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Rheology and Stability of Saudi Cement for Oil Well Cementing

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Abstract. The suitability of some locally produced cement for oil well cementing has been investigated by means of chemical and physical analyses of powder cement, rheology and thickening time of slurries, and the compressive strength of set cement. The stability of set cement surrounded by formation water of Saudi Oil fields at high temperature has also been discussed.

Nomenclature

C_3A	= tricalcium aluminate
C_2S	= dicalcium silicate
C_3S	= tricalcium silicate
CS	= calcium silicate
CA	= calcium aluminate
C_4AF	= tetracalcium alluminoferrite
CSA	= calcium sulfoaluminate
CF	= calcium ferride
CCLA	= calcium chloroaluminate
NaF	= Sodium ferride
WCR	= water-cement-ratio
τ	= shear stress
K'	= consistency index
n'	= flow behavior index
dv/dr	= shear rate

1. Introduction

Although millions of sacks of portland cement are used each year to cement oil and gas wells, this material can not stand for the severe well conditions. Variations in the composition of the natural products used to manufacture portland cement and the need to use many additives to extend its working range are the two factors that provide an incentive to search for suitable alternatives [1].

The measurements of the rheological characteristics of slurries used for cementing is a relatively simple method of analyzing the flow conditions existing in the well during cementing operations. Fluid properties of the slurry to be used should be available to determine what flow rates and consequently frictional pressure and horsepower should be attained [2,3].

Also, the common oil field brines, due to its content of magnesium and sodium sulfates have detrimental effects on cement hydration products. These sulfates react with the lime in the cement to form magnesium or sodium hydroxide and calcium sulfate. This latter reacts with the tricalcium aluminate to produce calcium sulfoaluminate which causes the cement to expand and disintegrate [4,5].

This work presents the rheological properties and the stability of a local produced cement to evaluate its use in oil and gas wells cementing.

2. Experimental Determination

Powder testing involves the chemical analysis and investigation of the physical properties of the local cement. The chemical composition of cement is obtained by the flame atomic absorption spectrophotometry method. The particle size or fineness is determined by the Blain permeameter by converting the permeability value into specific surface area expressed in sq. cm. per gram of cement.

The FANN V-G meter is used to measure shear stress in the presence of several pre-selected fixed shear rates. FANN dial readings and rotational speeds are converted to shear stress in lb/100 ft^2 and shear rate in sec^{-1} respectively. Once the flow mode is determined by plotting shear stress against shear rate, the parameters of the fluid: Plastic viscosity (μ_p) and yield point (τ_y) for Bingham Plastic, or flow behavior index (n') and consistency index (K') for the power law can be calculated [6]. The consistometer is used for determining the thickening time of slurries prepared by using sea water and common additives.

3. Results and Discussion

The physical and chemical properties of cement are reported in Table 1.

The number of various types of additives used in any given cement job is directly related to the depth, temperature, and type of formation encountered in the wells. With the large variety of additives in existence and the wide range of well conditions possible, some limitations had to be imposed on what was to be studied in this work.

Table 1. Physical and chemical analyses of the tested cement

Air permeability cm^2/gm	3000.00
Autoclave expansion (%)	0.07
Density (gm./cc.)	3.15
Air content (% volume)	6.00
Initial setting time (mn.)	140.00
Final setting time (mn.)	190.00
Loss of ignition (LoI)	1.20
Insoluble residue (IR)	0.30
SiO_2	19.22
Al_2O_3	6.63
TiO_2	0.35
Fe_2O_3	3.42
CaO	65.25
MgO	0.85
SO_3	2.37
K_2O	0.09
Na_2O	0.10

The shear stress-shear rate and the plastic viscosity against shear rate are investigated by using different water cement ratio (sea water is used as continuous phase) as well as by adding various percentages of common oil well cement additives (Figs. 1-4).

The sea water slurry starts to behave, in the likeness of a Bingham fluid as soon as initial pressure is applied, but does not follow the characteristic Bingham Plastic proportionality between shear stress and shear rate. The shear stress-shear rate relation (Figs. 1 and 2) follows the Power Law model represented by the equation

$$\tau = K' \left(\frac{dv}{dv}\right)^{n'}$$

The additions of the common cement accelerators, retarders, and extenders do not affect the shape of the rheograms. However, for the same shear rate, the shear stress increases with the addition of the accelerator ($CaCl_2$) and decreases with the addition of the retarder (HR-4) and the extender (bentonite). On the other hand, the viscosity also decreases by the increase of water cement ratio and the addition of lignosulfonates (HR-4) and calcium chloride ($CaCl_2$). (Figs. 3 and 4). It is well known that the chemically originated component of a fluid's apparent viscosity is lowered using various additives as dispersants: *e.g.* lignosulfonates, polyphosphates and organic acids which exactly coincides with our results. The flow behaviour index and consistency index are given in Table 2.

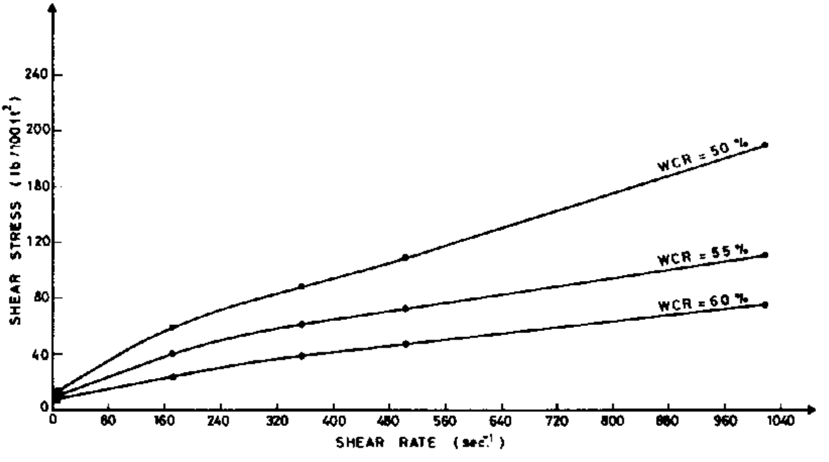

Fig. 1. Effect of water-cement-ratio on shear stress-shear rate relationship of slurries

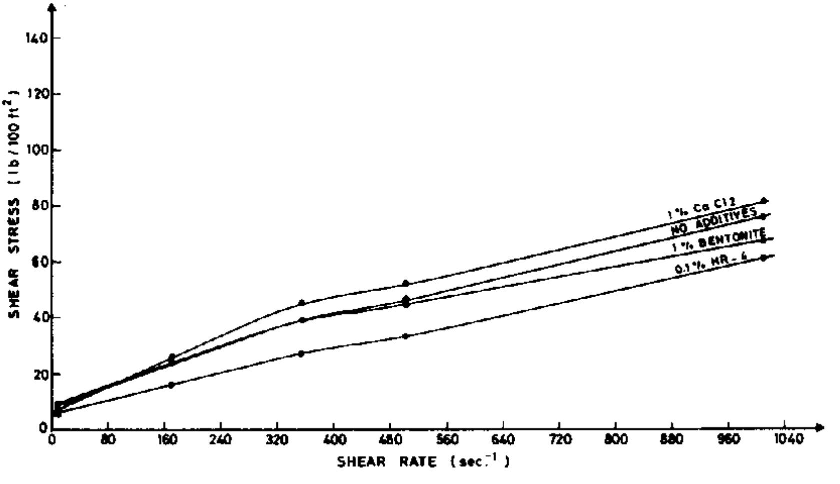

Fig. 2. Effect of cement additives on shear stress-shear rate relationship of slurries

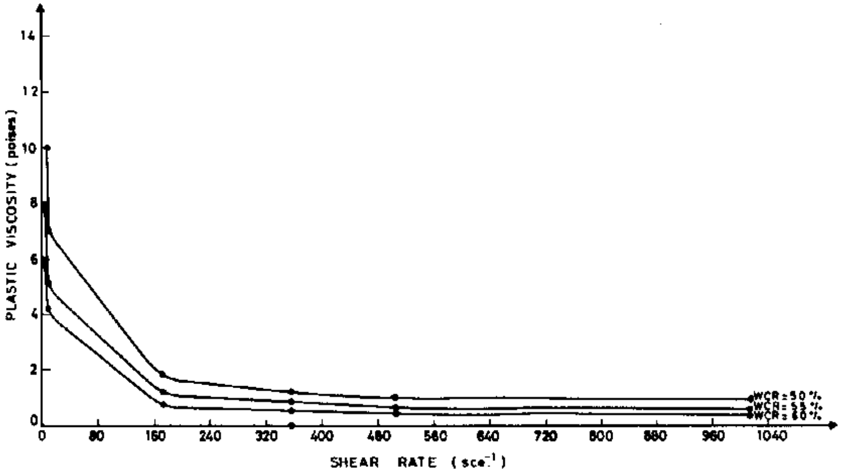

Fig. 3. Effect of water-cement-ratio on plastic viscosity of slurries

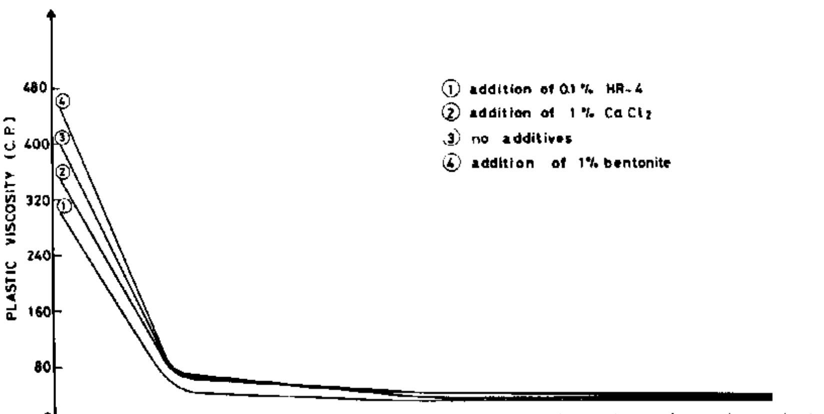

Fig. 4. Effect of cement additives on plastic viscosity of slurries

Table 2. Flow behaviour index (n') and consistency index (K')

Sample No.	Water type	WCR (%)	Additives used	K'	N'
1	Distilled water	60	–	2.958	0.445
2	Distilled water	55	–	3.656	0.482
3	Distilled water	50	–	4.446	0.521
4	Sea water	46	0.1% HR-4	2.339	0.432
5	Sea water	46	1.0% $CaCl_2$	2.576	0.443
6	Sea water	51	1.0% Bentonite	4.416	0.421

The addition of bentonite also decreases the slurry density from 15.6 (0% bentonite) to 13.8 ppg (5% bentonite by weight of dry cement). Primary cementation of weak zones with neat cement slurries often lead to losses as a result of the formation breakdown pressure being exceeded. In such a case, a good cementation job can be realized only by applying a multistage cementation process or by using some extenders to have low slurry gradients. Unfortunately, multistage cementation has the drawback of failures which may occur with D.V. tools. Moreoever, the cementation time is almost doubled. On the other hand, extended cement may fail to achieve 500 psi compressive strength which is generally accepted by industry standards. The results obtained by using local clays, however, realized these requirements as will be discussed later on.

Figures 5-7 show the consistency of cement slurries with time by adding different percentages of silica flour, lignosulfonates, and $CaCl_2$. The addition of silica has been adapted to provide a reliable cementing system for deep and hot wells [7,8]. Lignosulfonates and calcium chlorides have been added to study the thickening time control of slurries prepared from the local cements. When inorganic chemical accelerators are added to the cement slurry, they increase the ionic character of the aqueous phase causing the hydration of C_3S, C_2S and C_3A and releasing $Ca(OH)_2$ more quickly. This causes the rapid formation of the calcium-silicate-hydrates which are responsible for the cement's strength. On the other hand lignosulfonates inhibit hydration and precipitation of $Ca(OH)_2$ either by forming a chemical complex with the unhydrated cement compounds or by coating the unhydrated particles to prevent contact with water [9].

Experimental studies have shown that nearly all cement systems are subject to some deterioration at high electrolyte concentrations. Some cementation materials are better in the ability to resist formation brines significantly than others.

To determine the effect of formation water on the Saudi cement, the compressive strength of air cured cement prepared by using sea water, fresh water, and distilled water respectively are primarily tested (Fig. 8). Other cement cubes are prepared

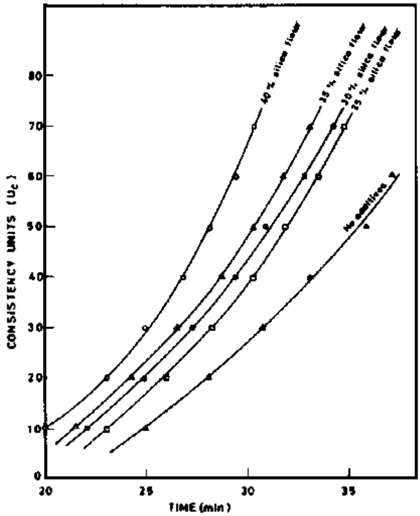

Fig. 5. Effect of silica flour addition on consistency of cement slurries

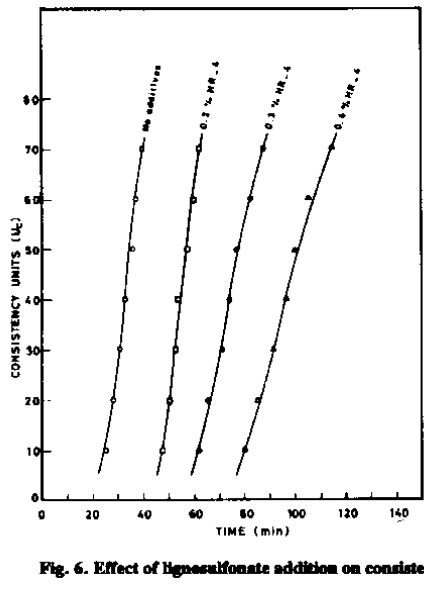

Fig. 6. Effect of lignosulfonate addition on consistency of cement slurries

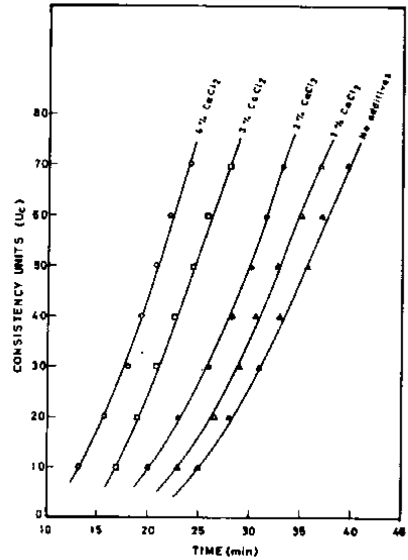

Fig. 7. Effect of calcium chloride addition on consistency of cement

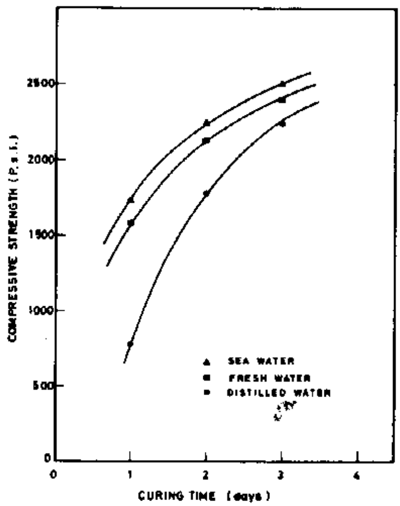

Fig. 8. Effect of water type on compressive strength of set cement

by using sea water, (the often used water in offshore drilling) and the cubes are allowed to cure while surrounded by Saudi formation water, the chemical analysis of which is given in Table 3. The compressive strength is then measured with time using calcium chloride, lignosulfonates; and bentonite at different percentages. The results are reported in Figs 9-11.

Table 3. Formation water analysis

(1) Ions	(2) Milligrams per liter mg/l	(3) Equivalent weight eq.wt	(4) Milliequivalent per liter meq/l	(5) % Reacting value as
A - Positive Radicals				
1. Alkalis				
Sodium, Na^+	67000.	23.000	2913.04	36.150
Potassium, K^+	0.	39.102	0.0	0.000
2. Alkaline Earth Metals				
Calcium, Ca^{+2}	18600.	20.040	928.14	11.518
Magnesium, Mg^{+2}	2270.	12.56	186.74	2.317
Barium, Ba^{+2}	0.	68.670	0.00	0.000
Strontium, Sr^{+2}	0.	43.810	0.00	0.000
3. Metals				
Aluminum, Al^{+3}	0.	8.733	0.00	0.000
Iron, Fe^{+3}	0.	18.616	0.00	0.000
Manganese, Mn^{+2}	0.	27.469	0.00	0.000
B - Negative Radicals				
1. Strong Acids				
Chloride, Cl^-	142500.	35.453	4019.41	49.879
Sulfate, SO_4^{-2}	260.	48.032	5.41	0.067
2. Weak Acids				
Bicarbonate, HCO_3^-	340.	61.000	5.57	0.069
Carbonate, CO_3^{-2}	0.	30.000	0.00	0.000
Sulfide, S^{-2}	0.	16.032	0.00	0.000
Total:	230970.		8058.31	100.000%

pH = 5.9
Specific Gravity = 1.1605 at 60°F
Conductivity = 169.1 Milli S/cm

Similar studies on portland cement and Madison Formation Brines showed that cement deterioration could be chemically evidenced as early as 24 hours. Continuing exposure showed that the chemical alteration of the competent cementitious components resulted in eventual physical deterioration of the entire samples.

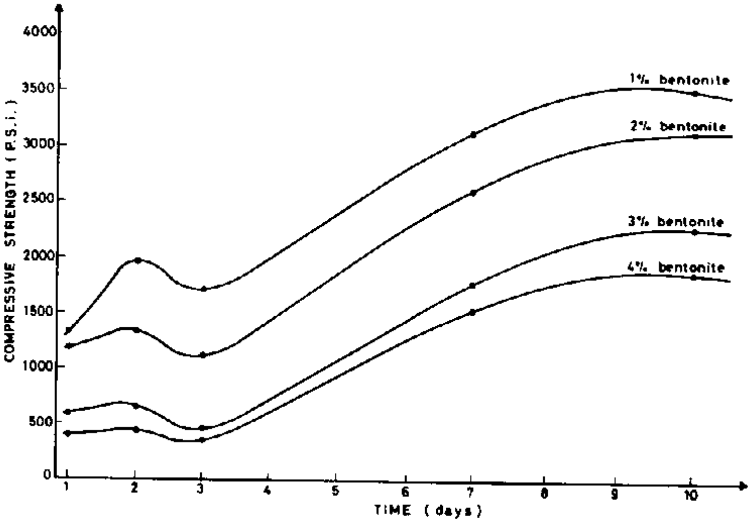

Fig. 9. Effect of bentonite addition on compressive strength of set cement

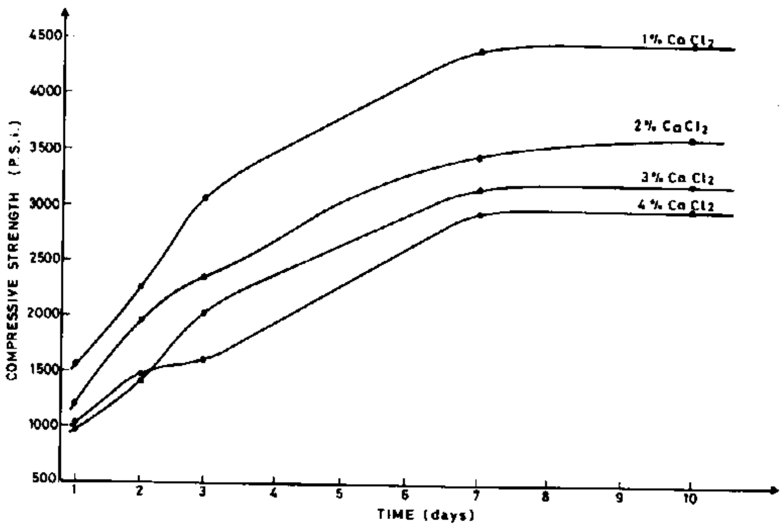

Fig. 10. Effect of calcium chloride addition on compressive strength of set cement

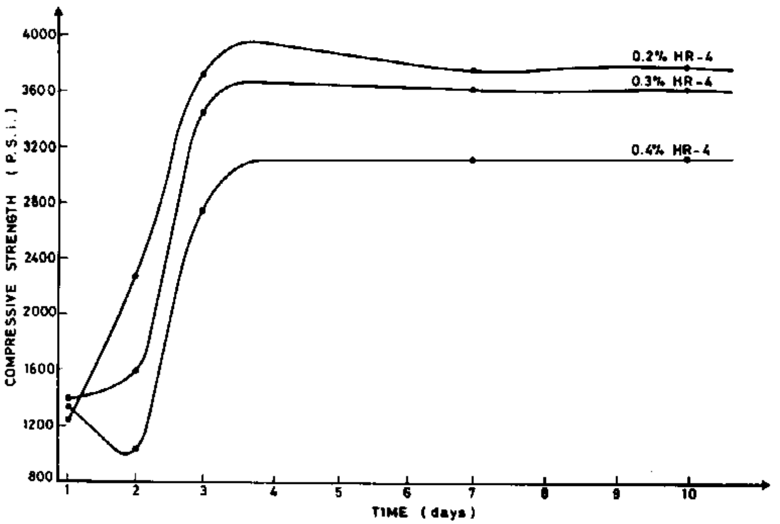

Fig. 11. Effect of lignosulfonate on compressive strength of set cement

The normal cement hydrolysis is expressed as follows [4]:

$$1)\ C_3A + C_4AF + C_3S + C_2S + CaSO_4 \xrightarrow{\text{hydrolysis}}$$
$$C_3A\,.\,6H_2O + C_2S + CF\,.\,XH_2O + CSA\,.\,31H_2O$$
$$+ CS\,.\,XH_2O + Ca\,(OH)_2 + Al_2O_3\,.\,H_2O$$

$$2)\ Ca\,(OH)_2 + C_3A\,.\,6H_2O + CaSO_4 \xrightarrow{\text{hydrolysis}}$$
$$CSA\,.\,31H_2O + CA\,.\,XH_2O$$

(Step 2 only occurs in the presence of enough $CaSO_4$).

It seems that the tested local cement is not greately affected when it is surrounded by the Saudi field formation water. In all cases, except at higher concentrations of bentonite, the compressive strength exceeds 500 psi (Figs. 9-11) in the first day. Also, the cement systems resist the environment of high brine concentration during the period investigated (10 days).

At higher concentrations of NaCl, however, an altered cement hydrolysis may result as follows [4]:

$$C_3A + C_4AF + C_3S + C_2S + CaSO_4 + NaCl \xrightarrow{\text{hydrolysis}} C_3A\,.\,6H_2O + C_2S + CF\,.\,XH_2O + CCLA + Na_2SO_4 + CS\,.\,XH_2O + Ca\,(OH)_2 + Al_2O_3\,.\,XH_2O$$

On the other hand, a small amount of NaCl will cause an increase in the solubility of the hydroaluminate, and will speed up the reactions with the available sulfates in solution to establish an earlier set of the cement (Fig. 8).

4. Conclusions and Recommendations

1) The rheological properties of slurries prepared from Saudi cement show a pseudoplastic behavior regardless of the types of water and the cement additives.

2) Thickening time and compressive strength of cement are dependent upon the type and percentage of the additives used.

3) The set cement exhibits good stability (no deterioration) in formation water and the 500 psi pressure recommended by the oil industry is attained in 24 hours.

4) It is important to investigate the rheology of cement slurry under dynamic conditions and the compressive strength under high pressure in order to simulate wellbore bottom conditions with the aim of assessing their use in oil well cementing.

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خواص سريان وثبوت الأسمنت السعودي في سمنتة آبار البترول

عبدالستار دهب وعدنان عمر

قسم هندسة النفط، كلية الهندسة، جامعة الملك سعود، ص.ب ٨٠٠،

الرياض ١١٤٢١، المملكة العربية السعودية

ملخص البحث: لقد تم بحث ملاءمة بعض خام الأسمنت السعودي في سمنتة آبار البترول وذلك من خلال التحليل الطبيعي والكيميائي لمسحوق وخواص السريان وزمن الشك لرزغة الأسمنت ثم مقاومة الانضغاط للأسمنت المتصلب وكذلك تمت دراسة ثبوت الأسمنت المتصلب المحاط بمياه تكاوين حقول البترول السعودية عند درجات الحرارة العالية.