Porosity of oil well cement slurries during setting

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The phenomenon of 'gas migration' during oil well cementing is believed to occur during the transition state between initial and final set of the cement. In order to evaluate the importance of pore openings and total porosity in the critical time gap, a suitable experimental technique was tested on some neat oil well cement slurries. The hydration was effectively stopped every 30 min at 20°C and every 20 min at 60°C by dropping plastic tubes containing the cement slurry into liquid nitrogen (i.e. quenching), cracking the tubes open and letting the frozen bits of paste thaw in ethanol. The change in porosity and pore size distribution was determined by helium pycnometry and mercury intrusion porosimetry as a function of time in the setting period for a plain API class G cement slurry (w/c = 0·50) at both 20°C and 60°C. These data were compared with the amount of chemically bound water in the same samples, and used to predict the total porosity at a given degree of hydration. The excellent correspondance of experimental and theoretical porosities validates the experimental procedure, which can also be used in explaining the variation in gas migration between commercial oil well cement slurries.

Introduction

Gas leakage in the annulus after primary cementing of oil and gas wells is still a problem, particularly in upper, unconsolidated, cavernous holes and in deep wells, i.e. under high temperature and high pressure conditions. Reasons for and mechanisms of gas migration are presented in Refs 1–3. Annular gas flow may occur when

(a) the hydrostatic pressure falls below the formation pore pressure due to shrinkage, fluid loss or gel strength build-up

(b) the cement slurry stays permeable or the initial gas forms channels, creates micro-annuli or fractures before the slurry has reached a certain strength.

Thus, the phenomenon of gas migration is believed to occur during the transition state between initial and final set of the cement, when the pressure transferred by the cement slurry column changes from being given by the density (i.e. $P = \rho g h$, where P is pressure, ρ is density, g is the gravitational constant and h is height) of the cement slurry to being given by the density of the percolating water phase, or is even lower.

As part of an initial study to elucidate the mechanism of gas intrusion into the cementing material, the importance of pore openings and total porosity in the critical time gap was evaluated. A suitable experimental technique was tested on some neat oil well cement slurries.

The effect of dissolved gas released when the pressure transferred by the cement slurry column is reduced, or simply when the solute (i.e. water) is removed by the hydration process, on gas migration is discussed elsewhere, as is the effect of chemical shrinkage due to cement hydration on gas migration.[4]

Experimental details

A slurry was made from Norwell G cement (American Petroleum Institute classification) and distilled water to a water–cement ratio (w/c) of 0·50. The cement was delivered by Norcem, Brevik, Norway, and had the following analysis: 64·82% CaO, 22·00% SiO_2, 4·78% Fe_2O_3, 3·53% Al_2O_3, 1·75% SO_3, 1·42% MgO, 0·87% free lime, 0·60% alkalis and 0·37% loss on ignition. The specific surface according to Blaine was 303 m^2/kg.

The slurry was distributed into stoppered polyethylene (PE) tubes (10 mm inner diameter). The PE tubes were then placed in water baths at 20°C and 60°C. The hydration of the slurry samples was stopped (i.e.

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quenched) by dropping the PE tube into liquid nitrogen at −196°C, cracking the PE tubes open and placing the frozen paste directly into 96% ethanol to thaw. Samples from the 20°C series were quenched every 30 min until 270 min; for the series at 60°C quenching was carried out every 20 min until 160 min. The chemically bound water for each series was measured by determining the weight loss between 105°C and 1000°C for each sample, taking account of the loss on ignition of the cement.

The samples intended for mercury intrusion porosimetry (MIP) were stored in ethanol for a few days prior to evaporation at 60°C until their weight was constant. The MIP experiments were carried out with a Carlo Erba porosimeter, Model 2000. The samples were cut into bits with a diameter of £ < 5 nm. This porosimeter records the pore size (radii) distribution of the sample between 5 and 50 000 nm. Spherical pores, a surface tension of mercury of 480 dyn/cm (0·48 N/m) and a contact angle of 117° were assumed. The total porosity and the material density of the samples were determined by a Micromeretics Accupyc 1330 Helium pycnometer (HeP).

Results and discussion

The amount of chemically bound water W_n, sample density ρ_s, solid material density ρ_m and total porosity ϕ_p of some samples from cement slurries cured at 20°C are given in Table 1 as a function of the curing time; analogous data for the cement slurry cured at 60°C are given in Table 2. The pore size distributions for three samples cured for 180, 240 and 270 min at 20°C are shown in Fig. 1; the pore size distributions for four samples cured for 10, 120, 140 and 160 min at 60°C are shown in Fig. 2.

When the frozen slurry samples were thawed in ethanol, many of them fell apart since they had not set properly (i.e. had not built up a sufficiently strong skeleton). In fact, the slurry cured at 20°C required 150–180 min to make a sample that retained its shape under the preparation conditions, while the slurry cured at 60°C required 100 min. This is why so few samples were investigated

Table 1. *The amount of chemically bound water W_n, sample density ρ_s, solid material density ρ_m and total porosity ϕ_p of some samples from a neat cement slurry with w/c = 0·50 cured at 20°C as a function of time t*

t: min	W_n: g/100 g cement	ρ_s: g/cm³	ρ_m: g/cm³	ϕ_p: %
0	1·72	—	—	—
30	1·78	—	—	—
60	1·88	—	—	—
90	2·09	—	—	—
120	2·19	—	—	—
150	2·37	—	—	—
180	2·79	1·3208	3·0382	56·5
210	2·98	—	—	—
240	3·50	1·3271	2·9953	55·7
270	3·34	1·2728	2·9845	57·4

Table 2. *The amount of chemically bound water W_n, sample density ρ_s, solid material density ρ_m and total porosity ϕ_p of some samples from a neat cement slurry with w/c = 0·50 cured at 60°C as a function of time t*

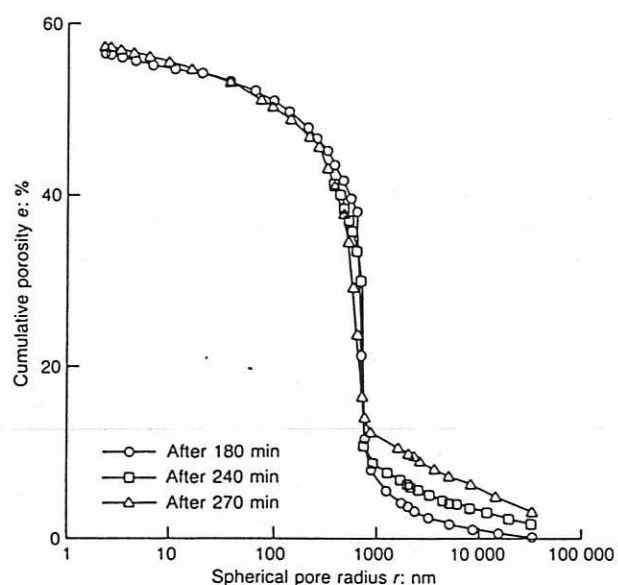| t: min	W_n: g/100 g cement	ρ_s: g/cm³	ρ_m: g/cm³	ϕ_p: %
0	1·09	—	—	—
20	1·26	—	—	—
40	1·57	—	—	—
60	1·68	—	—	—
80	1·87	—	—	—
100	2·57	1·2996	3·0537	57·4
120	3·27	1·2752	3·0105	57·6
140	4·49	1·3013	2·9558	56·0
160	4·95	1·3475	2·9103	53·7

Fig. 1. *Pore size distribution of a plain oil well cement slurry (class G) with w/c = 0·50 cured at 20°C for 180, 240 and 270 min (the profile after 240 min is uncertain)*
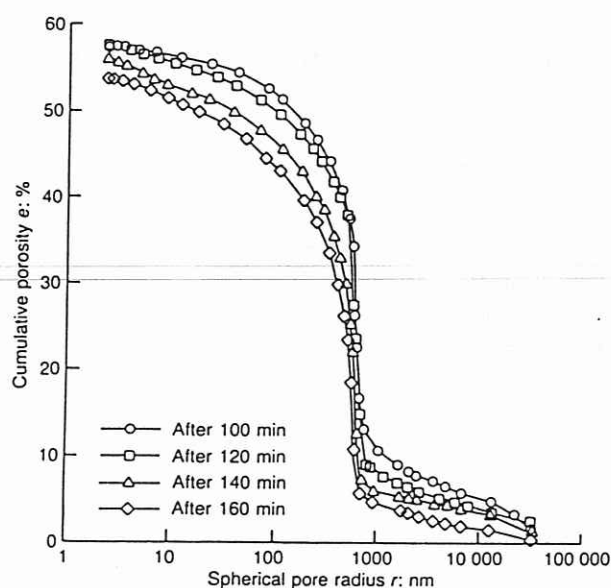

Fig. 2. *Pore size distribution of a plain oil well cement slurry (class G) with w/c = 0·50 cured at 60°C for 100, 120, 140 and 160 min*

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for porosity. The amount of chemically bound water (g/100 g burnt cement after the subtraction of loss on ignition of the dry cement) in Tables 1 and 2 can be used to estimate the degree of hydration $\alpha \approx W_n/0.25$. According to the W_n values, only about 10% hydration seems necessary for a plain API class G cement paste with w/c = 0.50 to retain its shape at atmospheric pressure.

Tables 1 and 2 show that the solid material density ρ_m is reduced with increasing curing time. This is a measure of the degree of hydration α, since the cement with a dry density of 3.15 g/cm³ reacts with liquid water (density 1.00 g/cm³) to form hydration products having intermediate densities. All the free, unreacted water and some of the physically adsorbed water are removed by the ethanol and the heat treatment. Thus, a higher degree of hydration gives a lower material density ρ_m.

Tables 1 and 2 also show that the total porosity ϕ_p is high immediately after setting; about 57% for samples from both curing schemes. However, while the porosity of the samples cured at 20°C seems to be constant over a time span of 90 mins, the porosity of the 60°C samples decreases substantially (-6.4% relatively) during 60 min. This observation is explained by the much higher hydration *rate* at 60°C than at 20°C (see Tables 1 and 2), which is also reflected in the change in, and values of, the material density.

All the pore size distributions reveal that the major part of the porosity has pore openings of radius 500–800 nm. The average particle size for the cement is about 40 μm. A closest packing of spheres (i.e. idealized cement grains) with diameter $d_1 = 40$ μm would have given initial space for a smaller sphere with diameter $d_2 = [\sqrt{(3/2)} - 1] d_1 = 9$ μm in the cavity formed between four of the larger spheres lying in the corners of a tetrahedron and with contact along the edge of it. The initial entry to this cavity is between three of the larger spheres in the corners of a triangle and with contact along the edge of it, which means that only spheres (e.g. gas bubbles) with a diameter $d_3 \leq (2 - \sqrt{3}) d_1/\sqrt{3} \leq 6.2$ μm could enter. However, the packing of cement particles, and the initial spacing between them, depends on the particle size distribution for the cement. The packing of particles with a range of sizes, and the partial filling of cavities and entries with hydration products, explains the fact that the experimental value (diameter $1.0-1.6$ μm according to Figs 1 and 2) of the major cavity entries is about five times lower.

The decrease in porosity in the range 800–8 nm as a function of time at 60°C (see Fig. 2), and the change in shape of these curves, reflects the filling of the coarser voids by hydration products. The latter have very fine micro-pores.

The *initial* 'porosity' (i.e. before hydration starts) of a cement paste with w/c = 0.50 is 61.2%, assuming specific densities of 3.15 and 1.00 g/cm³ for cement and water respectively. $\alpha = 0.10$ (2.5% water chemically bound) will give a porosity of about 56.5% after the sample treatment used in the present study (ethanol washing and drying at 60°C). These values agree well

with the measured values of ϕ_p in Tables 1 and 2.

There is apparently enough liquid volume to allow gas intrusion and percolation during the setting of oil well cement. However, the pore entries are so small ($1.0-1.6$ μm in diameter) that gas can enter only as small bubbles or when dissolved[4] without disruption of the matrix.

A potential drawback of the experimental procedure is the possible expansion of water as it freezes. However, the present cooling rate is so fast (i.e. quenching) that ice crystals may not form. If a substantial expansion should occur during freezing, it would probably lead to micro-cracking rather than alteration of the pore size distribution. Thus, the results obtained by MIP should be affected only in the upper detection range.

The experimental procedure seems to function adequately, judging from the excellent correspondance of experimental and theoretical porosity, and it will be used in further studies to investigate the effect of inert (e.g. precipitated calcium carbonate) and reactive (e.g. condensed silica fume) fine fillers on porosity during setting. The procedure can also be used to explain the variation in gas migration resistance between commercial oil well cement slurries.

Conclusions

Only about 10% hydration is necessary for a plain API class G cement paste with w/c = 0.50 to retain its shape at atmospheric pressure. Porosity measurements of initial set API class G cement paste with w/c = 0.50 at both 20°C and 60°C revealed that there is enough liquid volume to allow gas intrusion and percolation to occur during the setting of cement. However, the pore entries are so small ($1.0-1.6$ μm in diameter) that gas can enter only as small bubbles or when dissolved without disruption of the matrix.

The present procedure can also be used to explain variations in gas migration resistance between commercial oil well cement slurries and to investigate the effect of different additives (e.g. condensed silica fume) on porosity and pore entries.

Acknowledgements

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