



Oil swellable polymer modified cement paste: Expansion and crack healing upon oil absorption



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HIGHLIGHTS

- An oil swellable polymer (OSP) with oil absorptivity as high as 700% is synthesized.
- Addition of OSP decreases the total porosity of the hardened cement paste (HCP).
- Addition of OSP reduces the water adsorption rate and increases the oil absorptivity of HCP.
- Incorporation of OSP significantly increases the expandability of HCP upon oil absorption.
- A novel technique to achieve a crack self-healing property is developed.

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ABSTRACT

This paper proposes a novel approach to achieve self-healing property of cement sheath in the oil well triggered by oil leakage through cracks. An oil swellable polymer (OSP) with oil absorptivity as high as 700% was synthesized through emulsion polymerization. The OSP dispersion was added into the Portland cement paste. It is found that the oil absorption and the linear expansion of the OSP modified hardened cement paste (MHCP) are greatly increased compared to the blank hardened cement paste (BHCP). Pore structure measurements by N₂ adsorption show that the addition of OSP decreases the total porosity of MHCP which confirms that the formation of the polymeric film in MHCP. The self-healing ability of MHCP was evaluated by the oil flow test through a single crack in the cylindrical specimen. The oil flow tests indicate that the leakage of oil through the crack is gradually mitigated due to the expansion of the MHCP and thus the self-healing ability is successfully achieved.

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1. Introduction

Cracks, caused by shrinkage and external loads, are unavoidable in the cementitious materials because of their intrinsic fragile property [1]. These cracks facilitate the ingress of aggressive and harmful substances into the cementitious materials and indeed reduce the functionality and durability of the materials [1,2]. In oil well cementing, cement slurry is used to cementing a metal pipe (so-called casing) into the borehole. The hardened cement

paste, namely the cement sheath, fulfills many functions, including mechanically bonding and supporting the casing, chemically protecting the steel casing from corrosion, isolating fluids and gases between formations. Consequently, the sheath needs to withstand various stresses and erosions during the service life of an oil well. Cracking inside the cement sheath and debonding between the cement sheath and the borehole (or the metal pipe) are often taking place. The consequences of the occurrence of such cracks and gaps are: 1) leakage of oil/gas fluid and thus reduction of the productivity; 2) failure to protect the steel pipe from corrosion due to the invasion of aggressive species such as saline fluid, CO₂ and H₂S. Detection of the occurrence of such cracks and manual repair during operation of the oil well are almost impossible because these

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cracks can be located as deep as beneath the earth's surface in depth up to 9000 m. In this case, the only conceivable approach for the leakage problems caused by cracking is self-healing of the cracks in the hardened cement paste (HCP) triggered by the leakage of fluids, either aqueous fluids or oily fluids.

Self-healing of cementitious materials, such as concrete in natural environment was firstly reported by the French Academy of Science in 1836 [3]. The main mechanisms can be summarized as followings [4]: 1) Further hydration of the unreacted cement or cementitious material and the hydration products are able to block the cracks; 2) Formation of calcium carbonate on the surface of crack through the carbonation reaction of hydration product $\text{Ca}(\text{OH})_2$; 3) Blocking cracks by impurities in the water fluid or by loose concrete particles resulting from crack spalling; 4) Expansion of the hydrated cementitious matrix. Such self-healing phenomena are called autogenous self-healing because no additional components is needed in concrete formulations [3]. It is clear that water or moisture is one of the necessary elements in all autogenous self-healing reactions. However, in case of oil well, water is often absent. Therefore, the autogenous self-healing behaviors of oil well cement sheath cannot be realized in the absence of water (or moisture) based on the abovementioned mechanisms. It is demanded to trigger a novel concept to achieve self-healing properties of HCP triggered by oil (or gas) leakage.

Besides the autogenous self-healing properties of cracks in hardened cementitious materials, the other concept for self-healing is to introduce healing agents such as curable polymer resins (epoxy resin) or sodium silicate in the forms of microcapsules, fibers etc into cementitious materials [5–9]. The healing agents can be released and cure the cracks when the capsules or fibers are broken. As a result, the cracks are healed. In this case, the self-healing is triggered by mechanically breakage of the microcapsules or fibers. Proper design and control of the microcapsules or fibers are keys to the success of self-healing. It is not an easy work to keep the microcapsules or fibers intact during mixing of the cementitious materials and to properly activate the curing process of the healing agents at the location of cracking. The introduction of epoxy resin without any hardener into cementitious materials to achieve the self-healing is recently studied [10–13]. They concluded that the liquid epoxy resin remaining in the pores of HCP can be released and hardened under the catalysis of $\text{Ca}(\text{OH})_2$ and thus cure the microcracks. However, this method is practically inapplicable in oil well condition due to the high solubility of epoxy resin in the oil. On the other hand, especially, in the oil well cementing work, the cement slurries are prepared under super-high shear up to 10,000 rpm and the microcapsules or fibers are hardly able to withstand such high shear force during the mixing process.

Another emerging self-healing concept for cementitious materials in recent years is to involve a biological repair technique by the introduction of bacteria into concrete to aid in the precipitation of calcium carbonate to achieve crack self-healing [14,15]. However, the oil well cement sheath is subjected to high temperature up to 200 °C and high pressure up to 70 MPa in deep oil well and almost no biological species could survive in such severe conditions.

Apart from introducing the curable healing agents or bacteria to achieve self-healing, the expansion of hydrated cementitious matrix will also benefit to the self-healing of cracks. Calcium sulfoaluminate based expansive agents [16–19], super absorbent polymers (SAP) [20] were studied to achieve the self-healing ability of HCP through the dimensional expansion of HCP. Following these ideas, this paper develops a novel concept to achieve self-healing of HCPs stimulated by the leakage of oil fluid through cracks. Polymer nano-particles with high oil absorption capacity were prepared in the form of polymer latex by emulsion polymerization. The oil

swellable polymer nano-particles were incorporated into HCP by mixing the polymer latex into the cement slurry. For the fully cured HCP samples, their oil absorption and their linear expansion upon oil absorption were measured. The flow behavior of oil fluid through a single crack penetrating the cylindrical HCP specimens was studied to signify the self-healing behavior of the polymer modified HCPs.

2. Experimental

2.1. Materials

Analytical grade of chemicals, styrene (St), butyl acrylate (BA), octadecyl acrylate (OA), divinylbenzene (DVB), sodium persulfate (SPS), sodium hydroxide acrylamide (AM) and methacrylic acid (MAA) were used as received (all >98% purity). Anionic emulsifier MS-1 (alkylphenol ether sulfo succinate sodium salt, $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{COC}_3\text{H}_6\text{SO}_3\text{Na}$, 40 wt.% aqueous solution) and non-ionic emulsifier OP-10 (alkylphenol ethoxylates, $\text{C}_8\text{H}_{17}\text{C}_6\text{H}_4\text{O}(\text{CH}_2\text{CH}_2\text{O})_{10}\text{H}$ 40 wt.% aqueous solution) were provided by Haian petrochemical factory. Dispersing agent (water-soluble sulfonated acetone-formaldehyde resin) and fluid loss agent (modified polyvinylalcohol) used in the Portland cement paste preparation were provided by the Sinopec Research Institute of Petroleum Engineering. Deionized water (DI water) was used in all experiments in this study including the synthesis of polymers and the preparation of cementitious mixtures. Diesel was chosen as the oily medium. The physical properties of diesel were shown in Table 1.

According to Chinese standard GB10238–2005, G class oil well Portland cement produced by Sichuan Jiahua cement plant was used in this study. The chemical and mineral composition of this cement was measured by X-ray fluorescence spectrometry (XRF, LAB CENTER XRF-1800, SHIMADZU), and the mineral compositions were calculated according to the Bogue equation, the results were shown in Table 2.

2.2. Synthesis and characterization of the oil swellable polymer

2.2.1. Synthesis of the oil swellable polymer

It has been well documented that the oil absorptivity of polymer could be highly increased by incorporating long alkyl chains into the polymer, which can make the resulting polymer more hydrophobic [21]. In addition, molecular weight (M_w) as well as the crosslinking density of the polymer plays an important role in the oil absorption capacity of the polymer. High M_w and appropriate crosslinking density are beneficial to high oil absorptivity [22]. Taking all these factors into account, we synthesized the oil swellable polymer by co-polymerizing styrene, butyl acrylate and octadecyl acrylate as a functional monomer via radical polymerization. The oil swellable polymer was prepared by emulsion polymerization in a 1000 mL three-neck glass flask equipped with a mechanical stirrer and dosing units for both the monomers and the initiator. A water bath with fixed temperature of 90 °C was used to ensure the constant temperature during polymerization. Initiator solution was prepared by dissolving 3.6 g SPS in 252.0 g DI water. Monomer emulsion was prepared by mixing monomers (120.2 g St, 180.0 g BA, 148.5 g OA, DVB 1.7 g), emulsifiers (3.6 g MS-1 and 3.6 g OP-10) and 540.0 g DI water using a high-shear mixer at 10,000 rpm. Firstly, 225.0 g DI water and 12.8 g initiator solution were charged into the flask. The pre-charge was then heated up to 90 °C under stirring and kept for 5 min. The monomer emulsion prepared above and the rest initiator solution (242.8 g) were then separately dosed into the flask at constant dosing rates. The dosing time of both the monomer emulsion and the initiator solution were 4 h. After that, the flask was kept at 90 °C for another 0.5 h to complete the polymerization. Afterwards, the obtained polymer dispersion was cooled down to the room temperature. Solid content of the prepared polymer dispersions was measured by drying a certain amount of the polymer dispersion at 60 °C until constant weight was reached. The measured solid content of the prepared polymer dispersion was 27.9%.

2.2.2. Characterization of the oil swellable polymer

Particle size of the polymer dispersion was determined by dynamic light scattering (DLS) with a Malvern Zetasizer 3000hs (UK). The chemical structures of the polymers were characterized by FTIR (Nicolet 6700 FTIR, Thermo Fisher Scientific, USA) instrument with a resolution of 4 cm^{-1} . It is well understood that the latex may contain a tiny amount of residual monomers, oligomers, and free surfactants

Table 1
Physical parameters of diesel.

Viscosity at 25 °C	Surface tension ^a at 25 °C	Density at 25 °C	Density at 80 °C
0.00435 Pa s	27.8 mN/m	0.846 kg/m ³	0.827 kg/m ³

^a The surface tension was measured by using Tensiometers (K12, KRUS, Germany).

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