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## **Advanced Cementing Systems for Deep Sour Gas Wells**

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### **Abstract**

Cementing deep sour gas wells presents a number of challenges to well construction engineers. High bottom hole static temperature (BHST from 250 to 400°F) and pressure (mud density > 2.0 g/cm<sup>3</sup>), excessively long job times due to the constraints imposed by tight annular clearances (casing OD/hole size > 0.85), long cement columns (interval length > 450 ft), and harsh conditions (H<sub>2</sub>S, CO<sub>2</sub>, salt layer, high leakoff). All of these factors contribute to the operational risks not only during placement of the cement slurry in the wellbore, but also during the life of the well. Field data indicates that current cement systems were not able to address these challenges, and as a result, the outcome obtained from various cementing jobs was below expectation.

Advanced cement systems were developed to address the problems encountered in cementing deep sour gas wells. These systems were applied in the field with great success. Multi-functional fluid migration control systems together with engineering particle sizing technique significantly improved the performance of cementing jobs, including: superior fluid migration control, predictable thickening time, stable API properties at high slurry densities, and great resistance to H<sub>2</sub>S, CO<sub>2</sub> and salt corrosion. A unique retarder used in the lead slurry helped in developing compressive strength rapidly on the top of cement column. An effective laminar flow displacement technique was also used to displace drilling fluids effectively to enhance its placement and improve the cementing bond.

This paper details a thorough and systematic laboratory development of innovative cement systems and presents case histories to document their effectiveness for cementing deep sour gas wells.

### **Introduction**

Engineers pay more attention to the exploration and development of gas reserves due to the increasing demands of hydrocarbon resources in the last decades. However, most gas reserves in the world contain sour gases such as H<sub>2</sub>S and CO<sub>2</sub>. It is reported that more than 40% of deep sour gas reserves contain more than 2 mol% CO<sub>2</sub> and more than 100 ppm H<sub>2</sub>S (Arnold 1980).

Cementing high temperature deep sour gas wells presents a number of challenges to well construction engineers. High bottom hole static temperature (BHST from 250 to 400°F) and pressure (mud density > 2.0 g/ml), excessively long job times due to the constraints imposed by tight annular clearances (casing OD/hole size > 0.85), long cement columns (interval length > 450 ft) all contribute to the operational risks not only during placement of the cement slurry in the wellbore, but also during the life of the well.

Sour gases such as H<sub>2</sub>S and CO<sub>2</sub> bring additional challenges to deep gas well cementing. A few studies have been conducted to examine the effects of H<sub>2</sub>S on oil well cementing due to its high hazards and risks. Several studies however, are available that investigate the impact of CO<sub>2</sub> on oil well cements (Newton and Hausler 1984; Onan et al. 1984). H<sub>2</sub>S has destructive effect on oil well cements because it reacts with metal hydroxides in cements and forms metal sulfides, which could cause collapse of set cements (Guo et al. 2004).

On the other hand, gas migration control must be considered in cementing deep sour gas wells. The gas migrating paths must be eliminated by introducing various gas migration control mechanisms during cementing operations. These mechanisms include: (1) Ensure hydrostatic pressure greater than formation pore pressure, (2) Avoid formation of orifice or channels in annulus, and (3) Reduce permeability of set cement. Following slurry and set cement properties have to be maintained in order to provide the above gas migration control mechanisms. (1) Maintain less than 50 ml API fluid loss of cement slurry and thin, hard, impermeable filter cake (Carter and Slage 1984; Christian et al. 1976). (2) Avoid reduction of hydrostatic pressure caused by gel strength development (Cook et al. 1983) and chemical shrinkage (typically 4%) during cement hydration (Setter

and Roy 1987). (3) Reduce permeability of set cement and increase the displacement efficiency to avoid any mud channels connected to the formation in either set cement or cement slurry. (4) Avoid micro-annulus or mechanical failures due to variation of well temperature, pressure and formation stress during well operations.

Many chemical and mechanical techniques, such as isolation tools, right-angle set cement, expansive and flexible cement, and low fluid loss and low permeability cement systems, are utilized to avoid gas migration and sour gas corrosion on oil well cement. Low permeability and low fluid loss cement systems show more advantages among these techniques due to its gas migration and corrosion control effectiveness and wide range of application conditions.

New cement slurry systems were developed to address the problems encountered in cementing deep sour gas wells. A novel latex gas migration control system together with anti-corrosion techniques significantly improve the performance of cementing jobs, including: superior gas migration control, predictable thickening time and right angle setting, stable API properties at different slurry densities (low, regular and high densities) without chemical shrinkage, and great resistance to H<sub>2</sub>S, CO<sub>2</sub> and salt corrosion. A unique retarder used in the lead slurry helps to develop compressive strength rapidly on the top of cement column. An effective laminar flow displacement technique (Wan et al. 2010) was also used to displace drilling fluids effectively to enhance its placement and improve the cementing bond.

This paper details a thorough and systematic laboratory development of innovative cement systems and present case histories to document their effectiveness for cementing deep sour gas wells.

## Experimental Studies

### Apparatus and Materials

Standard experimental equipment were used and listed in **Table 1**. Except for special additives (from OPT Co.) and hollow microspheres (from 3M), cement, weighting agents, and cement extenders are provided by local suppliers, who supply the same materials to field operations (**Table 2**).

**Table 1: Experimental Apparatus and Equipment.**

Properties	Equipment	Model	Provider
Compressive Strength	Programmable Hydraulic Press	YAW-300B	S.G. Instrument
	High Temperature High Pressure Curing Chamber	HTD7370	Haitongda Instrument Co.
Viscosity	Fann Viscometer	35SA	Fann Instrument
Fluid Loss	Static Fluid Loss Cell	HTD7169	Haitongda Instrument Co.
	Atmospheric Consistometer	HTD1200	Haitongda Instrument Co.
Thickening Time	High Temperature High Pressure Consistometer	HTD8040	Haitongda Instrument Co.
Rheology	High Temperature High Pressure Rheometer	GRACE7500	GRACE Instrument
H <sub>2</sub> S corrosion	High Temperature High Pressure Corrosion Cell		Southwest Petroleum Univ.
Permeameter	Gas Permeability Tester	HKGP-3	Southwest Petroleum Univ.
Gas Migration	Cement Hydration Analyzer	7200 CHA	Chandler Engineering

**Table 2: Materials**

Name	Function	Provider
Oil well cement, class G	Cement	Local suppliers
Microsilica	Extender	
Hematite (sized or non-sized)	Weighing Agent	
Silica Flour	Anti-retrogression Agent	
Hollow Microspheres	Extender	3M
KCM012	Dispersant	OPT Co.
KCM028	Fluid Loss Agent	
KCM026	Retarder	
KCM018	Stabilizer	
KCM027	Anti-corrosion agent	
KCM004	Spacer	

### Procedures

Testing cement slurries follows procedures described in API RP10B. Tests include slurry preparation, free water, density, compressive strength, viscosity, thickening time, and fluid loss.

### H<sub>2</sub>S and CO<sub>2</sub> Corrosion Experimental Procedures

(1) Set cement preparation. Prepare three cement slurries according to API 10B procedures and place them into curing chamber at 20.7 MPa pressure and 145°C (raise temperature from ambient to 122°C in 2 hours and then raise it from 122°C to 145°C in another 2 hours). Cure cement samples for 48 hours before taking them out for testing.

(2) Core sample preparation. Measure cement compressive strength using 2 in. cured cement samples according to API 10B procedures and prepare core samples ( $\Phi = 25 \text{ mm} \times L = 50 \text{ mm}$ ) from set cement to conduct gas permeability and porosity testing (**Fig. 1A**) at 2.5 MPa confining pressure, 101.7 KPa atmospheric and  $\text{N}_2$  gas viscosity 0.01785 mPa•s.

(3)  $\text{H}_2\text{S}$  and  $\text{CO}_2$  corrosion testing. Open corrosion cell (**Fig. 1B**) and inject distilled water before placing set cement samples into the cell. Close the cell and apply  $\text{H}_2\text{S}$  up to 1.7 MPa before further fill the cell with  $\text{CO}_2$  up to 2.7 MPa. Total pressure of 10 MPa is reached by adding  $\text{CH}_4$  to the cell and finally heat up the cell to  $145^\circ\text{C}$  and maintain temperature and pressure for 7 days.

(4) Measure and record compressive strength, porosity and permeability of cement samples, and observe samples after  $\text{H}_2\text{S}$  and  $\text{CO}_2$  corrosion.

### Gas Migration Control Testing Procedures

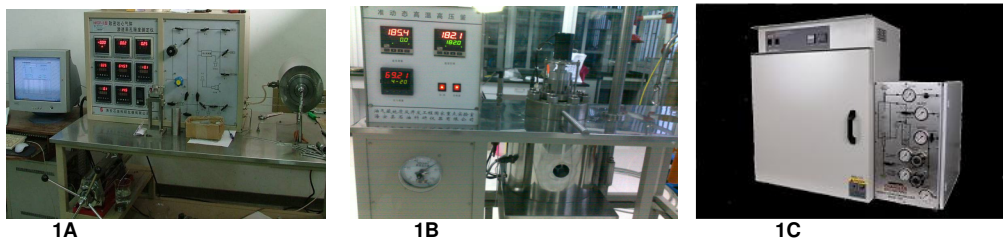
(1) Prepare equipment (Gas Hydration Analyzer Chandler Engineering Model 7200, **Fig. 1C**) as described in equipment manual and load cement slurry.

(2) Raise water confining and injection pressure to about 300 psi and 200 psi, respectively.

(3) Increase oven temperature as soon as possible to testing temperature  $122^\circ\text{C}$ .

(4) Start to control equipment with automatic mode so that gas injection could be started right after initiation of cement gel strength development.

(5) Record confining pressure, pore pressure, oven temperature, cement temperature, gas flow rate, and gas injection pressure.



**Fig. 1—Experimental Apparatus (1A—Gas Permeability Tester; 1B—Corrosion Cell; 1C—CHA 7200)**

## Results and Discussion

### API Properties of Advanced Cement Systems

API properties of advanced cement systems (formulation listed in **Table 3**) at three densities (1.30, 1.86, and  $2.35 \text{ g/cm}^3$ ) and bottom hole static temperature  $85\text{-}150^\circ\text{C}$  are summarized in **Table 4**. Slurries have typical plastic viscosity and yield point of 10-100 cp and 0 - 10 lb/100ft<sup>2</sup> respectively except for high density slurries (higher PV and YP). Normally no free water is observed for these slurries. Compressive strength of more than 7 MPa (24 hours) is obtained with low density slurries and more than 15 MPa obtained for regular and high density slurries at bottom hole static temperature. Typical thickening time of 2-10 hours can be adjusted by changing retarder concentrations.

**Table 3: Formulation of Advanced Cement Systems.**

Slurry	Cement BWOC%	Silica BWOC%	Fly Ash BWOC%	Extender BWOC%	W. Agent BWOC%	KCM012 BWOC%	KCM028 gps	KCM018 gps	KCM026 gps	KCM027 BWOC%
1	100		100	15		1	3.4	0.2		10
2	100		100	15		1	3.4	0.2		10
3	100		100			1	3.2	0.1		15
4	100		100			1	3.2	0.1		15
5	100	35				1	3.2	0.1	0.5	5
6	100	35				1	3.2	0.1	0.3	5
7	100	35				1	3.2	0.1	0.2	5
8	100	35				1	3.2	0.1	0.15	5
9	100				172	1	2.6	0.2		
10	100				172	1	3.2	0.05		

Synergistic effect between fluid loss agent, stabilizer and anti-corrosion agent (nano-particles) reduces fluid loss of cement systems significantly (less than 35 ml API fluid loss) and leads to form thin and hard filter cake for effective gas migration control.

Typical thickening time curves with various slurry densities are shown in **Figs. 2-4**. All thickening curves of advanced cement systems provide right-angle set behavior so that minimal (30-70 Bc developed in seconds) transition time is achieved for cement gel development and therefore reduces gas migration risks significantly.

In addition, the advanced cement systems can be used for all environmental-sensitive applications such as offshore cementing operations because major additives in the system are environmentally friendly.

Retarder used in the advanced cement system was effective and unique for cementing deep sour gas wells. It is not only insensitive to applicable conditions such as concentration, mixing water, temperature and pressure, and cement brands, but also provides synergistic effect with the fluid loss agent. As shown in **Fig. 5**, thickening time not only increases monotonically

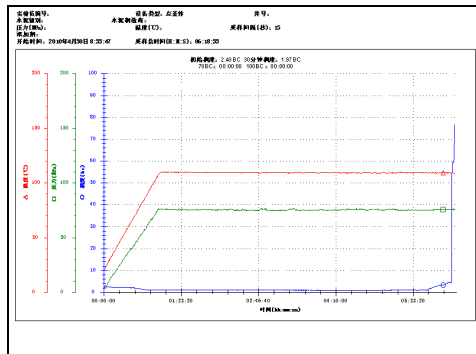
with increasing retarder concentration, but also insensitive to retarder concentration (about 0.1 gps KCM026 is required to extend thickening time from 210 to 280 min at 122°C). Typically, enough retarder is added into cement slurry to minimize operational risks in cementing deep sour gas wells. Consequently, slurry on top of the cement column is over-retarded due to much lower temperature at top of casing string or liner, resulting in excessively long WOC (wait-on-cement) time and risks of gas migration if high gas pressure presents. Therefore, retarder KCM026 is advantageous for cementing deep sour gas wells compare to other retarders because of its insensitivity to subtle concentration variation at high temperature.

### H<sub>2</sub>S and CO<sub>2</sub> Corrosion Tests

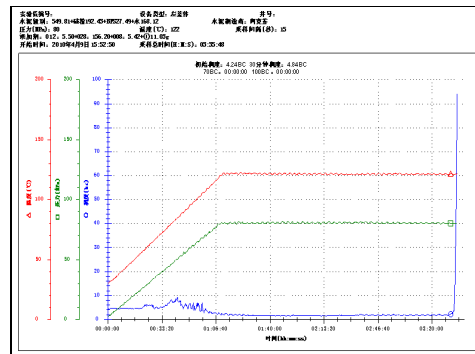
Compressive strength, porosity and permeability properties of set cement from different cement slurries are summarized in **Table 5**. Formulation of cement slurries are listed in **Table 6**.

**Table 4: API Properties of Advanced Cement Systems.**

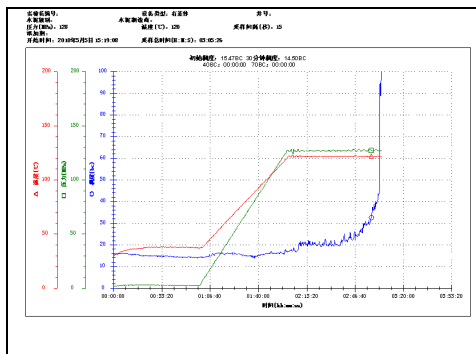
Slurry	Density g/cm <sup>3</sup>	BHCT °C	PV/YP, cp/lb/100ft <sup>2</sup>	API Fluid Loss ml/30min	Free Water ml	Thickening Time hr:min	24 h, C.S.	
							BHST, °C	MPa
1	1.3	110	6/0.5	32	0	6:18	130	7.0
2	1.3	110	7.5/2.5	30	0	4:08	130	
3	1.5	75	94/10	14	0	3:50	88	17.2
4	1.5	75	16/4	38	0	6:18	88	7.0
5	1.86	122	42/3	17	0	9:29	146	
6	1.86	122	81/13	22	0	4:52	146	
7	1.86	122	54/0.5	30	0	3:35	146	25.5
8	1.86	110	61/1	28	0	2:16	130	25.7
9	2.35	122	45/5	44	0	2:04	146	
10	2.35	122	117/73			3:05	146	



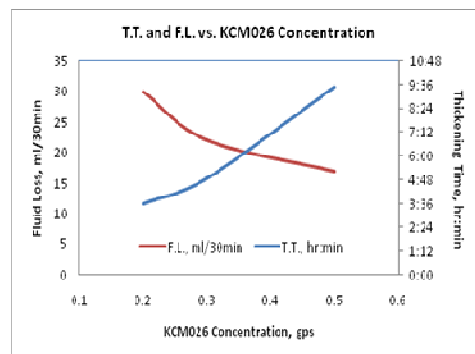
**Fig. 2—Low Density Slurry Thickening Time (1.3SG, 110°C BHCT).**



**Fig. 3—Regular Density Slurry Thickening Time (1.86SG, 122°C BHCT).**



**Fig. 4—High Density Slurry Thickening Time (2.35SG, 122°C BHCT).**



**Fig. 5—Relationship Between Retarder Concentration and Slurry Properties.**

Compressive strength values listed in **Table 5** indicate that set cement from gas migration control (2#) and anti-corrosion gas migration control systems (3#) show higher compressive strength than that from blank cement system (1#). After sour gas corrosion, set cement from blank system and gas migration control systems lost their compressive strength by 35% and 12% respectively, but cement compressive strength from anti-corrosion gas migration control system increases by 3%.

As shown in **Table 5**, permeability values of set cement from gas migration control and anti-corrosion gas migration

control systems are less than one tenth that of set cement from blank cement system. Accordingly, porosity values of set cement from anti-corrosion gas migration control systems is also much smaller than that from blank system and gas migration control system.

It is well known that high permeability and porosity can create gas flowing paths, which allow formation gas (including sour gases) to migrate into set cement and cause serious corrosion. Reduced permeability and porosity values by adding gas migration control and anti-corrosion control additives will certainly help to prevent sour gas from migrating and corrosion.

Meanwhile, synergistic effect between anti-corrosion agent and gas migration control additive in advanced cement systems provide stronger set cement even after sour gas corrosion so that no mechanical cracks or channels are formed for further gas migration and corrosion.

**Table 5: Properties of Set Cement Before and After Sour Gas Corrosion.**

Slurries	Compressive Strength (MPa)		Permeability (md) and Porosity (vol%)			
	Before	After	Before		After	
			Permeability	Porosity	Permeability	Porosity
1#	22.2	14.4	0.0467	29.3	0.0654	33.6
2#	25.6	22.4	0.0037	25.5	0.0065	28.7
3#	25.4	26.2	0.0025	17.2	0.0031	13.3

Note: 1#—Blank system; 2#—Gas migration control system; 3#—Anti-corrosion gas migration control system

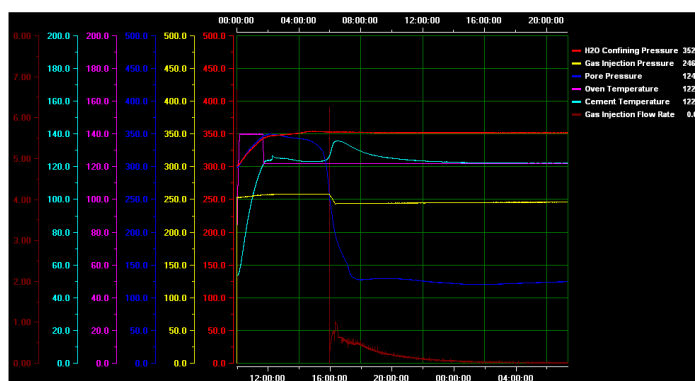
**Table 6: Formulation of Cement Systems.**

System	1#, g	2#, g	3#, g
Cement	573.04	569.77	569.77
Silica Flour	200.56	199.42	199.42
KCM012		5.70	5.70
KCM028		161.87	161.87
KCM018		2.81	2.81
KCM026		16.69	16.69 </td
KCM027			27.49
Fresh water	342.40 g	159.63 g	165.52

### Gas Migration Control Testing

Gas migration control effectiveness of advanced cement systems are evaluated with method described in experimental section and results are shown in Fig. 6.

As shown in Fig. 6, cement slurry starts gel development (light-blue line, exothermic peak) after about 4 hours at 122°C. Chemical shrinks taken place right after initiation of gel development reduces hydrostatic pressure significantly (dark blue line dropped from 350 to 125 psi). However no gas flow (red line) was observed after hydrostatic pressure loss even though constant gas injection pressure is maintained as 250 psi (yellow line). Results indicate that advanced cement systems perform effectively in gas migration control.



**Fig. 6—Evaluation of Gas Migration Control of Advanced Cement System.**

### Field Application

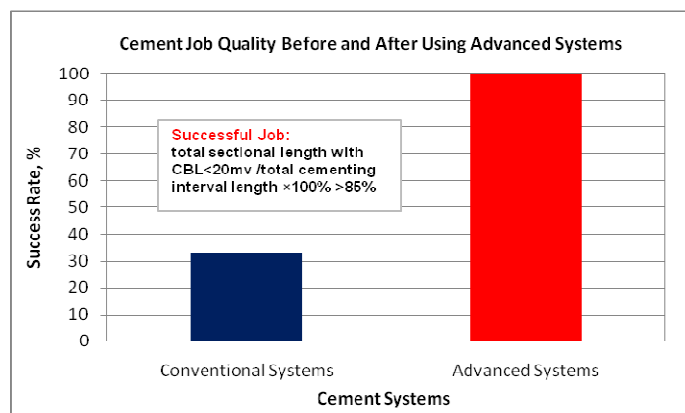
Innovative cement systems and the according laminar flow spacer systems were successfully used in deep sour gas exploration wells in Southwest China. Cementing programs are mainly liners at bottom hole static temperature ranging from 95°C to 125°C and density of 2.25-2.40 g/cm<sup>3</sup> (using both sized and regular weighting agents).

In order to quantitatively evaluate performance of novel cement system and laminar flow spacer, we define a cementing job with good bonding between cement and casing (Sonic signal at more than 85% of the cemented interval reads less than 20mV in CBL) as a successful job.

Five jobs in the same block were completed using advanced cement and spacer systems (2 jobs) and conventional cement and displacement techniques (3 jobs). Results shown in **Table 7** and **Fig. 7** indicate that job success rate increases from 33% to 100% by using advanced systems.

**Table 7: Summary of Field Application Cases.**

Well	Liner inch	Depth m	Density g/cc	Cement System	Results
A	6 5/8	7080	2.25	Conventional	Unsuccessful
B	10 3/4	5176	2.3	New	Successful
C	10 3/4	5176	2.35	Conventional	Unsuccessful
D	10 3/4	5089	2.2	New	Successful
E	10 3/4	4915	2.4	Conventional	Successful



**Fig. 7: Comparison of Job Success Rate Before and After Using Advanced Systems.**

### Conclusions

- (1) Both experimental and field application results indicate that the advanced cement system can be successfully used at density and temperature (BHST) ranging from 1.30 to 2.40 g/cm<sup>3</sup>, and 85 to 150°C, respectively. Advanced cement systems have typical plastic viscosity of 10-100 cp and yield point of 0-10 lb/100ft<sup>2</sup>. Normally zero free water and 24 hours compressive strength of more than 15 MPa is obtained for these slurries. Thickening time of 2-10 hours can be adjusted by changing retarder concentrations.
- (2) Less than 35 ml API fluid loss and thin and hard filter cake are available with advanced cement systems for effective gas migration control.
- (3) Right angle set behavior of advanced cement system minimizes duration of cement gel development and reduces the risks of gas migration.
- (4) Thickening time of advanced cement systems not only increases monotonically with increasing retarder concentrations, but also is insensitive to retarder loading. Such retarder insensitivity to subtle concentration variation not only favors the formulation of cement systems, but also reduces the operational risks of cementing deep sour gas wells.
- (5) Advanced cement systems not only develop its compressive strength rapidly, but also has no over-retardation on top of the cement column. Strength development insensitivity to temperature variation not only reduces wait-on-cement time, but also minimizes risks of formation fluid migration.
- (6) Synergistic effect of anti-corrosion agent and gas migration control additive in advanced cement systems not only reduces cement permeability and porosity significantly, but also increases cement compressive strength before and after sour gas corrosion. These mechanical and petro-physical properties of set cement improve its effectiveness in gas migration and sour gas corrosion control.
- (7) Results from gas migration tests indicate effectiveness of advanced cement systems in gas migration control.
- (8) Results of field cases indicate successful application of advanced cement systems. Job success rate increases from 33% to 100% using advanced cement and laminar flow spacer systems.

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## SI Metric Conversion Factors

gal	×	3.785238	E-03	=	m <sup>3</sup>
ft	×	0.333333	E+00	=	m
°F		(°F-32)/1.8		=	°C
lb	×	4.535924	E-01	=	kg
psi	×	6.894757	E+00	=	kPa

<sup>†</sup>Conversion factor is exact

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