S-H phases [32,33]. Furthermore, the buffer-effect of borax could decrease the pore solutions pH-value, decreasing Si solubility.

In general, it can be assumed that the organophosphonates preferably form complexes and stronger bonds with the Ca^{2+} ions compared to borates due to the principle of hard and soft acids and bases [34].

However, only little data is given for the phosphonate/borax retarder system and its properties in oil well environments, like rheological data, slurry stability, dosage control or interactions with additives. Additionally, first investigations within this work revealed potential of only small thermal thinning properties, enabling the reduction of anti-setting agents while obtaining slurry stability.

Therefore, the goal of this work is to prove low thermal thinning properties of the Na-EDTMP/borax retarder system and provide additional data, especially relevant for oil well application with focus on its rheological, retarding and stability behavior during high temperature and pressure conditions. HP/HT experiments of up to 200 °C and 19.0 kpsi were performed with the goal to achieve reasonable thickening times and viscosities. Supported by rheological measurements, free water, fluid loss, strength development and

Table 1
Measuring schedules of the HP/HT tests including API casing schedules [38].

API casing schedule	T [°C]	heating time [min]	heating rate [°C/min]	p [kpsi]
	100	38	2.6	8.0
7g	**119**	**44**	**2.7**	**10.2**
	132	48	2.7	11.5
8g	**145**	**52**	**2.8**	**13.4**
	160	56	2.8	14.6
	171	**60**	**2.9**	**16.1**
9g	180	62	2.9	16.8
	190	65	2.9	17.9
10g	**196**	**67**	**2.9**	**18.8**
	200	68	2.9	19.0

heat calorimetry experiments, the high potential but also challenges for the applicability of this system are shown.

2. Materials and methods

Experimental procedures were performed according to American Petroleum Institute (API) specifications and underlying corresponding device manuals [35]. Necessary and unavoidable deviations were noted. Additionally, non-API certified experiments which however are widely used in the oil well field are used do give further information. All used devices (except for the heat calorimeter and ultrasonic cement analyzer (UCA), chapter 2.7 and 2.9) were API certified.

2.1. Applied materials

As cement, an API certified Class G "black label" well cement from Dyckerhoff (Wiesbaden, Germany, plant Lengerich) was used [35].

For high temperature experiments (>115 °C), a commercial sample of silica flour (SSA-1) from Halliburton (Houston, USA) was added. According to X-ray fluorescence (XRF) analysis it contained (in wt.-%) 97.6 quartz, 0.56 CaO, 0.18 MgO, 0.17 Al_2O_3 and 0.06 TiO_2. Its specific density was 2.65 kg/L with a specific surface area of 1860 cm^2/g, determined by *Blaine* method. It showed an average particle size (d_{50} value) of 32.7 μm [36].

As first component of the retarder system, a commercial sample of CUBLEN E3115 from Zschimmer & Schwarz (Lahnstein, Germany) with a solid content of 31 wt% was used. The solution consists of the sodium salt (7 eq.) of ethylenediamine tetra(methylene phosphonic acid) (Na-EDTMP). As second component, analytical grade (Reag. Ph. Eur.) disodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$, borax) from Merck KGaA (Darmstadt, Germany) was used.

As fluid-loss control additives, commercial samples of HALAD-413 and HALAD-433 from Halliburton (Houston, USA) were utilized.

All experiments were performed with deionized water from a Barnstead Nanopore Diamond Water purification system (Werner Reinstwassersysteme, Leverkusen, Germany).

2.2. Cement slurry preparation

In general, a water-to-cement (w/c) ratio of 0.44 was applied for all experiments including the water contained in the retarder system. Therefore, all dosages of the used additives are given in wt.-% by weight of cement (% bwoc) considering the active content (water contained in the Na-EDTMP solution and borax is subtracted from given % bwoc values). For measurements above 115 °C, 35 % bwoc silica flour was added to avoid cement strength retrogression [37]. Silica flour, borax and fluid-loss additives were dry-blended into the cement, whereas the Na-EDTMP solution was added to the mixing water.

The aqueous solution was mixed for 15 s at 4000 rpm using a blade-type laboratory blender from Waring Products (Stamford, Connecticut, USA), followed by addition of the blended cement mixture within 20–25 s (according to API procedure 15 s) to achieve homogeneous slurries. Subsequently, it was mixed for 35 s at 12,000 rpm and directly used in the experiments. According to the device instructions, for consistometer measurements 600 g cement were prepared as basis, while 400 g were used for all other experiments. The applied retarder dosages are shown in the corresponding chapters.

2.3. Atmospheric pressure/moderate temperature consistometer tests

To determine the thickening times under atmospheric pressure and moderate temperatures (<85 °C), an atmospheric consistometer Model 1250 from Ametek Chandler (Berwyn, Pennsylvania, USA) was used. The consistency is described in Bearden Units of Consistency (Bc), a dimensionless unit describing the pumpability of a cement slurry without a direct conversion factor to common SI units (International System of Units). The heating rate was adjusted to 2.5 °C/min, starting at 27 °C. Measurements were performed at 27, 50 and 80 °C and the slurry was stirred at 150 rpm until a pumpability of 70 Bc was reached. The error of the consistency was assigned to ±5 Bc.

Table 2
Slurry composition used in isothermal heat flow calorimetry measurements for 4 g of cement.

sample	SiO_2 [wt.%]	Na-EDTMP [wt. %]	borax [wt.%]	ratio
1	0	0	0	–
2	35	0	0	–
3	35	0	0.154	–
4	35	0.008	0.146	0.055
5	35	0.035	0.119	0.294
6	35	0.099	0.055	1.79
7	35	0.154	0	–

2.4. High pressure/high temperature consistometer tests

To evaluate the consistency behavior at high pressures and temperatures, thickening time tests up to 19 kpsi and 200 °C were performed using a HP/HT consistometer Model 8240 from Ametek Chandler (Berwyn, Pennsylvania, USA). Psi (pound-force per square inch) was used to express the pressure in this work and is defined in SI units as:

$$1\ kpsi = 1,000\ psi \approx 6.895\ MPa = 68.95\ bar \tag{1}$$

API based casing schedules were used and extended with additional measuring points depicted in Table 1 [38]. During heating, the pressure was manually adjusted in a range of ±2 kpsi and when the desired temperature was reached between ±0.5 kpsi (except for chapter 2.8). The error of the consistency was assigned to ±5 Bc.

2.5. Rheological measurements of cement slurries

All rheological measurements were assessed on a Couette-type coaxial cylinder rotational viscosimeter Model PVS rheometer from Ametek Brookfield (Middleboro, Massachusetts, USA) using a B1 bob and 12.5 mL of cement slurry. The measurements were carried out at 27, 50, and 80 °C within ±1 °C and always at 1000 psi of N_2 pressure. During heating, a shearing rate of 150 rpm was applied and the slurries were measured while shearing at a sequence of 3-6-100-200-300-200-100-6-3-600 rpm. All measured values are given in [Pa]. The measurement error at 3/6 rpm accounts to ±0.01 Pa, for 100–300 rpm to ±0.05 Pa and for 600 rpm to ±0.1 Pa. The plastic viscosity (PV) and the yield point (YP) were calculated by following equations based on Bingham plastic fluids with errors of ±0.03 Pa (YP) and ±0.1 Pa (PV):

$$PV\ (Pa \cdot s) = \theta_{600} - \theta_{300} \tag{2}$$

$$YP\ (Pa) = \theta_{300} - PV \tag{3}$$

where θ is the dial reading at the indicated shearing rate in rpm [39].

2.6. Free water and density determination of cement slurries

Free water and density of the cement slurries were measured by a method based on ref. [40]. At first, 200 mL of the slurry were filled into a measuring cylinder and weighed. From these values the density was calculated. Subsequently, the measuring cylinder was sealed with foil and placed inside a preheated 80 °C drying compartment for 2 h. Afterwards, the amount of formed free water was weighed.

2.7. Isothermal heat flow calorimetry

In a 10 mL glass ampoule, 4 g of cement were dry-blended with selected additives. The mixing water was separately mixed with specific concentrations of Na-EDTMP. For all measurements, an overall retarder dosage of 0.154 % bwoc was applied. The corresponding compositions are shown in Table 2.

Subsequently, the water/Na-EDTMP mixture was added to an ampule containing the dry-blended cement, sealed and mixed for 2 min using a vortex mixer. Afterwards, the sample was immediately placed into the calorimeter (TAM Air Isothermal Heat Conduction Calorimeter, Thermometric, Järfälla, Sweden). The heat flow values were recorded for 450 h at 27 °C.

2.8. Slurry stability tests

To display particle sedimentation during the HP/HT consistometer measurements, stability tests at 160 and 190 °C were performed. Therefore, HP/HT measurements were conducted according to chapter 2.4 in which the stirring was paused for 15 min (off-cycle) after 1.5, 3 and 9 h. Within these breaks, no pressure regulation was applied. Once the stirring is started again, a spike in consistency would indicate occurred sedimentation [19].

Table 3
Fluid-loss: Amount of filtrate of the slurry at 180 °C and 1000 psi after specific times.

time	30 s	1 min	2 min	5 min	10 min	15 min	20 min	30 min
fluid [mL]	6.0	7.5	11.0	19.0	28.5	36.5	46.0	53.0

Fluid-loss [mL/30 min] is calculated by doubling the amount of filtrate after 30 min, corresponding to 106 mL/30 min.

Table 4
TT tests at atmospheric pressure and moderate temperatures showing exemplary retarder dosages. Bold = > 7 h until consistency reaches 70 Bc.

sample	T [°C]	Na-EDTMP [% bwoc]	borax [% bwoc]	total retarder [% bwoc]	ratio Na-EDTMP/borax	TT 25 Bc [h:min]	TT 70 Bc [h:min]
M-1	**27**	**-**	**-**	**-**	**-**	**05:25**	**07:09**
M-2	50	–	–	–	–	02:09	02:49
M-3	**50**	**0.035**	**0.119**	**0.154**	**0.294**	**07:00**	**07:42**
M-3a	**50**	**0.028**	**0.143**	**0.171**	**0.196**	**06:33**	**07:19**
M-3b	**50**	**0.042**	**0.095**	**0.137**	**0.441**	**08:03**	**08:38**
M-3c	50	0.020	0.068	0.088	0.294	03:48	04:26
M-3d	50	0.030	0.102	0.132	0.294	05:37	06:21
M-4	**80**	**0.035**	**0.119**	**0.154**	**0.294**	**07:17**	**07:35**
M-4a	80	0.025	0.085	0.110	0.294	04:17	04:30
M-4b	**80**	**0.040**	**0.136**	**0.176**	**0.294**	**09:20**	**09:40**

2.9. Compressive strength measurements via UCA

To assess the compressive strength development of the cement slurries, an ultrasonic cement analyzer Model 4262 from Ametek Chandler (Tulsa, Oklahoma, USA) was used. While this is not an API certified method, it is commonly used in the field [28]. The applied heating rates were similar to the thickening time measurements (Chapters 2.3 and 2.4, Table 1). All measurements were performed at 3000 psi of N_2 pressure.

2.10. Fluid-loss control experiments

Fluid-loss was measured on a Model 7120 stirred fluid-loss from Ametek Chandler (Tulsa, Oklahoma, USA). Conditions were set at 180 °C and 1000 psi with a heating rate similar to the HP/HT measurements (Chapter 2.4). For filtration, a 325-mesh screen was used.

For the test slurry, HALAD-413 (0.6 wt%), HALAD-433 (0.3 wt%), SiO_2 (35 wt%) and borax (1.85 wt%) were dry-blended to cement (400 g) and prepared according to chapter 2.2, including Na-EDTMP (0.62 wt%) which was added to the mixing water beforehand. The measured values of the filtrate are shown in Table 3.

3. Results and discussion

This work is divided into a moderate (<85 °C) and an HP/HT (>115 °C) condition part for clearer data visualization and comparability.

3.1. Atmospheric pressure/moderate temperature investigations

Investigations at atmospheric pressure and moderate temperatures <85 °C were performed to show if the Na-EDTMP/borax retarder system can act as an all-in-one retarder system. However, for moderate temperatures there are several established and optimized systems available [41].

3.1.1. Atmospheric consistometer tests

Exemplary retarder dosages at atmospheric pressure and at up to 80 °C with thickening times of targeted 7 h or more are depicted in Table 4 (M − 1 – 4).

Whereas at 27 °C (M − 1) no retarder addition was necessary to achieve desired TT's and pumpability (TT 25 Bc > 5 h), at 50 °C the strong accelerating effect of increased temperature is demonstrated, reducing the time of pumpability by over 70 % (M − 2). To increase TT's, addition of the Na-EDTMP/borax retarder system with a ratio of 0.294 and low dosage was applied (M − 3), which was adopted from the measurements shown in chapters 3.1.5 and 3.2.1. Interestingly, temperature increase from 50 to 80 °C (M − 4) does not require higher dosages which could be explained by the occurrence of the abnormal phenomenon mentioned by Guo et al. [42]. It describes elongated TTs with constant retarder dosage at temperature changes from 75 to 85 °C. It is explained by the significantly increased solubility of the C_4AF phase at higher temperatures, resulting in an increased ettringite formation and therefore $Ca(OH)_2$ consumption. As a consequence of the reduce $Ca(OH)_2$ content, more retarder molecules – which preferably bind to Ca^{2+} ions – are available to hinder C-S-H-phase formation resulting in delayed hydration kinetics.

Furthermore, higher retarding effect of Na-EDTMP compared to borax is shown. A lower ratio but higher total retarder dosage (M-3a) slightly decreases, whereas a lower total dosage but higher ratio extends TT's (M-3b). Also, a high retarder sensitivity can be seen

Table 5
Rheological measurements and calculation of the plastic viscosity and the yield point at temperatures up to 80 °C and at 1 kpsi N_2 pressure. M – 1 and 2 as well as M – 3 and 4 have the same composition respectively and are therefore summarized (see Table 4).

sample	T [°C]	shear stress [Pa] at rotational speed [rpm]										PV [Pa·s]	YP [Pa]
		3	6	100	200	300	200	100	6	3	600		
M-1/2	27	0.10	0.10	0.27	0.35	0.41	0.35	0.28	0.12	0.09	0.56	0.15	0.25
	50	0.10	0.12	0.42	0.51	0.57	0.51	0.43	0.12	0.09	0.71	0.15	0.42
M-3/4	27	0.06	0.07	0.15	0.21	0.26	0.21	0.15	0.07	0.06	0.40	0.14	0.12
	50	0.07	0.08	0.23	0.31	0.38	0.32	0.25	0.09	0.06	0.52	0.14	0.24
	80	0.08	0.10	0.33	0.46	0.57	0.47	0.33	0.09	0.07	0.73	0.16	0.41

Table 6
Free water amounts and density of selected moderate condition slurries.

sample	T [°C]	free water [wt. % (g)]	density [g/mL]
M-1/2	50	1.1 (2.2)	1.88
M-3/4	50	1.7 (3.5)	1.88
	80	2.9 (5.8)	1.88

Table 7
Compressive strength development of selected moderate condition slurries at 27, 50 and 80 °C at 3 kpsi.

sample	T (BHST) [°C]	CS 50 psi (0.35 MPa) [h:min]	CS 500 psi (3.5 MPa) [h:min]	CS 24 h [psi, (MPa)]	CS 72 h [psi, (MPa)]
M-1	27	05:45	11:50	1785 (12)	3424 (24)
M-2	50	02:19	03:54	3474 (24)	4361 (30)
M-3	50	07:40	09:33	2672 (18)	3720 (26)
M-4	80	09:35	10:37	3046 (21)	3957 (27)

when e.g. comparing measurements at 80 °C (M-4a – b). Dosage changes at the second decimal place can vary the TT by hours.

The consistency behavior during the consistometer measurements of selected samples (M – 1 – 4) is shown in SI Figure A1.

Overall, the viscosity of all cement slurries is low (<5 Bc) and therefore stability of the cement slurry cannot be guaranteed eventually causing sedimentation. Nevertheless, additives to overcome this problem at moderate temperatures are well known as described in chapter 1.

3.1.2. Rheological measurements

Rheological properties of selected slurries were measured *via* a PVS rheometer and are presented in Table 5.

Interestingly, the plastic viscosity – depicting the resistance of the slurry against shear – seems to be only slightly affected by the temperature and the retarder addition varying within the margin of error. This is also observed in the consistometer tests, which showed similar initial viscosities for all slurries.

The yield point – depicting the amount of force needed to liquefy a material and describing the ability of a slurry to hold particles dispersed – is lowered after the addition of the retarder (halved at similar temperatures) indicating some dispersing properties. Also, as is typical for water-based slurries, the YP increases again with rising temperature. Due to the low initial viscosity and retarder dosage, thermal thinning cannot be observed.

3.1.3. Free water and density determination

For well applications, low free water of the cement slurries plays a crucial role, especially for horizontal wells, to achieve zonal isolation and sufficient wellbore stability. Therefore, 0 % of free water are desired for horizontal jobs, and up to 2 % are acceptable for vertical ones [43]. In Table 6, free water amounts and densities of the moderate condition cement slurries are presented.

After addition of the retarders the amount of free water increases slightly. This is most probably caused by surface adsorption of the retarder molecules onto the particles, decreasing water adsorption. Like with dispersing agents – but less pronounced – the carrying capacity is reduced (chapter 3.1.2) [24]. At 80 °C, free water increases to 2.9 wt % showing thermal thinning and exceeding the desired amount [17].

3.1.4. Compressive strength tests via UCA

Compressive strength development was assessed by an ultrasonic cement analyzer. This method is especially useful to show the desired swift compressive strength development, which is important to minimize standing times in field application. The Na-EDTMP/borax system is known to possess these desired properties as long as the Na-EDTMP dosage is under certain concentrations [28]. The results are shown in Table 7 and an exemplary graphical illustration is presented in **Figure A 2, SI**.

In comparison to the reference slurries, with retarder addition a swift compressive strength development is observed. High compressive strength values for all samples are comparable after 72 h. Interestingly, compressive strength development within the first

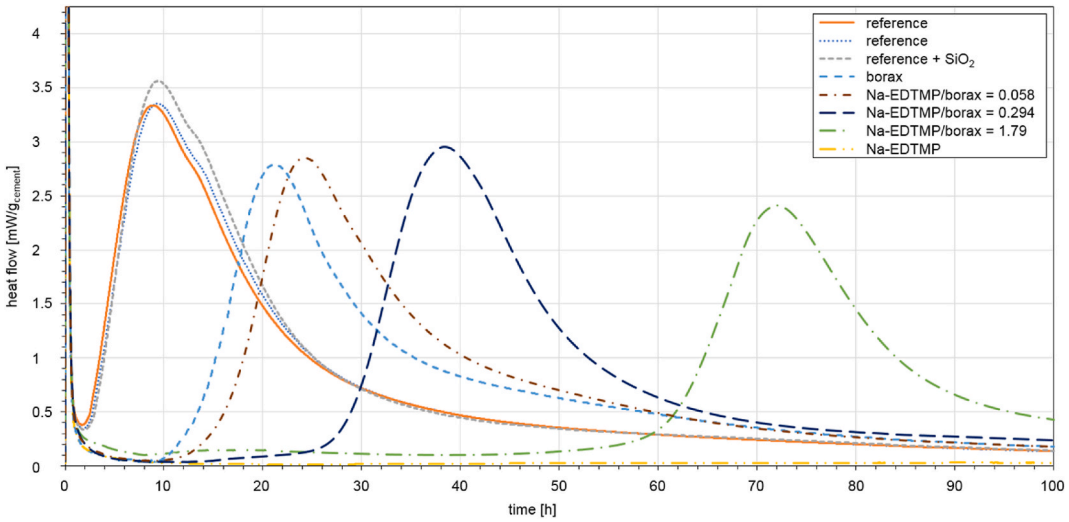

Fig. 1. Isothermal heat flow calorimetry measurements of cement slurries with different retarder ratios at 27 °C for 450 h (cut after 100 h). Total retarder dosages of 0.154 wt% were applied for all measurements except for the references.

Table 8
Thickening times for various high pressure and high temperature cement slurries containing different amounts and ratios of the retarders. P-1 and 2 were pre-experiments. * = gel formation.

sample	T [°C]	Na-EDTMP [% bwoc]	borax [% bwoc]	total dosage [% bwoc]	Na-EDTMP/borax ratio	TT 25 Bc [h:min]	TT 70 Bc [h:min]
H-1	119	0.22	0.748	0.968	0.294	07:17	07:42
H-2	132	0.28	0.92	1.2	0.304	06:36	07:34
H-3	145	0.4	1.292	1.692	0.310	06:56	08:00
H-4	160	0.42	1.36	1.78	0.310	08:42	09:12
P-1	171	2.5	0	2.5	/	n.m.*	n.m.*
P-2	171	0	1.5	1.5	/	/	0:37
H-5a						09:42	10:02
H-5b	171	0.47	1.46	1.93	0.322	12:01	12:05
H-5c						11:12	11:18
H-5d						10:22	10:30
H-6	180	0.53	1.646	2.18	0.322	10:36	10:44
H-6a	180	0.12	2.056	2.18	0.058	00:54	02:02
H-6b	180	1.396	0.78	2.18	1.790	01:25*	01:27*
H-7	190	0.62	1.85	2.47	0.335	13:24	13:30
H-8a						11:55	11:58
H-8b	196	0.67	1.97	2.64	0.340	09:59	10:18
H-8c						09:22	10:57
H-9	200	0.67	1.97	2.64	0.340	09:33	09:38

~12 h at 80 °C is delayed compared to 50 °C, although the same retarder concentration was applied which can be explained by the abnormal phenomenon mentioned before (chapter 3.1.1.) [42,44,45].

Summarizing, the Na-EDTMP/borax retarder system can be applied to retard cement slurries at temperatures below 85 °C. However, high dosage sensitivity and free water amounts limit application and suggest the use of other established retarder systems.

3.1.5. Isothermal heat flow calorimetry

The impact of the retarders on the hydration kinetics was measured *via* heat flow calorimetry and the results are shown in Fig. 1.

Heat flow measurements clearly show the extension of the dormant period caused by retarder addition as well as the higher retarding effect of Na-EDTMP compared to borax described by the mechanisms in the introduction. The slurry with solely Na-EDTMP – and therefore the highest Na-EDTMP dosage – showed extremely minor heat flow – illustrating hydration – within 450 h. These results support earlier research reporting many phosphonate-based retarders as super retarders, especially due to their extremely effective blocking of nuclei growth sites [46–48].

The width of the heat flow peaks for the retarded slurries is similar to those of the references, supporting the assumption that the hydration process itself is not significantly influenced by the retarders, only delayed. With a higher Na-EDTMP/borax ratio of 1.79 the overall heat flow is slightly lower compared to the sample with a ratio of 0.294. This could be caused by a higher amount of Ca which is permanently bound by the EDTMP ion and not available for heat generating C-S-H formation.

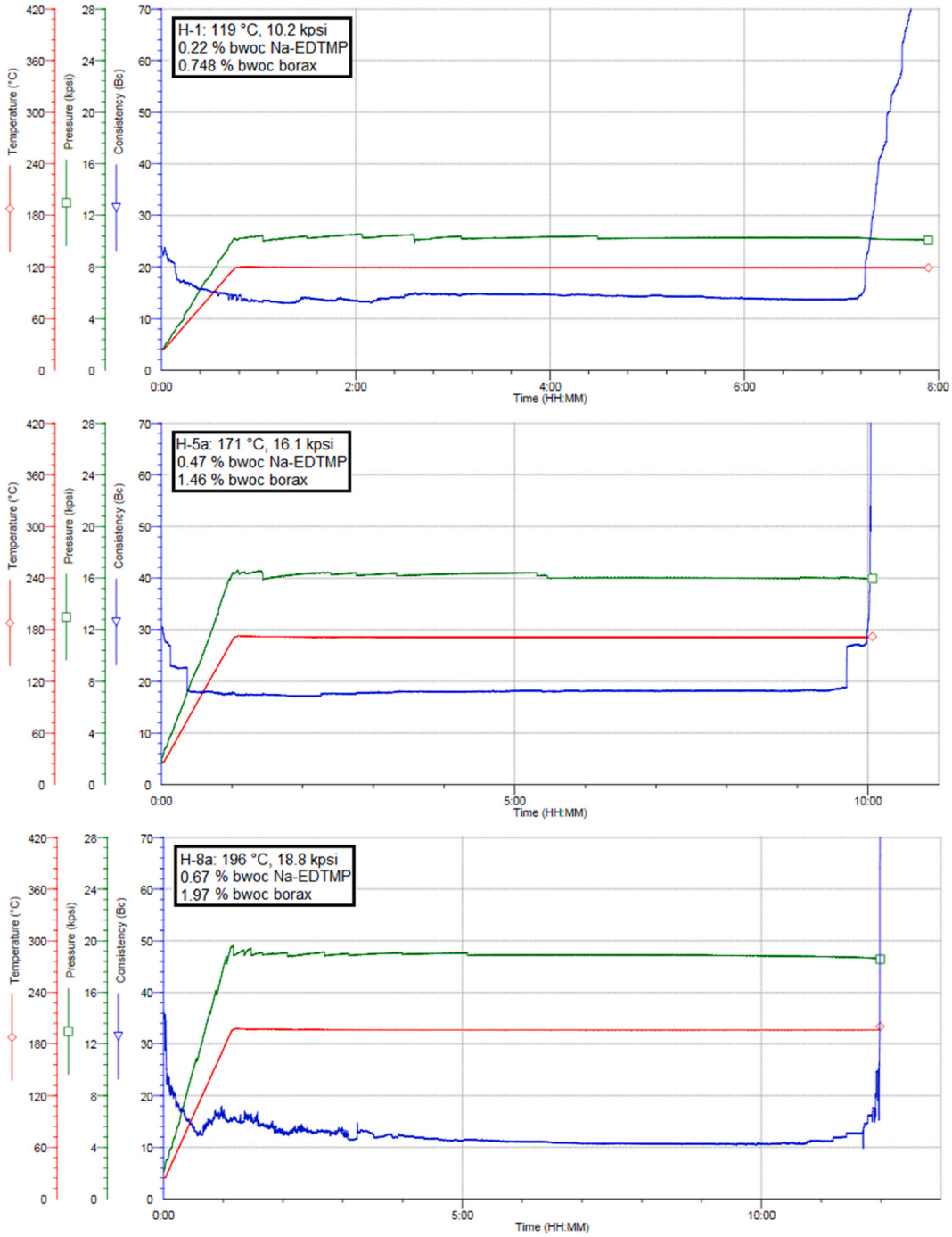

Fig. 2. HP/HT consistometer measurements at 119, 171 and 196 °C of exemplary HP/HT slurries.

3.2. High pressure/high temperature investigations

With temperatures exceeding 120 °C and especially >140 °C, achieving the desired slurry properties like sufficient thickening times, constant pumpability, high slurry stability, a decent initial viscosity as well as a swift compressive strength development are challenging. First published data shows promising properties of the Na-EDTMP/borax retarder system with TT's of >7 h at up to 232 °C. However, only very little additional data was given [28].

Hence, this work will give a comprehensive study about the Na-EDTMP/borax system by showing its potential at up to 200 °C by achieving at least 7 h of TT. Furthermore, the viscosity, slurry stability and hydration behavior will be monitored to give further

insights into the Na-EDTMP/borax retarder systems mechanical properties.

3.2.1. HP/HT consistometer tests

HP/HT consistometer tests were performed at various high pressures and temperatures to assess exemplary concentrations for the retarder system to obtain both, a sufficient thickening time from 7 h up to 13 h and a constant low viscosity to ensure sufficient pumpability [49] without occurring sedimentation (Table 8). Supplementary data is presented in Table A1**, SI** and Figures A2 and 3.

With higher temperature, the total dosages were increased from 0.968 % bwoc (119 °C) to 2.64 % bwoc (196/200 °C). In comparison to earlier literature [28,30], significantly higher Na-EDTMP/borax ratios were applied (see also chapters 3.1.5 and 3.2.1). As a result, longer TT's of 7 up to 13 h were achieved at comparable total dosages, especially when considering that in prior literature a Class H cement was used – showing already longer TT's by itself – compared to a Class G cement used in this work [28,30]. Additionally, further experiments (Table A1, **SI)** as well as the experiments H-6, a and b show that a higher Na-EDTMP/borax ratio of around 0.322 at a constant total retarder dosage possesses a significantly more pronounced retarding performance. This is most probably caused by the higher concentration of the far more effective Na-EDTMP retarder and increased synergetic effects between both retarders. However, too high Na-EDTMP dosage leads to enhanced gel formation and early increasing TT's without hardening of the slurry (P-1).

The slight increase of the Na-EDTMP/borax ratio with increasing temperatures from 0.294 to 0.340 only showed some impact at temperatures ≥190 °C. For example, at 171 °C, no significant differences in using a ratio of 0.294 instead of 0.322 (S-11, Table A1, **SI** and H-5a, Table 8) were found. Due to the starting degradation of Na-ETMP at temperatures >180 °C, increasing Na-EDTMP/borax ratio counteracts slightly [50]. For example, applying a ratio of 0.294 and similar total dosage as in measurement H-8a (Table 8), TT decreases significantly (S-17**,** Table A **1, SI**). At 200 °C, TT's cannot be further increased with more retarder added because of high Na-EDTMP degradation and strong gel formation increasing the initial viscosity as shown in **Figure A 4, SI** with a total retarder dosage of 4.4 % bwoc.

It is assumed that the synergetic effects are caused by the combination of the partly different retarding mechanisms of the two retarders [12–16,32–34]. In the beginning the already dissolved Na-EDTMP could directly form complexes with the Ca^{2+} ions of the clinker phases, slowing down clinker dissolution rate. The borax dissolves and forms Ca borate compounds while buffering the pore solution and decreasing Si-solubility by lowering the pH-value. In opposite to the fast-reacting EDTMP, borax could have some kind of depot effect [14]. With ongoing heating and dissolution of the clinker phases the Na-EDTMP preferably binds to Ca^{2+} ions at freshly formed C-S-H phases, slowing down their growth by nuclei poisoning. Meanwhile the Ca borate compounds precipitate onto the clinker grains and freshly formed C-S-H phases, thus minimizing "reactive" sites. This results in a higher sufficiency of the Na-EDTMP by "blocking" remaining C-S-H sites which delays setting of the slurry for longer time periods. Because of the HSAB concept it seems reasonably, that the $EDTMP^{-}$ ion binds more likely directly onto the surface due to higher charge density and the borate ion forms compounds with dissolved Ca^{2+} ions in the solution [34]. At some point, when the retarder is fully saturated and the Ca borate layer breaks, fast cement hydration reactions continue.

Solely addition of borax is far less effective because assumably clinker dissolution is less hindered in the beginning (borax has to be dissolved first) and the layer from precipitated Ca borate is most likely not "sealed" enough to hinder C-S-H growth effectively (see P-2).

Use of Na-EDTMP is limited by gel formation. At dosages necessary for sufficient TT's at higher dosages, initial viscosity would be increased too much (P-1 and H-6b).

Similar to experiments at moderate temperatures but less pronounced, the retarder system shows high sensitivity with a variation of ± 1–2 h regarding the TT at constant dosage (see samples H-5 a-d and H-8 a-c). Device-related errors like varying parameters during heating might have some impact. However, highly unpredictable variations of the TT's as mentioned by Casabonne et al. were not observed [28].

Fig. 2 shows exemplary HP/HT consistometer measurements and consistency developments of HP/HT slurries at 119, 171 and 196 °C to visualize the viscosity of the slurry during heating and simulated pumping times. Additional diagrams are presented in **Figure A 2** and **A 3, SI**.

At all temperatures, the initial viscosity remained at < 40 Bc, a desired consistency for field application. With higher retarder dosages (>1.93 % bwoc), the slurry started to slightly form a gel-like consistency directly after blending, therefore causing slightly increased initial consistencies.

Furthermore, at temperatures >100 °C significantly higher retarder dosages were needed in comparison to the moderate conditions. Still, minor thermal thinning during the heating process in comparison to polycarboxylate-based retarders as observed [19]. Initial viscosities decreased to about 10–25 Bc, indeed being ideal for field application. The consistency stayed constant throughout the whole measurement and showed a swift setting which is more pronounced at higher temperatures.

3.2.2. Rheological measurements

Rheometer measurements for the HP/HT slurries were performed at up to 80 °C. Measurements >80 °C showed high variations regarding PVs and YPs, probably caused by increased free water formation and therefore varying densities of the slurries due to the static environment within the testing apparatus. Nevertheless, HP/HT measurements showed that the most significant changes in consistency appear below 80 °C.

Furthermore, PVs and YPs were calculated (Chapter 2.5) and depicted in Table 9. The supplementary data is shown in Table A2**, SI**.

With increasing temperature, the PV decreases between 27 and 50 °C and less between 50 and 80 °C. In accordance with HP/HT results which show only little changes in pumpability at temperatures >80 °C a final PV > 0.2 Pa s can be expected for higher

Table 9
PVs and YPs of the HP/HT slurries at temperatures at up to 80 °C and at 1 kpsi N_2 pressure. Samples H 8 and 9 have the same composition.

	T [°C]	sample							
		H-1	H-2	H-3	H-4	H-5	H-6	H-7	H-8/9
PV [Pa·s]	27	0.94	0.93	0.97	1.00	0.98	1.03	0.95	0.96
	50	0.70	0.61	0.70	0.70	0.68	0.71	0.62	0.65
	80	0.54	0.46	0.48	0.56	0.60	0.58	0.44	0.57
YP [Pa]	27	0.07	0.05	0.09	0.08	0.08	0.10	0.14	0.15
	50	0.11	0.12	0.11	0.09	0.11	0.10	0.11	0.12
	80	0.17	0.14	0.15	0.12	0.12	0.12	0.16	0.15

Table 10
Free water amounts at 80 °C and density of HP/HT slurries. Samples H-8 and 9 have the same composition.

sample	free water [wt. % (g)]	density [g/mL]
H-1	2.3 (4.6)	2.01
H-2	2.0 (4.0)	2.00
H-3	1.9 (3.9)	2.00
H-4	1.8 (3.6)	2.01
H-5	1.6 (3.3)	2.02
H-6	1.6 (3.3)	2.01
H-7	1.5 (3.2)	2.02
H-8/9	1.7 (3.4)	2.00

temperatures, suitable for field-use. In contrast to the measurements at moderate conditions (chapter 3.1.2), the YPs of the slurries with lower retarder dosages increase with increasing temperature. This might be caused by free water formation and therefore slurry density increasement. At higher dosages, gel formation reduces free water formation also shown by increasing YPs at 27 °C with increasing dosage. This phenomenon of "abnormal gelation" can be observed by several polycarboxylate-based retarders, where it is assumed that through the high temperatures polymer structures can change as well as their interaction with the cement grains and the hydration products. The exact mechanisms of this complex systems are not understood completely yet [24]. Nevertheless, in case of the shown Na-EDTMP/borax retarder systems, such processes seem to only play an insignificant role, not endangering the pumpability but even more enhancing the slurry stability/counteracting thermal thinning in a reasonable scale.

Overall, within the tested area, the influence of the dosage on the slurry's PV and YP is low.

3.2.3. Free water and density of the HP/HT slurries

In Table 10 free water and densities of the HP/HT slurries are depicted.

The free water amount decreased with increasing retarder dosage until a plateau is reached at 1.6 ± 0.2 wt% which can be explained by a gelation effect of the retarder (chapter 3.2.2.), enhancing slurry stability.

This is an acceptable value for vertical wells, whereas for horizontal wells all free water amounts are significantly too high [43].

3.2.4. Slurry stability tests

Slurry stability is examined by sedimentation tests within HP/HT measurements at 160 and 190 °C presented in Fig. 3. Particle sedimentation is expressed by the formation of spikes after the off-cycles.

At 160 °C no hints for sedimentation can be observed. The spike after around 9 h was caused by beginning setting of the slurry. Interestingly, in contrast to the measurement without off-cycles (H-4, chapter 3.2.1.), the viscosity of the slurry increased within the measurement and does not stay constant. Most probably, this was not caused by a rapid increase of the slurry's viscosity itself, but a technical issue due to the limitations of the device. Due to the pressure changes, cement slurry might be pressed between sealing and mixing shaft. Nevertheless, the results confirm high slurry stability.

At 190 °C, after 9 h a small spike occurred, indicating minor particle settling. After the third off-cycle, a general increase in viscosity can be observed as before.

Summarizing, the Na-EDTMP/borax retarder system alone shows high slurry stability at elevated temperatures with only minor thermal thinning. The slight gel formation described in the chapters before might be advantageous for mitigating thermal thinning while enabling sufficient pumpability.

3.2.5. Compressive strength development via UCA

Similar to the results from chapter 3.1.4 (moderate temperatures), swift compressive strength development can be achieved. Measurements up to 160 °C were performed shown in Table 11. An exemplary diagram of an UCA measurement is presented in **Figure A 5, SI**.

Compressive strength of 50 psi is reached at around 2–3 h after a TT of 70 Bc was measured (Table 8), indicating similar hydration behavior in static (UCA measurement) as well as dynamic (HP/HT test) conditions. Final CS after 72 h is reasonably high with >40 MPa

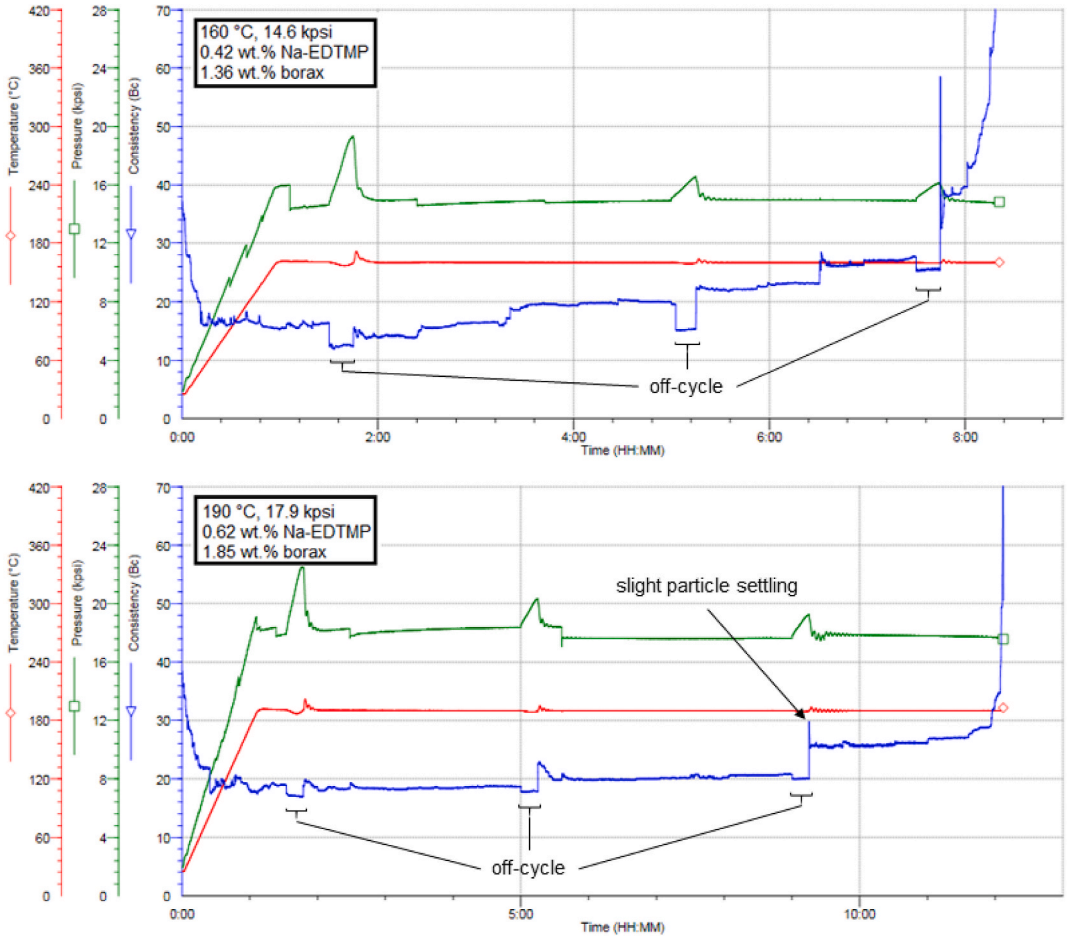

Fig. 3. Slurry stability tests at 160 (top) and 190 °C (bottom) during HP/HT consistometer measurements. Off-cycles were applied for 15 min after 1.5, 6 and 9 h to show appearing sedimentation of the cement particles. Pressure was not adjusted during the off-cycles.

Table 11
Compressive strength development of HP/HT slurries at various temperatures and 3 kpsi.

sample	T (BHST) [°C]	CS 50 psi (0.35 MPa) [h:min]	CS 500 psi (3.5 MPa) [h:min]	CS 24 h [psi, (MPa)]	CS 72 h [psi, (MPa)]
H-1	119	12:35	13:40	5104 (35)	6237 (43)
H-2	132	10:51	11:43	2975 (21)	6503 (45)
H-3	145	13:55	14:37	3421 (24)	6277 (43)
H-4	160	12:43	13:16	4573 (32)	6789 (47)

for all measured slurries.

3.2.6. Addition of fluid-loss additives

For field application it is often necessary to add fluid-loss control additives to the slurry to avoid loss of water by capillary drain of the porous environments. Depending on the well job, fluid-loss of <200 mL/30 min (oil wells), <50 mL/30 min (gas wells) or ~ 15 mL/30 min (special jobs) is required [51,52]. To demonstrate the compatibility of the Na-EDTMP/borax retarder system with common fluid-loss control additives, experiments using the commercial products HALAD 344 and 413 were conducted. A ratio of 1:2 (HALAD 344:413) and total amount of 0.9 % bwoc gave the best results regarding lowest fluid-loss (106 mL/30 min) combined with low initial viscosity and lowest thermal thinning. Additionally, no free water was observed at 80 °C, counteracting one drawback of the retarder system which originally was ~1.6 wt% at 80 °C (Table 10).

Increased fluid-loss additive dosages (1.2 % bwoc) decreased fluid-loss to below 50 mL/30 min but caused high initial consistencies (>60 Bc). However, at temperatures exceeding 50 °C the consistency decreased rapidly to <50 Bc.

To evaluate an impact on the retarding performance with fluid-loss additive addition, HP/HT measurements at 180 °C (comparison: H-6) with fluid-loss additives were performed (see **Table 12**).

Table 12
HP/HT measurements of slurries including fluid-loss additives.

sample	T [°C]	Na-EDTMP [% bwoc]	borax [% bwoc]	total retarder [% bwoc]	ratio Na-EDTMP/borax	TT 25 Bc [h:min]	TT 70 Bc [h:min]
FL-1	180	0.53	1.65	2.18	0.321	07:12	07:45
FL-2	180	0.62	1.85	2.47	0.335	13:10	13:13

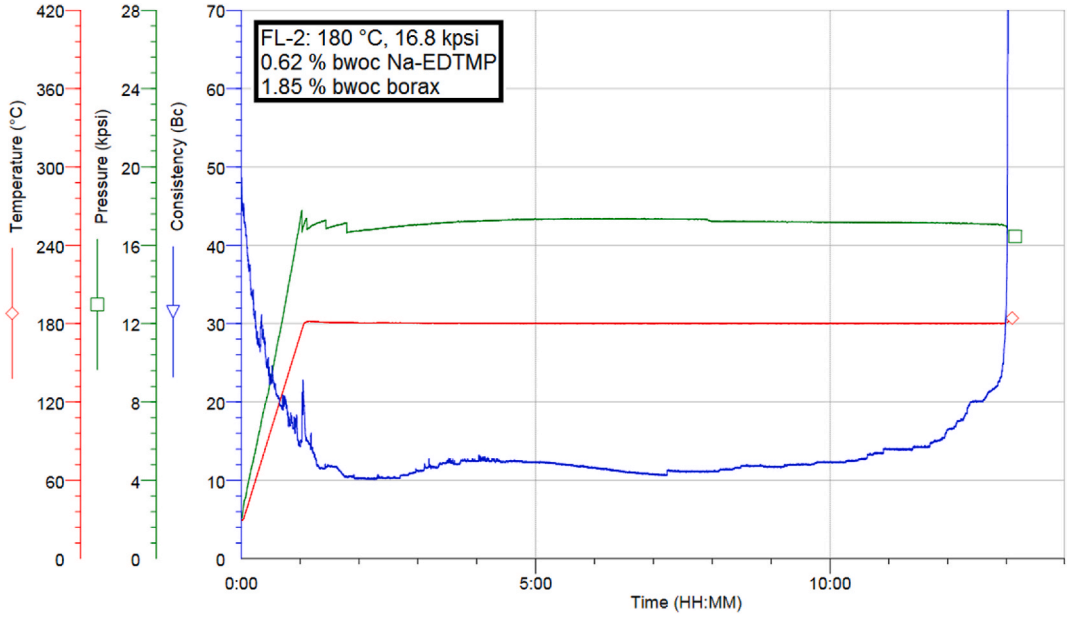

Fig. 4. HP/HT measurement at 180 °C of a retarded slurry containing HALAD 413 and 433 as fluid-loss additives.

Addition of fluid-loss additives decreased the TT's (FL-1). Nevertheless, with moderately increase of the retarder dosage (FL-2) TT's can be adjusted again as shown in Fig. 4. This could be caused by a slight competitive adsorption reaction between the fluid-loss additive and the retarder onto the cement grains as investigated with common retarders and fluid-loss agents by several authors [53,54].

In comparison to the previous slurries without fluid-loss additives, now the initial viscosity was slightly increased to nearly 50 Bc as a reason to the typical viscosifying properties of common fluid loss agents. Nevertheless, the consistency properties showed sufficient pumpability and no indication for sedimentation by Bc values < 10 Bc. Also, long TT's and swift setting of the slurry was obtained, displaying suitable properties for potential field application.

4. Conclusion

This work firstly shows a detailed study on the non-dispersing Na-EDTMP/borax retarder system for well cementing at pressures and temperatures up to 19 kpsi and 200 °C. Exemplary dosages for a variety of high temperatures and pressures were presented with sufficient thickening times and consistency properties, studied by atmospheric and HP/HT consistometer tests, rheological measurements, free water and density determinations and compressive strength development (UCA) tests. Heat flow calorimetry measurements displayed the retarders' effectiveness and additionally, slurry stability within HP/HT sedimentation measurements was confirmed. In the end, also fluid-loss control was investigated.

From the results it can be concluded that 1) the Na-EDTMP/borax retarder system is non-dispersing, preventing thermal thinning without the need of any anti-settling agent; 2) the system is applicable up to 200 °C with thickening times up to at least 13:30 h (at 190 °C). However, at higher temperatures Na-EDTMP degradation accelerates; 3) at temperatures of 120–200 °C a constant excellent pumpability (10–25 Bc) was achieved over 7–13 h with low initial consistencies (<40 Bc), followed by a swift setting and compressive strength development; 4) the main drawback of the system is the high sensitivity regarding retarder dosage, especially at moderate temperatures. Therefore, the final thickening time (TT) was only adjustable within a 2-h range; 5) in contrast to prior literature, higher ratios of Na-EDTMP/borax (0.294–0.340) were found to give better results regarding overall dosage, retarding effectiveness and consistency; 6) the YPs and PVs of the HP/HT slurries at up to 80 °C were only slightly affected by retarder dosage; 7) the free water amounts lay between 1 and 3 wt% and slurry density stayed constant independently of the applied retarder dosage without the need of any defoamer; 8) an improved slurry stability was confirmed by sedimentation tests at 160 and 190 °C; 9) an exemplary addition of common fluid-loss additives showed good compatibility and the possibility to obtain sufficient fluid-loss values by retaining desired

consistency properties.

In future studies, a fully formulated oil well cement system based on the Na-EDTMP/borax retarders and the fluid-loss experiments should be examined. For example, different fluid-loss additives could be tested and the whole system optimized regarding sufficient TT's, pumpability properties and fluid-loss control. Furthermore, mechanistic studies, especially considering both retarders would be of high interest. High temperature in-situ X-ray diffraction (XRD) or scanning electron microscopy (SEM) measurements could be possible methods. We hope that this study will help to make this advantageous system more accessible for field application and improves wellbore stability for high temperature jobs.

Data and code availability statement

Data included in article/supplementary material is referenced in the article.

CRediT authorship contribution statement

Dominik Staude: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Johann Plank:** Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e38921.

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