Effect of the chromium ion diffusion in polyacrylamide/chromium acetate gelation system with surrounding water on gelation behavior

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ABSTRACT

The diffusion of Cr^{3+} from the Cr^{3+}/HPAM system is simulated by quantifying the entrapment ability of the Cr^{3+} after dialysis analysis through a dialysis bag method to study the Cr^{3+} diffusion effect on the gelation types. After the gelant is put in the dialysis bag surrounded by the solvents, only the diffusion of the aqueous ions are allowed, which eventually can be detected in the dialysate. By monitoring the gelants with varying initial contents, we find that the Cr^{3+} dialysis kinetics and total dialyzed amount are changed. In this particular experiment, the gelation types are classified and the classification result differences for the same gelant with or without dialysis process are investigated and compared. In this study, we assess the gelant contents in terms of possible limiting scenarios for successful gelation and discuss their gelation results influenced by the Cr^{3+} diffusion The results demonstrate that Cr^{3+} diffusion, in different extent, influences the gelation types and gelation time of the Cr^{3+}/HPAM systems with varying HPAM molecular weight (MW), the Cr^{3+} initial concentration, the initial HPAM polymer concentration, or the degree of initial HPAM hydrolysis. Along with the gelation types and the accompanying morphological study, determine the relationships between the initial Cr^{3+} concentration and the true Cr^{3+} concentration entrapped on the polymers are possible, which are pretty distinct from each other. Neglecting to consider such diffusion effects will lead to overestimating of the crosslinking results. In addition, a sorption model is used to demonstrate the sorption trend changes before and after the gelation time.

1. Introduction

Chromium, widely known as a carcinogen, has various applications in a variety of metal alloys and in chemical refractory and foundry industries, serving as a catalyst, pigment/dye, and synthetic ruby, as well as finding use in such applications as electroplating and leather tanning (Huang and Wu, 1975; Unnithan and Anirudhan, 2001). Chromium can be presented in solution in various chemical forms. Chromium (III) (Cr^{3+}) is obtained and stabilized by dissolving elemental chromium in acids such as hydrochloric acid or sulfuric acid; the resulting solution can be used as a crosslinking agent for gel treatments in oil industry (Moradi-Araghi, 2000). During oil exploitation, most oil production is achieved by injecting water or gas to sweep the reservoir and drive oil towards the production wells (Jin et al., 2015). However, the injected water or gas will inevitably tend to flow into the higher-permeability pathways and leave large quantities of crude oil remaining in the reservoir, resulting in excessive water production and low oil recovery (Demitri et al., 2008; Sang et al., 2014). Excess water production is a major problem for most mature oilfields, which increases

economic and environmental concerns and can eventually shut down the well. Profile control processes with polymers or gels have already been used to solve this problem and improve oil recovery. Some polymer or gel is injected into injection or production wells to either block the flow or reduce water permeability (Ciesielski, 2005; Morris and Chang, 2011; Wu et al., 2012). Recently, a large number of gel treatment systems have been applied with the object of improving reservoir sweep efficiency during water or gas injection (Biswal and Singh, 2004). Among them, R. D. Sydansk et al. (Sydansk, 1993) found that the gelation process of a hydrolyzed polyacrylamide (HPAM) system (as a gelant) mixed with chromium acetate ($CrAc_3$) can be delayed during the gelant injection process so that gelation does not occur until the gelant reaches the target zones. Therefore, the HPAM/Cr^{3+} gelant system, made popular by its facile preparation, tunable properties, adaptability and low price, has been used worldwide for reducing fluid channeling in oil production (Grattoni et al., 2001; Zohuriaan and Shokrolahi, 2004).

Trivalent chromium (Cr^{3+}) has been considered responsible for the interaction between Cr^{3+} and HPAM carboxylate groups (Lin et al.,

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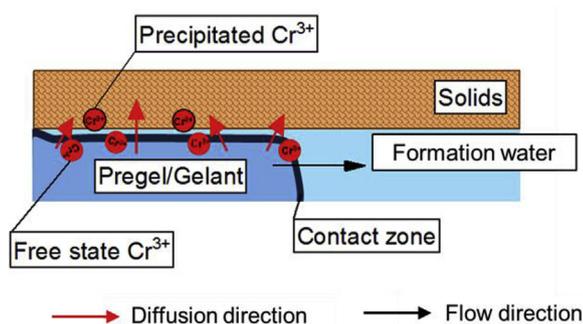* Corresponding author.
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Fig. 1. Cr^{3+} dialysis from gelant by ion-specific diffusion.

2002). This gelation technology is based on the idea that a crosslinking reaction is a ligand-exchange process that displays a typical coordination chemical reactivity (Georgieva et al., 2012). The introduction of acetate complexes of Cr^{3+} reduces the crosslinking rate of the HPAM-Cr^{3+} gel (Liu et al., 2015; Silvério et al., 2014), so some of the Cr^{3+} come out from the gelant before the crosslinking begins, after being transported over a long distance. The dialysis phenomenon of the Cr^{3+} from the gelant influences gelant gelation behaviors in formation water (underground) systems. In general, the Cr^{3+} amount in the gelant is reduced by ion-specific diffusion through formation water, self-chromatography, and precipitation of soil minerals or the aquifer sand surface (Kabir, 2001). The dialyzed Cr^{3+} cause the environmental issue and increased the cost of oil production.

As a precondition reaction, the ion-specific diffusion behavior (Yeager and Steck, 1981) observed in aqueous systems with polymer gel is a challenge and limitation because formation water (especially immobile water on the surface of the solids) acts as a bridge for the exchange of ions between the aqueous solution/colloid and solid-like rocks and sands (Fig. 1) (Boeykens et al., 2005; Dai et al., 2014). To some extent, ion-specific diffusion dominates other ion-specific phenomena, such as self-chromatography and precipitation. Recent studies have mainly addressed how gelation strength is affected by self-chromatography and the precipitation of Cr^{3+}. He et al. (2015) found that the network structures of acrylic-based gels were seriously weakened by self-chromatography during tubing transportation (Jin et al., 2015). G.P. Willhite et al. (2000) observed a large amount of Cr^{3+} precipitation on carbonate during long-term propagation (Zou et al., 2000). The uncertain Cr^{3+} losses can be reduced by controlling the above factors, but the fact that ion-specific diffusion theory is argued to account for the same or better development indicates a clear need for creating an improved method by which to measure Cr^{3+} diffusion.

The process of ion-specific diffusion is a special case of the general desorption process from the gelant. In some studies, the effect of Cr^{3+} loss on the gelation process and stability has been interpreted by observing the rheological behavior of the gelant after being transported through varying solids (Blowes et al., 1997; Huang et al., 1986). However, the results only show comprehensive Cr^{3+} loss behavior from which analyzing the ion-specific diffusion phenomenon separately is difficult. In the previous study, the experiments were done in a core system and the Cr^{3+} diffusion amount was assumed same as the Cr^{3+} amount absorbed on the rock (Zhang et al., 2016). In order to better investigate Cr^{3+} ion-specific diffusion in this study, we developed a novel dialysis bag method to simulate the Cr^{3+} diffusion process in the reservoir which produces more accurate dialysis results compared to conventional reference methods. The study starts by measuring the Cr^{3+} dialysis from the gelant system and its accompanying effect on the gelation, including gelation time and gelation type. The gelation time is determined by measuring the change of the viscosity, while the gelation type is achieved by combing the result of the Cr^{3+} dialysis, viscosity measurement, and morphology study. The dependency-relation rules between the dialysis/gelation test results and polymer molecule weight,

initial polymer or Cr^{3+} concentration, initial degree of hydrolysis (DH) and dialysis surface area were systematically investigated. Next, to determine the relations between initial Cr^{3+} amount in the gelant and the truly entrapped Cr^{3+} amount, the dialysis isotherm of the Cr^{3+} was determined. The results showed that there was a pretty distinct from them. Neglecting to consider such differences in the field operation will lead to overestimating of the gelation results and increase the possibility of the project fail. Furthermore, five gelation types were classified based on the dialysis analysis results of the typical samples which, on the contrary, were used to determine and prove the gelation processes of the rest samples.

2. Experimental

2.1. Preparation of materials and sample

An HPAM-Cr^{3+} gelant sample was prepared from HPAM stock solution and chromium acetate stock solution. Commercial-grade HPAMs were obtained from SNF. The degree of hydrolysis (DH) ranged from 1-5% to 27–32%. Chromium acetate (($CH_3COO)_7(OH)_2Cr_3$, 24% Cr(III)) solid was purchased from Alfa Aesar. All reagents were conducted on a weight basis and used without any further purification. The HPAM was diluted with deionic water (DIW) and stirred at a speed of 400 RPM in a blender for 5 min for dispersion to prepare 10000 ppm polymer stock solutions. Chromium acetate stock solutions with a 5000 ppm concentration were prepared by dissolving reagent-grade chromium acetate solids into deionic water (DIW). The stock solution was aged for 24 h for dispersion to ensure that the hydrolysis of the chromium acetate was constant. The stock solution was subsequently diluted to produce Cr^{3+} solutions of varying concentrations.

The reagent components and initial properties of the gelant used in the dialysis and gelation kinetic experiments are listed in Table 1 (samples #1–20). In the present experiments, we are dealing with the effects of polymer molecular weight, Cr^{3+} concentration, HPAM concentration, HPAM hydrolysis degree and interfacial area. A sample preparation follows as an example: 50 g of the polymer solution and 50 g of Cr^{3+} solution were mixed in a glass jar (Yuan et al., 2016) and agitated for 2 min; bubbles created during the agitation were removed through a 2-min ultrasound treatment. For Cr^{3+} dialysis analysis and dynamic viscosity measurement, samples were placed into dialysis bags. Earlier studies have indicated that the solution's pH is an important parameter affecting the dialysis of metal ions (Ertugay and Bayhan, 2008). Therefore, the initial pH of the gelants was controlled between 5 and 6.

2.2. Cr^{3+} dialysis analysis

The membrane dialysis system was used to measure the polymers or crosslinked polymers to the Cr^{3+}.

The dialysis bag was made by sealing two ends of the membrane tubing (Standard RC Tubing, MWCO: 6–8 kD). As one example of dialysis sample, HPAM/Cr^{3+} gelant of known weight were added to the dialysis bag, the gelant capacity of which was 20 mL ± 3 mL. This dialysis bag was permeable to small moieties such as water molecules and Cr^{3+}, but not permeable to the polymer chain. The bag was placed in a cylinder, and pre-weighted DIW (100 mL ± 1 mL) was added as the dialysate. In the dialysis experiments, the cylinders were then aged in a 45 °C water bath as the mixture samples gelled. The dialysates in the cylinders were renewed every 10 h after dialysis began, and the replaced dialysate was collected at the same time for ionic analysis. The dialysis process lasted at least 100 h to give the gelants enough time to diffuse and react. The Cr^{3+} concentration of the dialysate at the different periods were measured using inductively coupled plasma mass spectrometry (ICP-MS) at wavelength 339 nm.