Manufacture of water wet artificial core by chemical modification method

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ABSTRACT

A limited number of reservoir rocks can be drilled for laboratory experiments, so artificial core is often used to study the multiphase flow and EOR mechanism during physical simulation experiments. Artificial core manufacturing method includes epoxy cementing and high temperature sintering processes. Conventional epoxy resin cement core used was commonly oil wet. By adopting the method of high temperature sintering or surfactant cementation, the wettability requirements of reservoir rocks can be satisfied; however, it may have water sensitivity and unstable hydrophilicity issues.

The traditional process of epoxy cement is improved on the basis of above mentioned facts. In this paper the method of manufacturing water wet artificial core was improved and simplified by chemical modification. The non-ionic hydrophilic group for epoxy molecule is added by the chemical reaction of E-51(epoxy) and glycine, and then the chemically modified epoxy and curing agent can cement quartz sands directly. The mixture of chemically modified epoxy resin and curing agent before solidification can be diluted by water directly instead of acetone which is toxic for human body. The test of contact angle shows that cured epoxy resin and cemented core slice are both water wet. Strength, porosity and permeability of cementing core are essentially the same with the conventional cementing one; moreover, the pore distributions by NMR test are the same. Furthermore, the water sensitivity phenomenon does not exist, and its' properties (strength, porosity and permeability) basically remain unchanged after soaking by kerosene or water for 48 hours. This kind of water wet core manufacturing method is simple since the process doesn't need high temperature curing and it's more suitable to study the fluid flow in porous media and EOR method in light of the stable property.

INTRODUCTION

Most scientists working on the problem have concluded that it is difficult to obtain valid measurements without operating under conditions as close as possible to those in the reservoir. In the field of reservoir engineering, it is important for the core samples used in laboratories to have properties representing the real reservoir. Although often neglected, core samples always degrade to some degree in the process of cutting the core, handling it, and studying it. This necessitate for artificial core sampling as an alternative. Artificial core manufacturing methods which include high temperature sintering or surfactant cementation improve wettability requirements of reservoir rocks and makes the sample representative. Unfortunately, water sensitivity and unstable hydrophilicity is still challenging under this method.

Most scholars generally change additives or processing methods to meet the requirements of different wettability [1]. For the core produced by epoxy cement, the method of adding clay and surfactant substances, is generally adopted to change the wettability (weak oil-wet is changed into weak water-wet) [2-3]. For the high-temperature sintering core and natural water-wet core, the method of silicone oil immersion is generally adopted to change the wettability (weak oil-wet is changed into weak water-wet). However, silicone oil and surfactant can be removed by core flooding. When clay is added, there is strong water-sensitivity. Moreover, the acid and alkali resistance of high-temperature sintering core is poor [5-6]. Therefore the reusability and wetting stability of core are still unresolved.

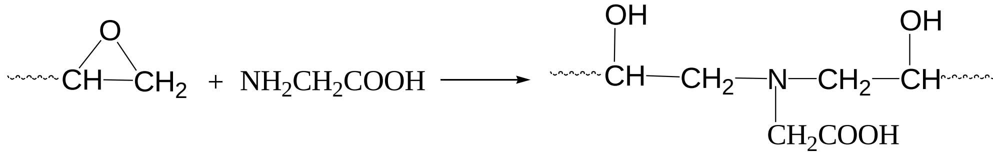
Chemical modification is a common way to change the surface properties in material science field, and water-borne epoxy resin technology has been developed in these years [7-8]. So chemical modification adopted as remedy to improve and simplify the method of manufacturing water wet artificial core and hence give solution for the above mentioned challenges. The traditional process of epoxy cement is improved on the basis of the above mentioned criteria.

PROCEDURES

Chemical Modification of Epoxy

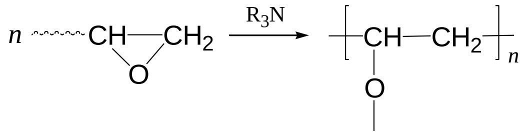
The cement and quartz sand should be sufficiently stirred and cured during core manufacturing process. The thin film is formed by cement on the surface of quartz sand. The ordinary epoxy is oil-wet; as a result, the cemented core is also oil-wet. The core's wettability can be influenced by properties of epoxy and curing agent.

Bisphenol-A-type epoxy resin E-51(Epoxy value: 0.48-0.54, industrial products with lower viscosity) and glycine (analytically pure) were selected for chemically modified epoxy resin manufacturing. Mole ratio is n (epoxy group): n (glycine) = 3:1 (mass ratio is about 8:1). E-51 epoxy resin, the glycine and surfactant were mixed together and heated to 80°C (keep 3.5 hours for reaction). Using sodium hydroxide solution to neutralize the mixture and therefore the water-based epoxy system was produced [6]. The equation for the chemical reaction is:



(1)

Modified epoxy resin is transparent liquid with light yellow color. Triethanolamine (TEA, industrial product) is used as a curing agent. The equation for the cure reaction is:



(2)

Solidification of Epoxy and Artificial Core

Firstly, mix ordinary epoxy or modified epoxy resin with TEA adequately and smear the mixture evenly on the glass. Then place it into a thermostat (65°C) for 5 hours to solidify. After the solidification, measure the solid-oil-water contact angle for cured epoxy and modified epoxy resin.

Secondly, mix ordinary epoxy or modified epoxy resin with TEA and quartz sand adequately. Quartz sand of 100~120 mesh was used as cement particles and the mass ratio of epoxy (including curing agent) to quartz sand is 0.07:1. Then push the mixture into the cylindrical mould (diameter = 1 inch, pressure = 10MPa) and place it into a thermostat (65°C) for 5 hours to solidify. After the solidification, we get the artificial core and then measure the contact angle, stability in oil or water (valued by stress sensitivity) and pore structure using NMR.

RESULTS AND DISCUSSION

Wettability

Using water and kerosene (dyed by Sudan III), the oil-water contact angle on the solid surface for different epoxy coatings at 20°C was measured. The results are given by Fig 1 and Fig 2. The contact angle of oil-water on ordinary epoxy coating surface is about 106° which is the critical value between weakly oil-wet and oil-wet. But the contact angle on water-wet epoxy coating surface reaches about 40.5°, which shows that it is strongly water-wet or hydrophilic.

The artificial cores were cut into small slices with a thickness of 3mm and the contact angle results of oil-water phase on the surface are given in Fig 3 and Fig 4. Since ordinary epoxy resin core is oil-wet, slow spontaneous imbibition will occur to the oil drop, so ought to measure the contact angle when the kerosene were just touching the slice. Contact angle on ordinary epoxy resin core slice is 103^o, which shows that it is weak oil-wet. On the other hand, contact angle on waterborne epoxy resin core slice is 47^o, which shows that it is stronger water-wet than the previous.

The analysis of results show that the contact angles of cement core are very close to epoxy resin. Although quartz is hydrophilic, after mixing the epoxy resins and curing agent, cementing agent will form the thin film on the surface of quartz particle. After the cementing agent solidified, the quartz particles will be brought together to form the core. So the surface properties of cemented core are related closely with curing agent.

Core stability

8 artificial cores were made at same conditions, but with different epoxy. The permeability and porosity were tested by N_2 at 20°C. Table 1 shows that these cores have

basically the same permeability and porosity. After soaking in kerosene and brine (5%wt) for 48 hours, stress sensitivity of cores was tested by changing confining pressure, the results were used to value the core stability. In Fig 5 and Fig 6, k and k_i represent permeability under different confining pressure and initial permeability respectively. The stress sensitivity curves are very similar and close for cores soaked in kerosene or brine for both kind of cores. Therefore the kerosene and brine have little effect on the strength of this kind of cores. Stress sensitivity is low for both cases since the permeability under 10MPa is still above 85% of initial permeability. Comparing Fig 5 and Fig 6, the oil-wet core has a higher permeability than water-wet core at the same effective stress. In particular, when stress is 15MPa for both cases, the permeability for oil-wet is 5% higher as compared to that of the water-wet core.

The cured epoxy resin ensured the strength and weak stress sensitivity for the artificial cores. Since some epoxy groups of chemical modified epoxy have been replaced by hydrophilic groups, the strength of cured resin modified epoxy becomes lower and the effective stress of water-wet core stronger. However, the difference of 5%, which is shown in the results has little influence on normal displacement experiment.

Pore structure

Finally, the NMR tests were conducted for two kinds of cores (O4, W4) as shown in Table1 and Fig7. They all have the feature of single crest in the NMR spectrum. Since the pore samples were made of sand and epoxy of the same size and amount, the porosity, permeability and proportion distributions is almost the same. So a better comparability for the influence of wettability on multiphase flow in porous media is shown.

CONCLUSION

(1) The wettability of core mainly depends on the surface characteristics of epoxy. Using chemically modified epoxy the manufacture of water wet artificial cores becomes simple and convenient

(2)Artificial core has low stress sensitivity and better stability even when soaked in oil or water.

(3)Generally, artificial cores have almost the same properties except for wettability, so they are more suitable for porous media flow under different wettability.

ACKNOWLEDGEMENTS

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Tab 1. Properties of artificial cores

Core number	Length /mm	Diameter /mm	Gas Permeability /$10^{-3}\mu m^2$	Porosity	Processing mode	Wettability
W1	62.43	25.02	1453	0.352	-	water-wet
W2	59.40	24.96	1512	0.357	Soaked in kerosene for 48h	water-wet
W3	60.88	25.08	1478	0.353	Soaked in brine (5%wt) for 48h	water-wet
W4	21.02	24.88	1512	0.354	-	water-wet
O1	61.52	24.86	1450	0.353	-	oil-wet
O2	62.34	24.96	1489	0.355	Soaked in kerosene for 48h	oil-wet
O3	61.72	25.12	1503	0.354	Soaked in brine (5%wt) for 48h	oil-wet
O4	20.56	24.90	1485	0.358	-	oil-wet

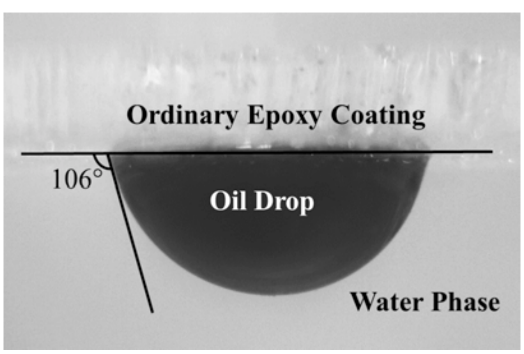

Fig 1. Contact angle on ordinary epoxy coating surface

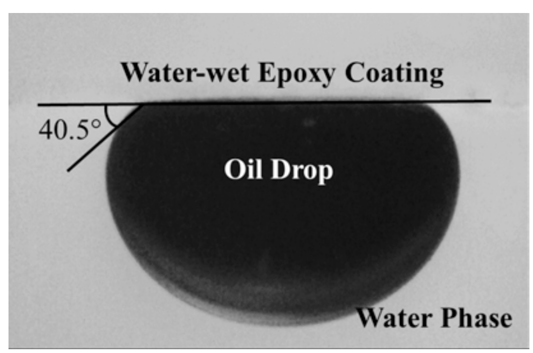

Fig 2. Contact angle on modified epoxy coating surface

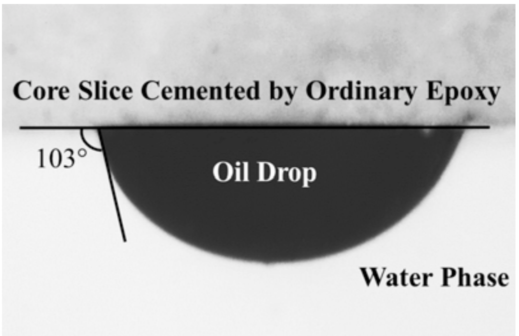

Fig 3. Contact angle on surface of core slice cemented by ordinary epoxy

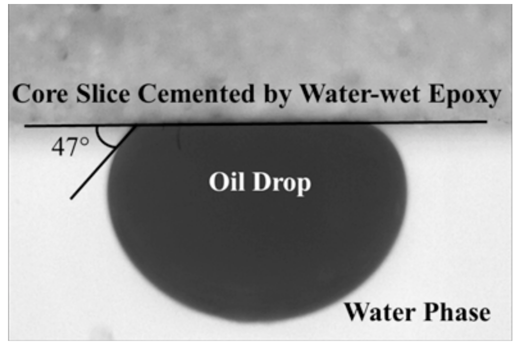

Fig 4. Contact angle on surface of core slice cemented by modified epoxy

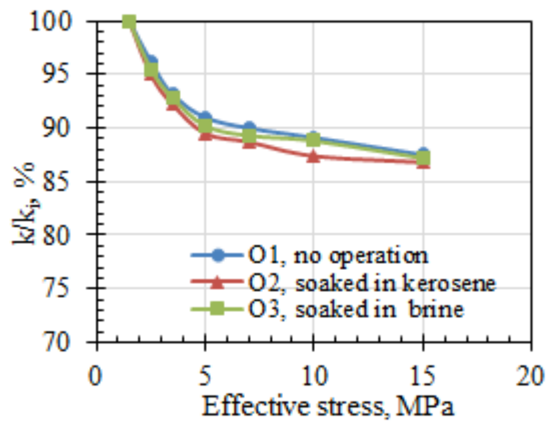

Fig 5. Stress sensitivity of oil-wet cores using ordinary epoxy

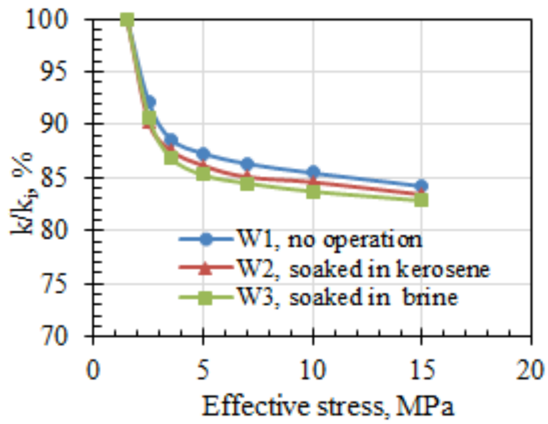

Fig 6. Stress sensitivity of water-wet cores using modified epoxy

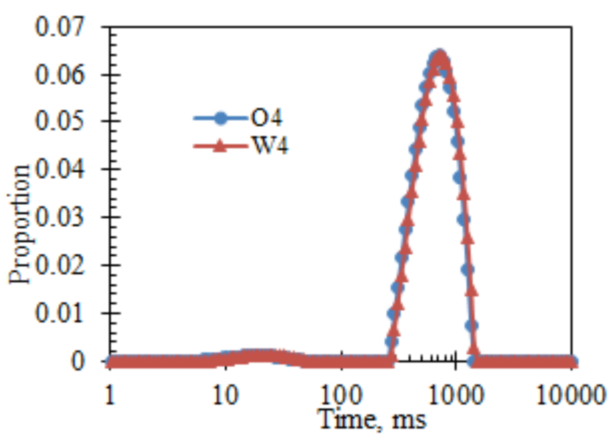

Fig 7. NMR result (proportion distribution) for two kind of cores