Transport and Retention Modelling of Iron Oxide Nanoparticles in Core Scale Porous Media for Electromagnetic Heating Well-Stimulation Optimization

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Abstract. Understanding the transport and retention of iron oxide nanoparticles is critical in optimizing electromagnetic heating well stimulation. If the injected concentration or injection rate is too big, nanoparticles can build-up inside the pore throat, which can reduce the permeability of the reservoir. A numerical model has been created to describe the behavior of iron oxide nanoparticles in porous media. The model is coupling material balance equation and fluid flow in porous media equations. There are six parameters to be estimated through matching with experimental data: irreversible attachment rate, reversible attachment rate, irreversible attachment capacity, reversible attachment capacity, reversible detachment rate and permeability. All parameters were obtained directly through coreflooding result in previous study. We add Langmuir static isotherm test to limit the maximum adsorption capacity to provide a better estimation of concentration distribution. We use 1% NaCl solution as the base fluid and 45-50 mesh sand as the porous media. From the Langmuir static isotherm test, the maximum adsorption concentration is determined. Then, coreflooding is conducted using 10 ppm nanofluid and 12 cc/min injection rate. The proposed model is matched with the experimental data and its parameters are consistent with the maximum adsorption capacity provided from the test.

1. Introduction
Currently, nanoparticles have been extensively applied in various fields such as medicine, chemical, electronic and engineering. Nanoparticles, also called engineered nanomaterial, could be designed for certain purpose. Some of the nanoparticles types are highly responsive when they are induced with electromagnetic field. UV-visible, microwave and infra-red spectra may be used as sources to provoke translation, rotation and vibration motion of those magnetic nanoparticles [1]. Absorbed energies are then converted into heat. This process is known as electromagnetic heating assisted with nanoparticles.

The usage of nanoparticles to improve oil recovery has been popular with many methods and mechanisms applied to increase oil production. Some purposes such as stabilization of foam and emulsion, oil wettability alteration on the sand surface and interfacial tension (IFT) reduction could be conducted by nanoparticles support [2]. There are many developing nanoparticles application in oil exploration and production. Carbon dioxide in water foams may be generated by nano silica without
surfactant addition, as reported by Espinosa et al. (2010) [3]. Huang et al. (2008) used nanoparticles to coat hydraulic fracture proppant to control fines migration without decreasing productivity [4]. Zhang et al. (2010) stated that oil-in-water and water-in-oil emulsions which are stabilized with different surface-coated silica nanoparticles of uniform size remain stable for several months without coalescence [5].

Although nanoparticles have many usages in oil production, one of the most critical issues is how to transport nanoparticles into the reservoir and fulfill the properties of colloidal transport in porous media. Emulsion properties depend on some factors like concentration of nanoparticle, fluid salinity, and initial injected volume ratio [6]. Aggregation, retention, adsorption and absorption phenomena can occur in porous media. Other than that, previously adsorbed nanoparticles may attach other particles injected afterwards [7]. Godinez and Darnault (2011) reported that the aggregation of nanoparticles and the electrostatic interaction between surfaces of porous media and nanoparticles are impacted by the solution ionic strength and pH [8].

Presenting those phenomena with equations will provide further understanding and furthermore, can be applied to another cases without conducting the same experiment. Modifying computational flow design also gives a chance to modify the equations easily. In this paper, we modify material balance equation and couple it with fluid flow in porous media equation to describe nanoparticles flow behavior. Coreflooding is conducted to validate our proposed model.

2. Mathematical Model

Zhang et al. (2016) proposed a mechanistic model for nanoparticle retention in porous media. The model is an independent two-site model (ITSM) [9]. The ITSM is based on mass conservation, irreversible attachment, and reversible attachment. We proposed a modification of ITSM model by coupling it with diffusivity equation which provides continuously changing interstitial velocity, depends on pressure gradient instead of a constant interstitial velocity in ITSM.

2.1. Independent Two-Site Model

\[
\frac{\partial c}{\partial t} + \frac{\rho_b}{\phi} \frac{\partial s_1}{\partial t} + \frac{\rho_b}{\phi} \frac{\partial s_2}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} \tag{1}
\]

\[
\frac{\rho_b}{\phi} \frac{\partial s_1}{\partial t} = k_{irr} \left( 1 - \frac{s_1}{s_{1\text{max}}} \right) \frac{c}{c_{b}} \tag{2}
\]

\[
\frac{\rho_b}{\phi} \frac{\partial s_2}{\partial t} = k_{ra} \left( 1 - \frac{s_2}{s_{2\text{max}}} \right) \frac{c}{c_{b}} - \frac{\rho_b}{\phi} k_{rd} s_2 \tag{3}
\]

Equation 1 is mass conservation equation, Equation 2 and 3 are irreversible attachment and reversible attachment equation respectively where

- \( c \) : nanoparticle dispersion concentration, fraction
- \( \rho_b \) : bulk density, ML^{-3}
- \( \phi \) : porosity, fraction
- \( D \) : hydrodynamic dispersion coefficient, L^{2}T^{-1}
- \( v \) : interstitial flow velocity, LT^{-1}
- \( s_1 \) : irreversible attachment concentrations on solid surface, fraction
- \( s_2 \) : reversible attachment concentrations on solid surface, fraction
- \( s_{1\text{max}} \) : irreversible attachment capacity, fraction
2.2. Fluid Flow in Porous Media

\[ \frac{\partial P}{\partial t} = \frac{k}{\phi \mu c_i} \frac{\partial^2 P}{\partial x^2} \]  

where

- \( P \): pressure, \( \text{ML}^{-1}\text{T}^2 \)
- \( \phi \): porosity, fraction
- \( \mu \): dynamic viscosity, \( \text{ML}^{-1}\text{T}^{-1} \)
- \( c_i \): total compressibility, \( \text{M}^{-1}\text{LT}^2 \)
- \( k \): permeability, \( \text{L}^2 \)

2.3. Boundary Condition and Constraint

In the experiment setup explained in the next section, the boundary conditions are

1. injection condition at inner boundary (Neumann boundary)
   \[ \frac{\partial P}{\partial x} \bigg|_{x=0} = -\frac{\mu QB}{kA} \]

2. constant outlet pressure at outer boundary (Dirichlet boundary)
   \[ P \bigg|_{x=L} = P_{\text{atmosphere}} \]

3. constant injected concentration at inner boundary (Dirichlet boundary)
   \[ c \bigg|_{x=0} = c_{\text{injection}} \]

4. no concentration flux condition at outer boundary (Neumann boundary)
   \[ \frac{\partial c}{\partial x} \bigg|_{x=L} = 0 \]

5. initial pressure at all points in the core is confining pressure
   \[ P \bigg|_{t=0} = P_{\text{confining}} \]

6. initial concentration at all points in the core is zero
   \[ c \bigg|_{t=0} = 0 \]

7. with the constraint
   \[ s_{2\text{max}} < s_{\text{Langmuir, Test}} \]
2.4. Stokes-Einstein Equation

In calculating the hydrodynamic dispersion coefficient, Stokes-Einstein equation [10] can be applied

\[ D = \frac{k_B T}{6 \pi \mu r} \]  

(5)

where

- \( k_B \): Boltzmann’s constant, \( \text{ML}^2\text{T}^{-2}\text{\theta}^{-1} \)
- \( T \): Temperature, \( \theta \)
- \( \mu \): dynamic viscosity, \( \text{ML}^{-1}\text{T}^{-1} \)
- \( r \): radius of nanoparticle, \( \text{L} \)

2.5. Darcy Equation

Darcy equation is a common equation used for fluid flow in porous media.

\[ v = -\frac{k}{\mu} \frac{\partial P}{\partial x} \]  

(6)

where

- \( v \): interstitial velocity, \( \text{LT}^{-1} \)
- \( k \): permeability, \( \text{L}^2 \)
- \( \mu \): dynamic viscosity, \( \text{ML}^{-1}\text{T}^{-1} \)
- \( \phi \): porosity, fraction
- \( \frac{\partial P}{\partial x} \): pressure gradient, \( \text{ML}^2\text{T}^{-2} \)

2.6. Calculation Algorithm

There are 6 parameters to be estimated. The parameter estimation is done by means of this algorithm

\[ \begin{align*}
\text{Guess parameters} & \quad \rightarrow \quad \text{Solve Equation} \quad \rightarrow \quad \text{Calculate } v \\
\text{Experimental} & \quad \rightarrow \quad \text{Calculate squared error} \quad \rightarrow \quad \text{Solve Equation} \quad \rightarrow \quad \text{Error} \\
& \quad \text{Estimated parameters = Guessed Parameters}
\end{align*} \]

*Figure 1.* Parameter Estimation Algorithm.
3. Experimental Procedure

In order to obtain the five constant data (irreversible and reversible attachment rate, reversible detachment rate, irreversible attachment capacity and reversible attachment capacity) for the simulation purpose, we conducted coreflooding test using iron oxide nanoparticles in loose sand core. The coreflooding test mimics the real fluid flow in reservoir. Langmuir test was also conducted to provide the data for the boundary condition.

3.1. Materials and Tools

3.1.1. Materials
For making nanofluid, we use iron oxide nanoparticles from Sigma-Aldrich, which known properties are <50 nm in size and 5 mg in weight. As a comparison, we use base fluid consists of NaCl powder for making 10 ppm brine solution. A loose sand core is also used as a representative to create a porous medium with average porosity of 38.4%.

3.1.2. Tools
Apparatus used include flooding setup, core holder (including wire net, rubber, and lids), laboratory glasswares, and digital scale.

3.2. Nanofluid Preparation
Aqua DM and NaCl were used to make 10 ppm synthetic brine. Then, 5 mg of iron oxide nanoparticles was gently added into 500 ml of synthetic brine to make 10 ppm nanofluid which is mixed with sonicator (Ultrasonic Cleaner, Krisbow 150179) for approximately 15-20 minutes.

![Figure 2. Nanofluid used in the flooding experiment.](image)

3.3. Core Preparation

3.3.1. Loose Sand Core Making
A Loose sand core was prepared from quartz. The wire net was installed near the core holder lids, thereafter sand was added and pressurized gradually using the core making device. The purpose of using wire net is to keep the sand from being carried away by the fluid during flooding experiment.
3.3.2. Pore Volume Determination

To calculate pore volume in this experiment, we first measured the mass of an empty set of core holder and the mass of a core holder with sand using the digital scale. From this procedure, we obtain the net mass of sand inside the core. Afterward, flooding was initiated using 10 ppm brine solution to saturate the entire core. The core was then briefly removed from hassler core holder to measure its mass. We will obtain the mass of fully saturated core.

Aside from the mass of each parameter, we also need to measure the dimension of the core to further obtain the bulk volume. Based on the measurement we have commenced, the loose sand core has a bulk volume of 17.73 cc. The results of core measurement are summarized in Table 1.

![Figure 3. Loose sand core.](image)

**Table 1. Core Data**

| Rate          | Mass of an empty core holder | Mass of a core holder + sand | Mass of a saturated core holder + sand | Net sand mass | Fluid mass | Porosity (fraction) |
|---------------|-----------------------------|-----------------------------|----------------------------------------|---------------|------------|---------------------|
| 12 cc/min     | 111.1 g                     | 148.4 g                     | 155.2 g                                | 37.3 g        | 6.8 g      | 0.38                |

3.4. Flooding Scenario

The flooding scenario was divided into 3 steps. The first step of the flooding was to saturate the loose sand core with 10 ppm brine solution using 1 cc/min injection rate. After the whole core was fully saturated, the mass was measured using the digital scale to calculate PV. The second step was injecting 10 ppm nanofluid with 12 cc/min injection rate for 15 cuvettes (about 4 cc/cuvette) or 8.8 PVs. Subsequently, post flush with 10 ppm brine solution and 12 cc/min injection rate for 15 cuvettes.

![Figure 4. Schematic of flooding apparatus.](image)
3.5. Langmuir Isothermal Test
In this section, we carried an experiment to generate Langmuir Isotherm plot. The first step was to create nanofluid samples comprised of 10 ppm brine with different nanoparticles concentration from 0 – 16 ppm and then measure them with UV – Vis spectrophotometer to obtain their initial concentration ($c_0$). Afterward, quartz and each sample were sonicated for 15 - 20 minutes. Each nanofluid sample should have a different concentration of nanoparticles ($c_1$) after sonication period. The adsorption concentration can be obtained by subtracting $c_0$ with $c_1$.

4. Results and Discussion
The estimated parameters are shown in the table below

| Table 2. Core Data          |
|-----------------------------|
| Parameter | Estimated value |
| $k$       | $8 \cdot 10^{-21}$ m$^2$ |
| $k_{ijr}$           | $9.9 \cdot 10^{-2}$ 1/s |
| $s_{1\text{max}}$     | $5 \cdot 10^{-5}$     |
| $k_{ra}$            | $8 \cdot 10^{-5}$ 1/s |
| $s_{2\text{max}}$     | $5 \cdot 10^{-8}$     |
| $k_{rd}$            | $4 \cdot 10^{-5}$ 1/s |

Solving Equation 1 and Equation 4 with these estimated parameters and overlaying it with the experimental data result in Figure 5 below. The proposed model is matched with the experimental data.

![Figure 5. Effluent history simulation result overlayed with experimental data.](image)
As we can see from the results, reversible detachment capacity ($s_{2\text{max}}$) is smaller than irreversible attachment capacity ($s_{1\text{max}}$), which we suspect is a notable sign of absorption phenomena.

![Langmuir Isotherm](image)

**Figure 6.** Langmuir isotherm plot for iron oxide shows maximum adsorption concentration of $8 \times 10^{-6}$.

Langmuir isotherm plot is conducted to confirm the estimated value of reversible detachment capacity. We can see the right part of Langmuir isotherm plot is decreasing. It is caused by agglomeration of the iron oxide nanoparticle. The maximum point before it decreases is the maximum adsorption concentration (MAC) which value is $8 \times 10^{-6}$. This result provides a more powerful sense of $s_{2\text{max}}$ value. Langmuir isotherm test is conducted in static condition while $s_{2\text{max}}$ is in dynamic condition, which means the value of $s_{2\text{max}}$ should be less than MAC. While the estimated value of $s_{2\text{max}}$ is less than $8 \times 10^{-6}$, the estimated value is confirmed to be correct.

5. **Conclusion**

From the simulation results, it can be concluded that the combined model to predict the transport and retention of iron oxide nanoparticles in porous media has been successfully developed. The model is developed using material balance (ITSM) equation and coupled with fluid flow in porous media equation.

Langmuir adsorption test result is used as a new constraint to increase the accuracy of prediction. The value of $s_{2\text{max}}$ inside the ITSM model should be less than concentration obtained from the MAC test.

6. **References**

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