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THE INFLUENCE OF THE SHEAR FIELD ON THE MICROSTRUCTURAL AND CHEMICAL EVOLUTION OF AN OIL WELL CEMENT SLURRY AND ITS RHEOMETRIC IMPACT

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ABSTRACT

Well cementing is one of the most important operations performed in an oil well. An adequate rheological characterization of the slurry is required to optimize cementing parameters. A study of chemical and microstructural development of a cement slurry and its impact on rheometric behavior was carried out. Scanning electron microscopy, X-ray diffraction analysis and rotative rheometry were used. Hydration of the slurry was followed at rest and under shear. It is shown that chemical reaction kinetics, microstructure development and rheometric behavior depend markedly on the shear conditions during hydration. © *1997 Elsevier Science Ltd*

Introduction

When a well is drilled and the string of casing is run into the well, a cement slurry is pumped into the casing to fill the annular column between the casing and the geologic formations exposed to it (Fig. 1). The most important function of the cement sheath is to provide zonal isolation to the wellbore, e.g. to exclude fluids such as water, gas or oil from one zone to another. Cementing is considered as one of the most important operations performed in a well. An adequate rheological characterization of cement slurries is important to design and execute it.

A cement slurry is a reactive system: chemical reactions between solid phases and mixing water lead to the formation of new species, possessing connecting properties. This is the hydration procedure, that brings about alterations to the slurry mechanical properties. The chemical and microstructural evolution of cement slurries during the first hours of hydration has been the subject of several studies (1- 5). Cement slurry rheometry is also a very widely studied subject. Reviews of the relevant work can be found in the litterature (6-8). However, very few authors have looked for correlations between chemical, microstructural and mechanical behavior of the slurry before setting (9-12).

The objective of this work is to examine the influence of a shear field on the rheometric, microscopic and chemical development of cement slurries. Our approach of the problem consists of using adapted methods in Rheometry, Scanning Electron Microscopy and X-ray

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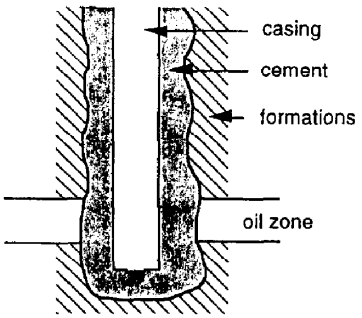
FIG. 1.
Schematic representation of a cemented well.



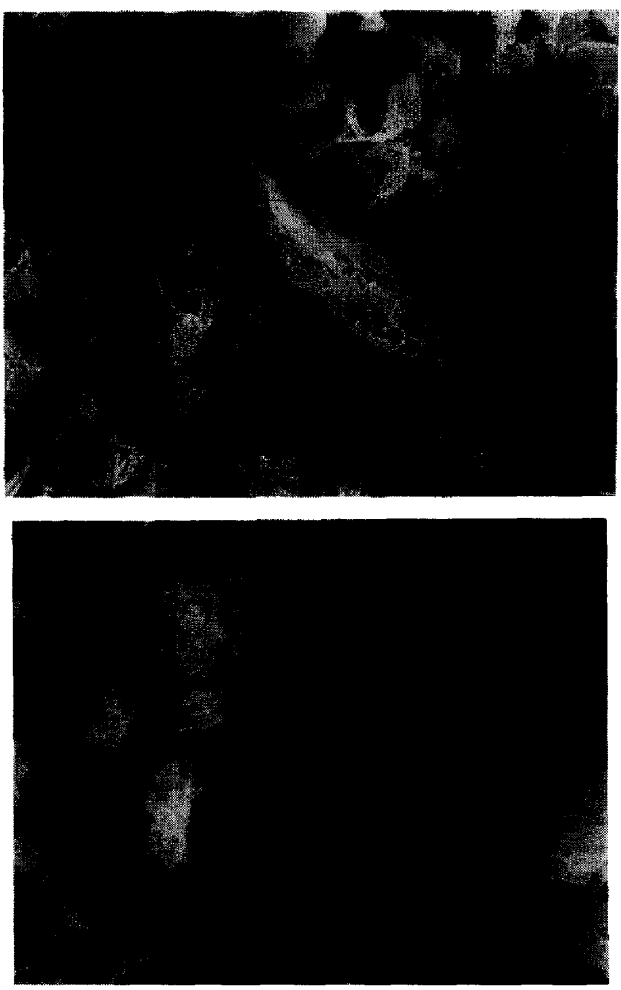


FIG. 2.
(MEB) Dry cement powder.

TABLE 1

Chemical Analysis of Class G Dyckerhoff Cement

Element	Ca	Si	Fe	Al	Mg	S	K	Na	LOI
% by Weight	46.78	10.38	2.91	1.98	1.24	0.67	0.51	<1	0.92

Diffraction to follow the evolution of the slurry, when it hydrates at rest or under stirring at 150 rpm (stirring speed of the consistometer used in the oil industry). More precisely, we followed the steady state flow curve and the viscoelastic parameters G' and G" as a function of the hydration time. We followed, in parallel, the microstructural and chemical development of a slurry, by SEM observations and XRD analysis. We have tried to find correlations between chemical and physical evolution of the system.

Operational Mode

The Materials. Oil well cements are Portland cements, that follow particular specifications with regard to their size distribution and their exact composition.

We used a Class G oil well cement, supplied by the German manufacturer Dyckerhoff. Fig. 2 presents two SEM micrographs of dry cement powder. Cement grains are of very varied shapes and their size lies from some nm to several tens of μm. This wide size distribution causes the simultaneous action of colloidal and gravity forces on the rheometric behavior of the slurry.

Cement particles are polymineralic, composed essentially of silicate and aluminate phases. Chemical and mineralogical composition and some physical characteristics of the cement used in these work are given in Tables 1 and 2.

Several admixtures are used in the oil industry. They are agents that we add to the slurry in small quantities, to adjust their properties to the particular conditions of each well. In this work we used a modified lignosulfonate (ML) to delay setting, and a hydroxyethylcellulose (HEC) to reduce filtration. The action of the admixtures is very complicated and still a matter of controversy. The influence of these two additives on the rheometric behavior of the slurry has been studied in 8 and 13.

TABLE 2

Mineralogical Composition and Physical Characteristics of Dry Cement

	% by Weight
C_3S $[3(CaO)SiO_2]$	62
C_2S $[2(CaO)SiO_2]$	17
C_3A $[3(CaO)Al_2O_3]$	3
C_4AF $[4(CaO)Al_2O_3Fe_2O_3]$	16
Other Oxides (Mg, K...)	2

Mean Size	17.8 μm
Density	3,230 kg/m^3

TABLE 3

Composition of the Slurries

Water/Cement Ratio $\frac{W}{C} = 0.44$	Mass Concentration Cw = 69%	Volume Concentration $\Phi v = 41\%$	Density d=1,920 kg/m3

HEC = 0.55%*	M.L. = 0.28%*

*by weight dry cement

The Experimental Approach. The composition of the slurries used is given in Table 3. This composition has been chosen, because it provides slurries with an acceptable behavior for an on site use. Thickening time* of this formulation at different temperatures is reported in Table 4.

Slurries were prepared at ambient temperature (20 ± 2°C) as specified by the API (14). A standardized Waring mixer was used. It is a two-speed propeller-type mixer. It was operated at 4,000 rpm for about 15 seconds, during which cement and admixtures were added to the mix water, followed by 35 seconds at 12,000 rpm. After mixing, slurries are divided into two parts:

- the first part is hydrated under stirring of 150 rpm, in a vertical paddle agitator
- the second part is hydrated at rest in a container, or in the rheometric gap for the oscillatory tests.

We followed the evolution of each of these parts, from right after mixing until the end of the thickening time.

Concerning rheometry, the experiments were performed at ambient temperature (20 ± 2°C), using a Carrimed Weissenberg rheometer. This is a rotative, shear rate-controlled rheometer. With this apparatus, rotational speed is assigned on one tool and the torque, transmitted through the sample under test on the other tool, is measured. For liquid samples (that flow under their own weight) we used a rheometric geometry adapted to coarse suspensions, constructed at the Laboratoire de Rhéologie. It is equivalent to a parallel plate geometry, with plates of 26 mm radius and a gap of 2 mm. This tool is presented and evaluated in the reference 8. For pasty samples, a classic parallel plate geometry with 25 mm radius and 2 mm gap was used. Plates had rough surfaces, with a roughness of 200 μm.

TABLE 4

Thickening Times of the Slurries

Temperature (°C)	Thickening Time
20	20 h
60	6 h
120	< 30 min

*The thickening time of a slurry is a standardized parameter, defined as the time during which the slurry is sufficiently fluid to be pumped. A specific apparatus (the consistometer) is used for its determination. The operational procedure to be respected is contained in the API Specification 10, Section 8, Appendix E (14).

We followed the evolution of the steady state flow curve with hydration time. For this, samples were taken at several stages of the hydration, transferred in the measurement geometry and submitted to the following experimental protocol:

- 30 s pre-shear at 40 s^{-1}
- 30 s rest
- series of four ascending steps of $\dot{\gamma}$, applied for 1 min each, a time long enough for the establishment of the steady state flow

The range of $\dot{\gamma}$ was limited because of problems of flow regime establishment and because of the necessity to keep experiment duration short enough to neglect the influence of the hydration reaction. Results were reproducible with a relative error of about 10%.

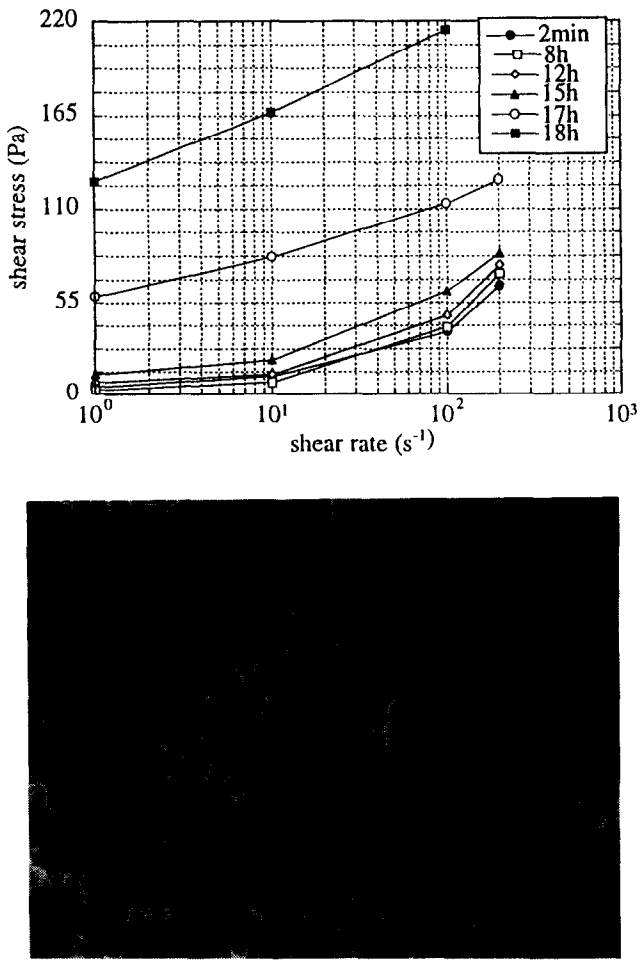


FIG. 3.
Rheometric and microscopic evolution of a cement slurry, hydrated under stirring at 150 rpm.

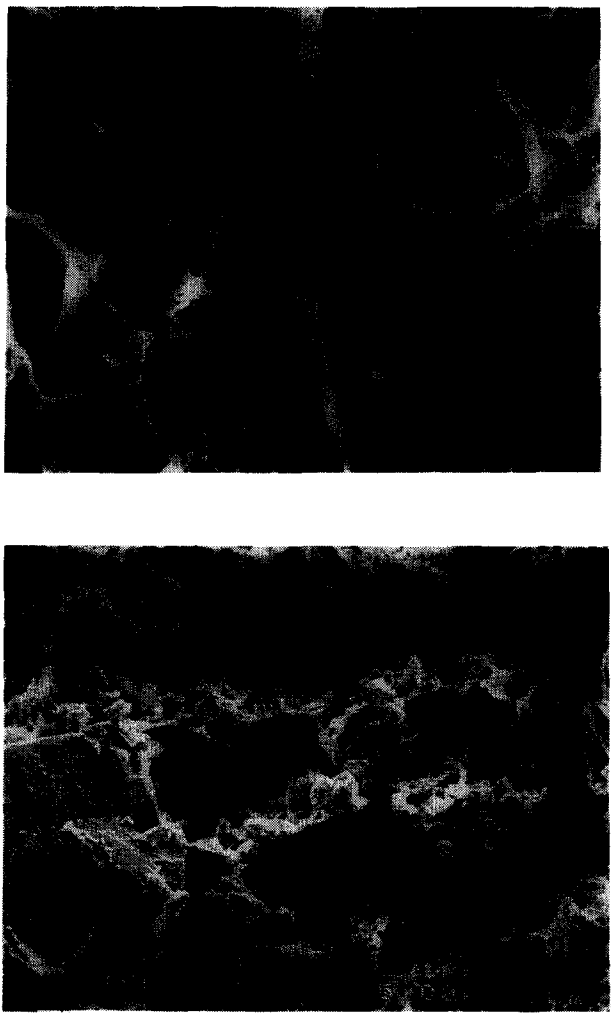


FIG. 3.
(Continued).

Oscillatory experiments were performed in order to examine the evolution of the viscoelastic properties with hydration time at quasi-static conditions. During these experiments we apply an oscillatory strain of very small amplitude. We measure the resulting shear stress, which oscillates with the same frequency, but not necessarily in phase. We followed the evolution of the storage modulus G', which represents the elastic, in-phase component of stress (accounts for the stored elastic energy), and of the loss modulus G", which represents the viscous, out-of-phase component of stress (accounts for the dissipated through viscous effects energy). The strain amplitude and the oscillation frequency were chosen so that we are in the linear viscoelastic domain of the material.

In parallel, we followed the microstructural and chemical evolution of the slurry, based on SEM observations and XRD analysis.

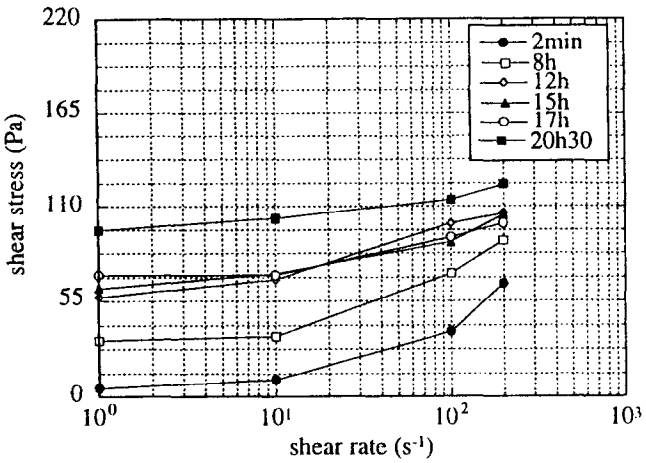
For the SEM, samples of about 0.5 g are taken from the bulk slurry, placed on an adapted sample-holder, frozen rapidly by soaking into nitrogen slush, fractured, lyophilized very slowly and covered with a very thin film of platinum (≅ 5 nm). Then they were observed in the microscope, in a vacuum of about 10^{-5} Torr.

For XRD analysis, samples are immersed in acetone, to stop the hydration procedure, washed with petroleum ether and dried before analysis.

The SEM and XRD experiments were performed in the Physico-chimie Appliquée et Analyse division of the Institut Français du Pétrole.

Discussion

The flow curves and the SEM images of the slurry hydrated under stirring are put together in Fig. 3. Three micrographs are presented in this figure. The first one corresponds to the state



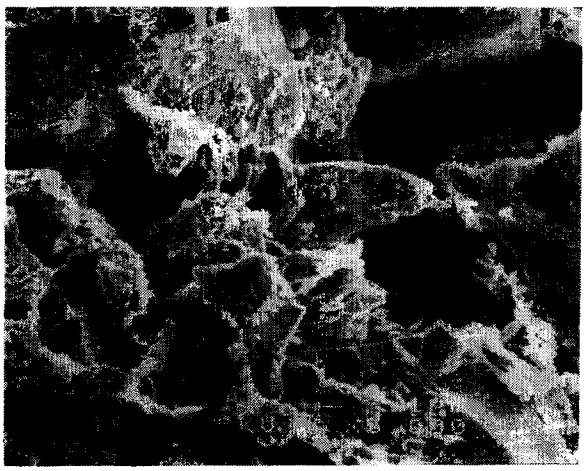


FIG. 4.
Rheometric and microscopic evolution of a cement slurry, hydrated at rest.

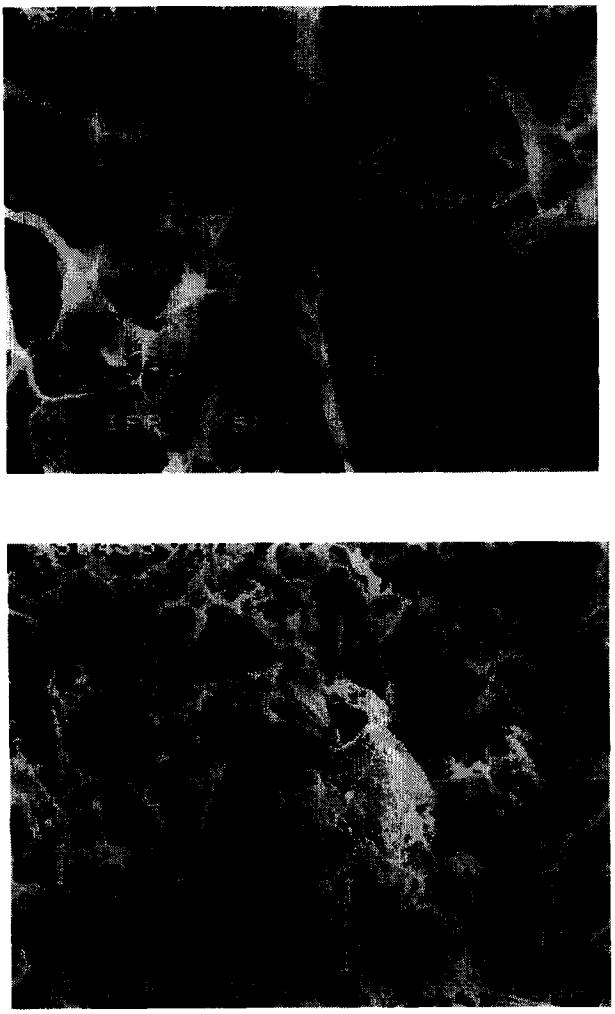


FIG. 4.
(Continued).

of the slurry when it gets out of the mixer. We can distinguish anhydrated cement grains, dispersed in a kind of spider's web, formed by the polymeric admixtures.

The second one is taken at 8 h of hydration. Several small particles are formed in the interparticle spaces. Their size is of the order of a micrometer, and they are the products of the hydration of the aluminate phases (1,2). On the micrograph taken at 18 h of hydration, these particles are much more numerous. At this stage, other forms of crystals appear equally. Particularly, we see big plates of portlandite $\{Ca(OH)_2\}$, as well as the first fibers of C-S-H (product of hydration of the silicate phases) on the grain surfaces (5,6). All these formations completely encumber the porosity between the grains, and increase the concentration in solid particles.

Concerning flow curves, we can see that they practically not evolve during the first 12 h of the hydration. We observe a slight evolution at 15 h. Afterward, thickening of the paste

happens very rapidly. In fact, the formation of the first hydration particles doesn't influence the flow curve, because these particles do not create bonds between them, but they circulate freely into the interparticle spaces. During the first hours of the hydration process, their quantity is low and, as their size is small, they don't induce a significant increase of the solid volume fraction. But as fast as their quantity increases, and especially when bigger crystals appear, flow curve moves towards much higher shear stresses.

Fig 4 presents the same information for a slurry hydrated at rest. With regards to hydrates creation, we notice a different situation. At 8 h of hydration, we observe fine hydrates that grow from the surface of the grains and sometimes meet each other. We can also distinguish some polymer filaments, which could signify that the reaction has not sufficiently progressed to consume them. At 20 h, the situation doesn't change a lot. There is still a layer of hydrates on the grain surfaces and a lot of porosity. This situation is very different from the rich and dense structure of the stirred paste.

Rheograms also evolve in a different way: We observe an important evolution during the first hours, and a slowing down afterwards.

To facilitate comparison of the flow properties in the two cases, we present in Fig. 5 the apparent viscosity measured at $\dot{\gamma}$ equal 10 s^{-1}, as a function of the hydration time. The shear rate of 10 s^{-1} has been chosen because it is approximately in the middle of the range used for the shear flow experiments. The picture is quite alike for the other values of the shear rate. Fig. 5 illustrates that, for the slurry hydrated under stirring, viscosity remains approximately constant during several hours. This is the time corresponding to the formation of small spheres of hydrates of the aluminate phases. During this time, the slurry keeps good fluidity properties, that facilitate its use. Then the paste thickens rapidly, with the multiplication of these crystals and the appearance of other more massive ones, that launch the setting process. On the contrary, slurries hydrated at rest present a much more precocious increase of their viscosity, after which their evolution slows down.

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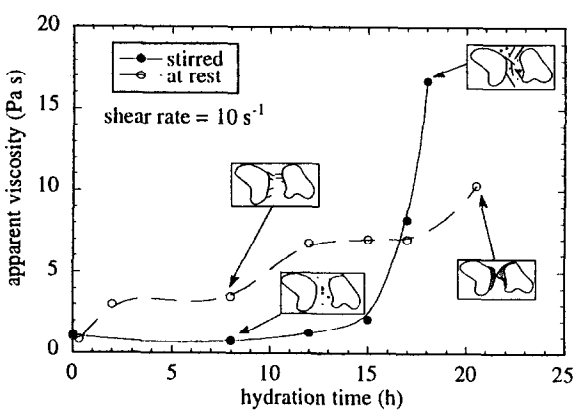

FIG. 5.
Evolution of the apparent viscosity as a function of hydration time, for cement slurries hydrated under stirring at 150 rpm or at rest.

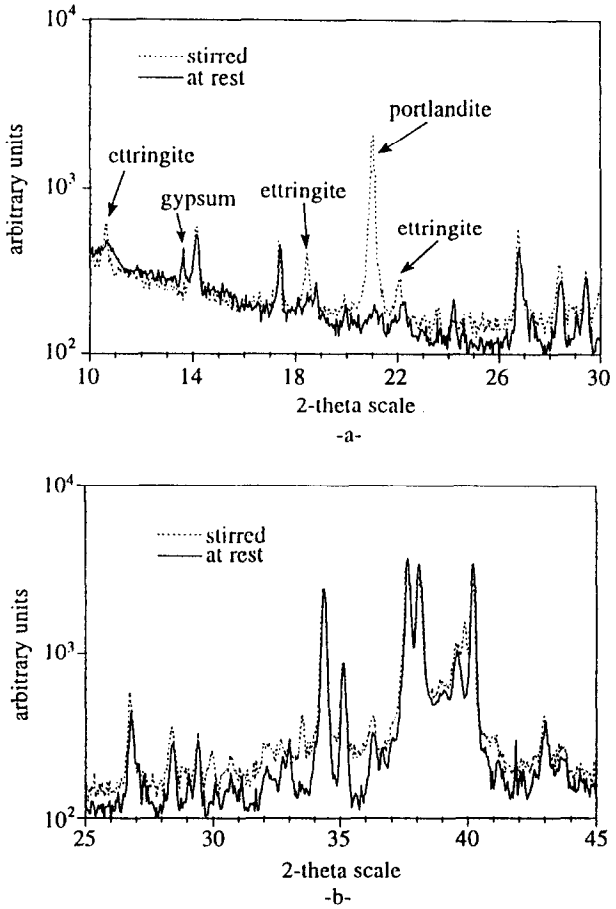

FIG. 6.
Comparison of X-ray diffraction spectra of cement slurries hydrated during 20 h under stirring at 150 rpm or at rest.

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The X-ray diffraction spectra of the slurries after 20 h of hydration under stirring or at rest are compared in Fig. 6. We irradiate the sample with an X-ray beam, and we measure the intensity of the diffracted radiation, as a function of the diffraction angle, generally referred to as 2θ. A crystalline materials, such as ettringite, gypsum and portlandite, produces diffraction peaks at characteristic angles. Their relative quantity present in the sample can be measured by the relative intensity of the corresponding peaks. On the contrary, an amorphous material, having no long range order, produces a disordered diffusion, and corresponding spectra contains a broad and bad-defined maximum.

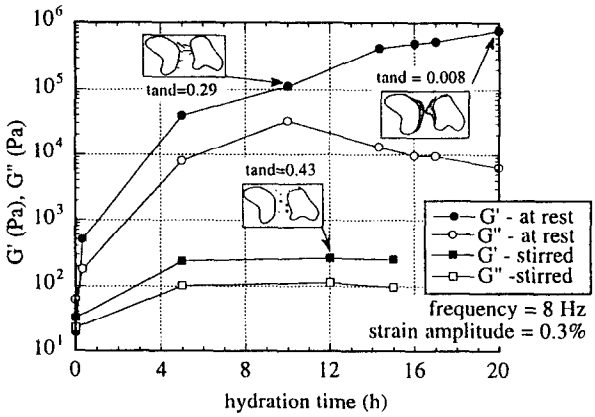

FIG. 7.
Evolution of the G' and G" moduli of cement slurries hydrated under 150 rpm stirring or at rest.

The comparative observation of the two diffractograms shows, as we would expect, that reaction has much more progressed in the case of the stirred sample. In fact, for the stirred slurry, gypsum is completely consumed and we notice the creation of ettringite and of a significant quantity of portlandite (Fig. 6a). We also measure a small quantity of amorphous products, which is shown by the elevation of the bottom of the diagram, evident in Fig. 6b. It is the beginning of the amorphization of the C_3S and C_2S, with the formation of C-S-H gel.

The slurries hydrated at rest contain small quantity of ettringite, bad organized or crystallized in small crystals, which is at the origin of broad peaks. Moreover, we don't measure any portlandite or amorphous products.

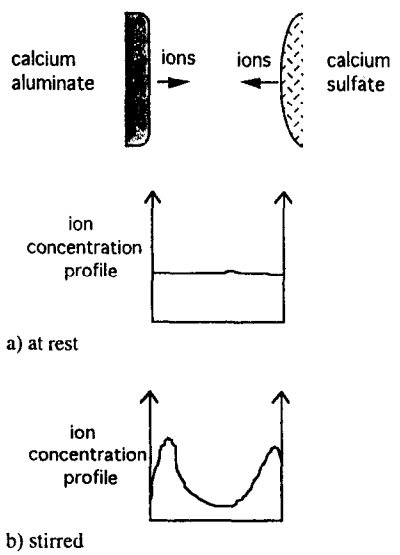

FIG. 8.
Mechanisms of precipitation of hydrates.

Next, we will examine the evolution of the storage and loss modulus, G' and G" respectively, with hydration time, for the two cases of interest. These parameters are drawn in Fig. 7. Just after mixing, the ratio G"/G' is 3.3. Consequently, the viscous character is preponderant. For the slurry at rest, G' increases ten-fold in 20 min, whereas G" increases in a much more moderate manner. G' keeps increasing all over hydration. On the contrary, G", starts to decrease from the moment when hydrates growing on the surfaces form a network which spreads over the whole sample. From this time, the elastic character becomes more and more important.

For the slurry hydrated under stirring, where free particles in the interparticular space are formed, viscoelastic properties remain essentially constant during 15 h of hydration.

Fig. 8 illustrates the way in which we could resume the situation. We schematically represented two cement grains and the diffusion zone between them. Ions dissolution takes place from grain surfaces, immediately after mixing with water.

In the case of a slurry hydrated at rest, progression of ions happens only because of diffusion. Their concentration in the space between the two grains follows the profile shown in Fig 8a. This concentration reaches early high values in the neighborhood of the grains, and crystals precipitate in this region or on the grain surfaces. These crystals are very small, because they stem from an over-saturated solution. They form the gel layer, observed by several authors (1,5,6). After formation of this layer, reaction slows down, and microscopical and chemical aspect of the slurry don't change considerably. This slowing down is usually attributed to the action of these hydrates as a "protective layer". However, other mechanisms cannot be excluded. For example, for Mehta P.K., 1976 (2), this layer is not sufficiently compact to justify the mechanism of the "protective layer", and he explains the slowing down action on the bases of the reduced solubility of the C_3A in a solution saturated in sulfate. Anyhow, the hydrates form bonds between particles, that provoke, for instance, the increase of the G' of the suspension. But these bonds are fragile: in high shear they are break and the slurry regains a certain fluidity.

In the case of the stirred slurry, the ions are fairly distributed in the available space (Fig. 8b). Crystals are formed before over-saturation of the solution, and this in the whole sample volume. They are, consequently, of bigger size, and appear everywhere in the porosity. Reaction doesn't slow down. So we have, at 18 h of hydration, an intergranular structure very rich and compact, with very little porosity. In this case, slurry keeps good fluidity properties during several hours, but it thickens rapidly at the end of the thickening time, with the beginning of setting.

Conclusions

In this work, through adapted experimental methods, we have suggested correlations between chemical evolution, microstructural development and rheometric behavior of an oil well cement slurry.

The evolution of the system can be summarized as follows: when water and cement powder are brought in contact, a rapid dissolution of ions from the grain surfaces takes place. If the fluid is stagnant, an over-saturation of ions in the grain neighborhood leads to a rapid formation of crystals in this region. These are mainly aluminate hydration products of colloidal size. They cover the surface of the grains, slow down the reaction and give to the suspension the characteristics of a gel, although fragile. This is reflected, at macroscopic level, by a continuous growth of the storage modulus, or of the viscosity at low shear rates.

If, on the contrary, the fluid is stirred, ions are dispersed all over the sample volume and dissolution goes on until saturation. Afterwards, crystals of nominal diameter of several μm precipitate. They consume water molecules and increase the solid volume fraction. At the first stages of the hydration, their influence on the rheometric properties of the slurry is negligible. But at later stages, they lead to a rapid increase of the viscosity of the paste.

Globally, chemical reaction progresses more rapidly for the stirred pastes, although locally (at the surface of the particles) and momentarily (in the first minutes after mixing with cement) reaction rate is very rapid in the stagnant pastes. It would be interesting to investigate the mechanical characteristics after setting, associated to these two preparation modes.

Acknowledgements

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