High Temperature Stability and Low Adsorption of sub-100 nm Magnetite Nanoparticles Grafted with Sulfonated Copolymers on Berea Sandstone in High Salinity Brine

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Abstract

The synthesis of polymer grafted nanoparticles that are stable at high salinities and high temperature with low retention in porous media is of paramount importance for subsurface applications including electromagnetic imaging, enhanced oil recovery and environmental remediation. Herein, we present an improved approach to synthesize and purify sub-100 nm IONPs grafted with a random copolymer poly(AMPS-co-AA) (poly(2-acrylamido-3-methylpropanesulfonate-co-acrylic acid)) by means of catalyzed amide bond formation at room temperature. The improved and uniform polymer grafting of magnetic nanoparticles led to colloidal stability of IONPs at high temperature (120 °C) in API for a month. The transport behavior of the polymer grafted IONPs was investigated in crushed and in consolidated Berea sandstone. The high poly (AMPS-co-AA) polymer level on the surface (~34%) provided electrosteric stabilization between the NPs and weak interactions of the NPs with anionic silica and sandstone surfaces. This behavior was enabled by low affinity of Ca^{2+} towards the highly acidic AMPS monomers thus enabling strong solvation in API brine. In crushed Berea sandstone, the retention was reduced by three fold and nine fold relative to our earlier studies, given the improvements in the grafted polymer layer. For intact core flood experiments in Berea sandstone carried out at elevated temperature (65°C) and pressure (1000 psi net confining stress), the retention was 519 $\mu\text{g/g}$, comparable to the value for crushed Berea sandstone. Furthermore, the addition of a relatively small amount (0.1% v/v) of commercially available sacrificial polymer (e.g., HEC-10) further reduced IONP retention to 252 $\mu\text{g/g}$ or 0.17 mg/m^2 by blocking retentive sites.

Keywords

Magnetic Nanoparticles; Co-precipitation; Transport; Porous media; Polyelectrolyte; Polymer grafting.

1. Introduction

The design of nanoparticles (NPs) including silica, carbon nanotubes, and iron oxide have been investigated recently for various upstream applications in subsurface reservoirs, for example enhanced oil recovery (EOR), [1-3] CO₂ capture, [4] electromagnetic reservoir imaging, [5-7] and environmental remediation [8-10]. Magnetic NPs, especially magnetite (Fe₃O₄), offer unique advantages including superparamagnetism, low Curie temperatures, high magnetic susceptibility, low toxicity, and relatively low cost [11-13]. Given these characteristics, magnetite NPs have been investigated as contrast and imaging agents for magnetic resonance imaging (MRI) applications [13, 14] and for subsurface oilfield applications such as magneto-motive acoustic imaging and cross-well electromagnetic tomography [15, 16]. Ultimately, electromagnetic imaging with highly mobile magnetic nanoparticles with high susceptibilities could provide improved spatial resolution of flow patterns in reservoirs, which could be used to enhance reservoir management during secondary and tertiary production, relative to traditional seismic techniques [17].

Despite the potential of NPs in down-hole electromagnetic imaging in a variety of applications, the harsh conditions of oil reservoirs (e.g., high salinities (>1 M ionic strength), presence of divalent salts (Ca²⁺ and Mg²⁺), and high temperatures (~ 150 °C) present unique challenges for NP stabilization and transport. For example, the high salinities weaken electrostatic repulsion of the particles, typically resulting in NP aggregation and strong adsorption onto mineral surfaces. These factors limit the mobility of the NPs through porous media over the desired distances of 10s and 100s of meters [5, 7, 18-20]. Low molecular weight organic ligands and surfactants are often employed to passivate iron oxide nanoparticle (IONP) surfaces for size control during synthesis and also to provide resistance against aggregation and oxidation [11, 21, 22]. However the range of steric and electrosteric stabilization may be increased markedly with polymer functionalized IONPs, which is important given the high degree of screening of electrostatic repulsion at high salinity [13, 23].

Various polymers have been coated on NP surfaces to provide electrosteric stabilization against colloidal aggregation. In general, polymer coatings are more likely to stabilize NPs if the polymer by itself is solvated in the same media and does not undergo phase separation [24]. Steric stabilization is limited for nonionic polymeric stabilizers such as polyethylene glycol

(PEG), polyacrylamide (PAM), and polyvinyl pyrrolidone (PVP) that are not sufficiently solvated at high salinities [25-28]. Weakly acidic polyelectrolytes such as polyacrylic acid (PAA) remain soluble in 1 M NaCl at ambient temperatures but precipitate in presence of divalent cations [29, 30]. In contrast, sulfonated polymers with low divalent cation binding affinities tend to remain solvated at high salinities and temperatures [31, 32]. Furthermore, it has been demonstrated that strong polyanions, such as sulfonated PHEMA (poly(2-hydroxyethylmethacrylate)) and PSS poly(sodium styrene sulfonate), are more effective under neutral to acidic conditions whereas polyanions capable of forming coordinative bonds with the iron oxide surface, such as PNaVP poly(sodium vinyl phosphonate) and PNaA, (poly(sodium acrylate)) (PNaA) should be used under basic conditions [33].

Recently, our group has demonstrated electrosteric stabilization of IONPs in very high salinity American Petroleum Institute (API) brine (8% NaCl and 2% CaCl₂ by weight) at elevated temperatures up to 90 °C using a series of sulfonated random and block copolymers [5, 6, 34-36]. Poly(AMPS-co-AA) random copolymers were found to be effective stabilizers for ~100 nm IONP dispersions at 90 °C for up to 30 days. The ratio of AMPs to AA was varied from 1:1 to 20:1 to optimize the stabilization of IONPs. It was determined that a ratio of 3:1 was sufficient to provide stabilization of the IONPs without any benefit from higher ratios [35]. The high acidity of the AMPS moieties provided resistance against Ca²⁺ specific binding while the reactive AA units afforded multiple reactive grafting points for robust attachment. To provide sites for grafting of poly(AMPS-co-AA) with a ratio of 3:1, the IONPs were amine functionalized with aminopropyltriethoxysilane (APTES), followed by (N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) (EDC) catalyzed amidation [35] or thermal amidation as shown in Figure 1 [36]. The grafting was performed at high ionic strengths to screen charges on anionic polymer chains in order to increase the grafting density. Thermal amidation reaction was performed on IONPs coated with silica shells to improve APTES functionalization which in turn improved grafting density. The covalent grafting was further confirmed by performing an extreme dilution test by diluting polymer grafted IONPs by 40,000 fold, and demonstrating the polymer was still present by thermal gravimetric analysis. The IONPs, grafted with poly(AMPS-co-AA) either thermally [36] or EDC [35] catalysis, were stable in API brine at elevated temperature (90 °C) for 1 month and exhibited relatively low adsorption in dynamic flow experiments through Ottawa sand and crushed Berea sandstone

packed columns [35, 36]. Also, it was found that homopolymers including anionic PAMPS and zwitterionic sulfobetaine[3-(methacryloylamino)- propyl]-dimethyl(3-sulfopropyl)ammonium hydroxide (PMPDSA) could be tethered to IONPs *via* a “grafting through” approach. For the zwitterionic IONPs, the adsorption on crushed Berea sandstone was found to be an order of magnitude lower than for that of poly(AMPS-co-AA) grafted IONPs [37, 38]. Polyzwitterions are converted from a collapsed globule to a coil-like structure with increases in ionic strength and temperature, and have been used to stabilize silica nanoparticles in salt up to 120,000 mg/dm³ at 90 °C [39].

To improve the mobility of IONPs in porous media, it is important to further decrease the NP adsorption onto the mineral surfaces. An important way to achieve this goal would be to improve the uniformity and graft density of the polymer chains onto the IONPs surfaces. Thermal grafting of IONPs may limit the complete covalent grafting thus limiting surface coverage [36]. Thus, catalyzed grafting of polymer chains under optimal conditions onto IONPs would be a method of choice to enhance the graft density. The EDC or EDC/(N-hydroxysuccinimide) (NHS) system is extensively used for the formation of robust amide bonds, for example in biomolecular applications [40, 41].

Herein, we present an improved approach to synthesize and purify IONPs grafted with a random copolymer poly(AMPS-co-AA) that are colloiddally stable in API brine at 120 °C and smaller than 100 nm, about two fold smaller than in our previous studies [34-36]. The polymer chains were grafted onto IONPs *via* an EDC catalyzed amidation reaction at room temperature at high ionic strength under sonication. The IONPs were synthesized by a co-precipitation method and coated with a thin layer of silica to improve the robustness of NPs and to take advantage of higher reactivity of APTES on silanol groups relative to the naked iron oxide surface as shown in Figure 1. Furthermore, the polymer to IONP ratio was increased from 5 to 10% while the polymer solution was first mixed prior to addition of EDC to take full advantage of EDC activation of the carboxylate groups. It is hypothesized that bath sonication of reaction mixture during initial EDC grafting may reduce the aggregation of the IONPs and improve multipoint attachment of AA groups to individual IONPs, thus lowering the amount of bridging between the IONPs. The IONPs were extensively characterized at various stages by thermogravimetric analysis (TGA) to determine organic content, zeta potential to determine the surface charge, and

dynamic light scattering (DLS) to determine the hydrodynamic diameter. The improved grafting method, as well as purification by tangential flow filtration (TFF), rather than magnetic separation and centrifugation used previously [34, 36], is shown to reduce the degree of aggregation with hydrodynamic diameters smaller than 100 nm in API brine, even after storage in brine at 120 °C for up to 30 days. In contrast the diameters were ~ 150-200 nm in previous studies [5, 34, 36]. With smaller more stable particles and more uniform grafting, the NP adsorption in crushed Berea sandstone decreased markedly by a factor of 3 compared to our previous study [34-36]. The adsorption and transport behavior of polymer grafted IONPs in intact cores of Berea sandstone at high salinity are also reported for the first time. The ability to decrease the NP adsorption is very important for subsurface applications given the large surface areas in the formations and large quantities of NPs required. Furthermore, to the best of our knowledge, this is the first study to demonstrate stability of IONPs at a higher temperature of 120 °C in API brine using poly(AMPS-co-AA), relative to previous studies at 90°C [34-36].

2. Materials and Methods

2.1. Materials

Iron(II) chloride tetrahydrate, iron(III) chloride hexahydrate, citric acid monohydrate, 30% ammonium hydroxide, tetraethyl orthosilicate (TEOS), 3-aminopropyl triethoxy silane (APTES), glacial acetic acid, N-(3-(dimethylamino)propyl)-N'-ethylcarbodiimide hydrochloride(crystalline) (EDC), N-hydroxysuccinimide (98%) (NHS), calcium chloride dihydrate, sodium chloride, hydrochloric acid, sodium hydroxide, acrylic acid, potassium persulfate, sodium metabisulfite and hydroxyethyl-cellulose (HEC-10) (~145 mPa.s, 1 % in H₂O at 20 °C, product no 09368) were obtained from Sigma-Aldrich (St. Louis, MO) and Fisher Scientific (Pittsburgh, PA) and used as received. The monomer 2-amino-2-methylpropanesulfonate (AMPS) was a gift from Lubrizol corporation and used as received. Uniform 8 µm silica microspheres with the trade name Angstrom Sphere Monodispersed Silica Powder (Catalog #SIO2P800-01-1KG) were purchased from Fiber Optic Inc. (New Bedford, MA), and were washed at least five times with pH 9 water and dried at 80 °C before use.

2.2. Synthesis of Poly(2-acrylamido-3-methylpropanesulfonate-co-acrylic acid) (poly(AMPS-co-AA)).

The polymer with an AMPS/AA ratio of 3 was synthesized according to our previously reported procedure while details are provided in the SI [34, 35].

2.3. Synthesis of Iron Oxide Nanoparticles (IONPs, Silica Coating and Amine functionalization

The nanoparticles were synthesized by co-precipitation of iron chlorides with a stoichiometric ratio of 1:2 between Fe(II) and Fe(III) exactly as reported previously [36]. The key advances over previous syntheses [5, 35] were the use of citric acid as a stabilizing agent and maintaining the pH at 10. The nanoparticles were coated with silica using TEOS as described previously [35] with a new method for separation. Once the reaction is complete, the pH was lowered to 10 with 1.0 N HCl and the silica coated NP were purified by using Spectrum Labs KrosFlo Research II ultrafiltration unit (SpectrumLabs, Los Angeles, USA) with a Tangential Flow Filter (TFF) made of 30 KDa molecular weight cutoff (MWCO) poly(ether sulfone) (PES) hollow fibers. Aqueous APTES was employed to introduce amine groups on the surface of TEOS coated IONPs following our earlier procedure [36] with one modification. The sample was bath sonicated for 30 minutes and then purified by using a TFF composed of 30 KDa MWCO PES hollow fibers in diafiltration mode.

Detailed synthetic protocols and characterization techniques are provided in the SI. These techniques include FAAS, DLS, zeta potential, titration of amines, TGA, TEM, and a dilution test to show that the polymer remained on the nanoparticle surfaces.

2.4. Polymer Grafting of Amine Functionalized IONPs

The amine functionalized IONPs were grafted with poly(AMPS-co-AA) by using a modified approach from our previously published procedure. [35] The primary changes were to increase the polymer/IO ratio and to mix simultaneously the IONPs, the EDC and the polymer. The polymer, poly(AMPS-co-AA), was first dissolved in DI water to make a 10% solution and the pH was adjusted to 5.0 using 2.5 N NaOH. The concentration of APTES functionalized IO@SiO₂ NPs to be grafted was maintained close to 5 mg/mL and the dispersion was bath sonicated in an ice-bath for at least 30 minutes prior to grafting reaction. In a typical synthesis, 1 mL of 10 wt. % poly(AMPS-co-AA) was taken in a 5 mL glass vial and placed in a bath

sonicator. To the polymer solution, 2 mL of APTES functionalized IO@SiO₂ NPs were added dropwise over a period of 2 minutes under constant sonication. To this reaction mixture, 27.63 mg (0.14 mmol) of EDC (AA:EDC =1:1 molar ratio) was added and the pH was adjusted to 5.7. After 15 minutes of sonication, 0.5 mL of 20% NaCl (such that the final NaCl concentration in solution is 3 wt. %) was added to lower the electrostatic repulsion between the polymer chains to facilitate grafting. The bath sonication was continued for another 90 minutes after which the reaction vial was transferred to a stir plate and continued stirring for overnight at room temperature. The reaction was scaled up accordingly for synthesis of polymer grafted IONPs while keeping the ratios of polymer to IONPs and EDC the same. The polymer grafted IONPs at large scale were purified using TFF composed of 300 KDa MWCO PES hollow fibers in diafiltration mode followed by concentration.

2.5. Column Studies

2.5.1. Unconsolidated Porous Media Experiments

Transport experiments were performed as described previously [35], using a syringe pump (model 22, Harvard Apparatus, Inc., Holliston, MA), a borosilicate glass column (10 cm length × 2.5 cm i.d.; Kontes, Vineland, NJ) and a fraction collector (CF-1, Spectrum Chromatography, Houston, TX). Briefly, dry 80-100 mesh acid-washed Ottawa sand (specific surface area, SSA = 0.01875 m²/g), or unwashed crushed Berea sandstone of 60-170 mesh (SSA = 22.54 m²/g) [42] was packed into the column in 1 cm increments. Immediately after packing, the column was purged with CO₂ gas for 20 min, followed by the injection of 10 pore volumes (PVs) of background solution (API brine) in an up-flow direction to completely saturate the column media. For column experiments containing oil residual, 1.5 PVs (ca. 35 mL) of neat IsoparTM-L, a synthetic isoparaffinic hydrocarbon solvent (>98% C₁₁-C₁₃), were introduced into the saturated column in a down-flow mode at a flow rate of 1.0 mL/min. The flow was then reversed and 10 PVs of API brine was injected from the bottom of the column at the same flow rate to displace the mobile oil phase. A nonreactive tracer test (2.0 M NaBr in DI water) was performed after complete saturation to assess water flow and hydrodynamic dispersion as previously described [43]. Following the tracer test, approximately 4 PVs of a poly(AMPS-co-AA) grafted IONPs suspension (2500 mg/L as Fe₃O₄ in API brine) was adjusted to pH 7 with 1.0 M NaOH and was injected into the column at a flow rate of 1.78 mL/min, which corresponds to a pore-water (seepage) velocity of approximately 12 m/day. The IONP injection was followed by 4

PVs of NP-free background solution (API brine) at the same flow rate. Quantification (% breakthrough) of influent and effluent IONPs concentrations was performed using a UV-vis spectrophotometer (UV-1800, Shimadzu Scientific Instruments, Columbia, MD) operated at 600 nm. Accuracy of the UV method was confirmed through analysis of nine duplicate samples that were prepared using a Discover SP-D microwave digester (CEM Corporation, Matthews, NC) with concentrated nitric acid, followed by quantification of total iron using an Optima 7300 DV inductively coupled plasma-optical emission spectrometer (ICP-OES, Perkin Elmer, Waltham, MA). X-ray diffraction (XRD) analysis of Ottawa sand indicated a silica content of >99%. Similarly, XRD analysis of the Berea sandstone indicated a quartz content ranging from 83-88% and clay content ranging from 5-7%, including illite, chlorite, and kaolinite [43].

2.5.2. Intact (Consolidated) Core Experiments

Intact core flood experiments at elevated temperature and pressure were carried out at a commercial laboratory (Stim-Lab Division of Core Laboratories, Duncan, Oklahoma). The cores (1.5 inch diameter $\times$ 6 inch length) were cut from a block of Berea sandstone. The average porosity was 0.204 and the SSA was approximately 1.6 m²/g. The remaining sandstone carcass was crushed and sieved to obtain the crushed 60-170 mesh sized Berea sandstone that was used in unconsolidated column experiments described above. The Berea sandstone core experiments were carried out using a Hassler-style core holder under conditions of 65 °C, 2000 psi confining pressure, and 1000 psi pore pressure (1000 psi net confining stress). Three injections were carried out in separate cores: (1) 2400 mg/L (as Fe₃O₄) IONPs, (2) 1000 mg/L IONPs, and (3) sacrificial polymer pre-flood (1000 mg/L hydroxyethyl cellulose, HEC-10 (~145 mPa.s, 1 % in H₂O (20 °C)) followed by 1000 mg/L IONPs. HEC-10 is used as a viscosity modifier and stabilization agent in a variety of industries ranging from beauty products to oil and gas production. Column effluent samples were collected and analyzed using the same procedure described above for the unconsolidated media column experiments.

3. Results and Discussion

3.1. Synthesis of Polymer Grafted IONPs

A schematic of the synthesis steps in the preparation of polymer grafted IONPs, along with corresponding TEM images, is shown in Figure 1. The IONPs were synthesized using a slight modification of the well-established co-precipitation of stoichiometric amounts of ferrous

(Fe²⁺) and ferric chlorides (Fe³⁺) in an alkaline solution [5, 11, 35]. Thus, according to LaMer theory, a short burst of nucleation was followed by slow growth of NPs, without additional nucleation to produce monodisperse NPs. The synthesized NPs were redispersed in a citric acid solution and stored at pH 10 to enhance their colloidal stability. The volume weighted hydrodynamic diameter distribution measured with DLS revealed small clusters of 19-26(90) nm with a small fraction of 67-77(10) nm.

To enhance the robustness, colloidal stability and surface reactivity, the citrate functionalized IONPs were coated with a thin shell of silica by sol-gel processing [44]. A thin silica shell is expected to maintain the magnetic properties of the IONPs while at the same time providing oxidation resistance for practical applications [45]. It has been argued that silica is the best choice for screening interactions between IONPs because of well-known chemical silica-surface modification [46]. The deprotonation of the highly acidic silanol (Si-OH) groups led to a zeta potential lower than -40 mV from pH 4 to 12 and an isoelectric point at pH 2 (Table 1 and Figure 2), indicating a highly negatively charged surface with high coverage. The average size of the NPs after silica coating was 22-26(78) with a small fraction of 57-90(20) for 3 samples, indicating the IONPs did not agglomerate and the silica shell is relatively thin after sol-gel processing. The silica shell thickness determined from the mass ratio of nanoparticles to added TEOS, assuming complete conversion, was 3-4 nm and is not expected to affect the magnetic properties of the IONPs. The electrostatic silica coated IONPs were stable for more than 12 months under ambient temperature at pH above 9.

Given that only a limited number of molecules can be covalently bonded to the IONPs [44], coating IONPs with silica provides a more useful platform for further surface functionalization, especially amines. Similarly, it has been shown that silica shell enhances (approx. 2.5 times) the amine functionalization of IONPs due to higher reactivity of APTES molecules [47] on silica than iron oxide. APTES hydrolyzes in the presence of water and in subsequent reaction the silanol groups condensate with OH groups on the silica coated IONPs to form strong Si-O-Si covalent bonds. The silanol groups of APTES can react with themselves as well, forming oligomers [47]. The oligomer formation of APTES was taken advantage of in the current synthesis approach to ensure a sufficient amine density. The efficiency of APTES grafting was confirmed by a) positive zeta potential below pH 9, b) direct measurement of the amine density using a conductometric titration, and c) TGA. The size of the amine functionalized

IONPs@SiO₂ increased to approx. 50-59(79) with a 20% fraction in the size range of 132-166 nm which is indicative of some aggregation taking place during the amine functionalization, increasing the diameter by a factor of 3. The zeta potential curve (Fig 2) exhibited an isoelectric point around pH 9. The zeta potential increased to a maximum of +32 mV around pH 5 due to protonation of the amine groups and is consistent with previously reported results [36, 47].

The “grafting from” approach often leads to higher graft densities as compared to “grafting to” approach; however, the expensive catalysts can be prohibitive for lost cost magnetite. Thus, our group has focused on “grafting to” approach for the covalent attachment of poly(AMPS-co-AA) using the catalyst (EDC) [34, 35], or thermal grafting [36]. In contrast to our previous work with EDC catalyzed polymer grafting onto IONPs [34, 35], modifications were made to improve the grafting efficiency: (i) the IONPs were coated with a thin shell of silica prior to APTES functionalization to enhance the stability IONPs and the uniformity of the amination, (ii) the polymer to IO ratio was increased from 5% to 10%, (iii) the polymer solution and APTES functionalized IO@SiO₂ NPs were first mixed together in a bath sonicator before addition of EDC, (iv) 20 wt. % salt was added after 15 minutes of addition of EDC, and (v) the reaction mixture was bath sonicated for 90 minutes and then mixed overnight using a magnetic stirrer.

The pre-mixing of IONPs and polymer before addition of EDC allowed the spontaneous reaction of EDC-activated carboxylate groups with the amine groups for amide bond formation. Additionally, a higher polymer concentration and bath sonication increased the degree of multipoint grafting on individual IONP clusters and avoiding bridging with adjacent clusters. The average hydrodynamic diameter of polymer grafted IONP clusters in API brine was 54-79(74% by volume cumulative), and 159-190(20) nm (26% by volume cumulative), (Table 1). At the onset of the amidation reaction, the electrostatic attraction is favorable between the free polymer chains and the cationic protonated amine surface. However, as the graft density increases the electrostatic repulsion between the like-charged polymer chains will further impede covalent grafting. To overcome this limitation, the grafting was carried out in the presence of 3 wt. % NaCl to screen the charges [48]. The zeta potential curve shows charge inversion from positive to negative after polymer grafting with values in the range of -50 mV from pH 4 to 11 (Figure 2), imparting enhanced stability to the IONPs in API brine at elevated temperatures (*vide infra*).

Another advancement in the current synthesis is the use of TFF to purify the IONPs after silica and APTES coating, as well as after polymer grafting. Two different sizes of TFF mPES hollow fiber membranes were employed; 30KDa after addition of silica and APTES, and 300 KDa after polymer grafting. In our earlier work [34-36], purification and separation of IONPs were carried out by magnetic separation followed by repeated centrifugation and redispersion of IONPs. These steps may lead to irreversible aggregation, are very time consuming, give limited yields and would be impractical for industrial scale up processes. For example, in our previous studies, the average size of polymer grafted IONPs ranged from 130 to 170 nm [35, 36]. In the current study, excess ligands and impurities were removed by diafiltration and IONPs were later concentrated by TFF without subjecting the particles to the high concentrations encountered in both magnetic separation and centrifugation. The IONPs obtained were less aggregated and the purification was achieved within 1-2 hours as compared to days when magnetic separation and centrifugation were used to purify large batches of IONPs [34, 49]. The yield of the IONPs in each TFF step was approximately 90% while the overall yields were 60-70%.

3.2. Composition and Surface Chemistry of IONPs.

The composition of the IONPs was determined by TGA during various stages of synthesis as shown in Figure 3 and Table 1. The hydrodynamic diameter from DLS increases with each layer,; however, the relatively large increase with added APTES suggests some aggregation was present. For silica coated particles, the 7.8% weight loss may be attributed to absorbed water in the silica layer. For the APTES functionalized IONPs, the total weight loss was $16.4 \pm 1.6\%$ arising from the release of water and aminopropyl groups. For the final poly(AMPS-co-AA) grafted IONPs, the net weight loss from polymer, water, and propylamines was $49.4 \pm 2.4\%$. Thus, 32.9 % of the NP mass was poly(AMPS-co-AA). Our previous work of EDC mediated polymer grafting reported a total weight loss of $7 \pm 3\%$ at the amine coating stage, and $15 \pm 3\%$ for the poly(AMPS-co-AA) grafted IONPs corresponding to ~9% poly(AMPS-co-AA) polymer after grafting [34]. Similarly, our thermal grafting approach [36] reported 18% weight loss at APTES level and 37% weight loss at the polymer level, corresponding to 23% polymer on the IONPs. The polymer content obtained using the modified synthesis is 3.6 times higher than previous EDC grafting approach and 1.4 times higher than the thermal grafting approach which ultimately led to superior transport and stability of IONPs (*vide-infra*).

It has been previously reported that sol-gel reaction of APTES on silica coated IONPs leads to at least 2.5 times greater amine densities as compared to bare IONPs [47]. Similarly, pre-oligomerization of APTES prior to grafting was used to build a multilayer, thus providing more sites for covalent attachment of polymer chains through AA groups. According to conductometric titration, the surface amine density of the aminosilica coated particles measured with 0.01 M HCl was $3.56 \pm 0.5 \mu\text{mol/mg}$ IONPs, which corresponds to $42 \pm 3 \mu\text{mol/m}^2$ and 25 ± 1 amines/nm² and matches closely with our recently reported results (Figure 4) [36].

The multipoint grafting of AA groups in the polymer layer limits the ability to accurately calculate its thickness. However, the minimum polymer layer thickness was estimated from the 34% TGA polymer content to be 9 nm for an IO core size of 51.8 nm, assuming the poly(AMPS-co-AA) chains on the surface were at the bulk density of 1 g/mL. For this approximation, it is assumed that the chains are fully collapsed on the surface of the nanoparticles. The hydrodynamic diameter of the poly(AMPS-co-AA) employed herein, with a MW of 200 kDa, is 10 nm in DI water or API brine [34]. Thus, the above thickness of 9 nm corresponds to a full monolayer of polymer grafted onto the IONPs, indicating high surface coverage.

3.3. Stability of Poly(AMPS-co-AA) Coated IO NPs in Brine

The stability of poly(AMPS-co-AA) grafted IONPs was investigated at both room and elevated temperatures in API brine. The polymer grafted IONPs formed stable and clear dispersions in API brine at room temperature without showing any signs of settling. Furthermore, the IONPs exhibited unprecedented stability at 120 °C without any settling or precipitation for a month (the studies were discontinued after 30 days), relative to several previous studies that were limited to 90 °C, to keep the pressure below one atmosphere. It is pertinent to mention that amide bonds in the poly(AMPS-co-AA) polymer are stable for extended periods of time under current conditions. The amide bond hydrolysis is often accelerated when subjected to highly alkaline conditions (~pH 14)[50, 51]. The high stability of IONPs indicates that the polymer chains remained solvated in brine and provided steric stabilization, as further characterized by DLS data shown in Table 2. The hydrodynamic diameter decreased in API brine as compared to DI water. The smaller diameter in API brine may be attributed to a higher density of the IO clusters due to weaker electrostatic repulsions [52] and /or contraction of the polyelectrolyte chains upon screening of the negative charges

[53]. Furthermore, aggregates of the grafted particles formed during synthesis may break up with salt addition as the polyelectrolyte chains contract. In DI water, these aggregates dissociated into smaller species upon exposure to elevated temperature via Brownian motion. Upon storage, approximately 70% of IONPs by volume stayed below 100 nm and only after storage of more than 3 weeks did the IONPs show signs of growth when the hydrodynamic diameter increased above 200 nm (~30% by volume).

To further investigate whether poly(AMPS-co-AA) chains are covalently grafted, an extreme dilution test was performed to attempt to desorb any ungrafted polymer. The IONP dispersion was diluted 20,000 times in DI and allowed to equilibrate overnight. After dilution, the sample was found to be stable at 120 °C in API brine with no appreciable change in diameter (Table S2), and a stable zeta potential value around -50 mV at pH 8. Both factors indicate that the polymer remained covalently grafted. Furthermore, the multipoint grafting of polymer chains through AA groups ensured steric stabilization even if a few covalent amide bonds are degraded during the high temperature exposure or extreme dilution test. On the contrary, when polymer was adsorbed electrostatically i.e., without any EDC, the IONPs aggregated immediately in API brine after the dilution test. As expected, after such extreme dilution, the physically adsorbed hydrophilic polymer desorbs from the NP surfaces, as also shown previously by TGA [34, 35].

Our group had demonstrated previously poly(AMPS-co-AA) coated IONPs remain stable at 90 °C for a month [36] and IONPs grafted with a poly(sulfobetaine) homopolymer were stable for the maximum time tested, one week [37]. Similarly, polyzwitterionics of MA/SBMA block copolymers have been used to stabilize silica dispersions at 90 °C for a month in different electrolyte environments [39]. Recently, metal nanoparticles stabilized by polysulfabetaines derived from methacrylate (PSBMA) and methacrylamide (PSBMAM) were shown to remain stable at elevated (~100 °C) and ambient temperature in 2 M NaCl solution [25]. However, to the best of our knowledge, this is the first example of stabilizing IONPs at 120 °C in divalent salinity with any polymer.

The high stability may be expected due to only partial collapse of polymer chains at high temperature and salinity, given the charge screening. The interaction potential between two adjacent polymer grafted IONPs is a function of steric repulsion, electrostatic repulsion, and van der Waals attraction [24, 34]. In API brine, the charges on the polyelectrolyte layer are screened

and steric repulsion becomes dominant stabilization mechanism, with a small degree of electrosteric repulsion. Factors such as the size of IONPs, molecular weight of polymers, composition of polymers, and pH also affect the stability of NPs [25, 54]. The smaller size of the nanoparticles, versus the 150 to 200 nm NPs reported previously [34] favors greater steric stabilization relative to the VDW attractive forces. In salt solutions, monovalent ions such as Na^+ exhibit weak affinity towards carboxylate or sulfonate anions thus contribute towards charge screening, while divalent ions such as Ca^{2+} bind strongly to carboxylate groups and bridge polymer chains between particles and within the polymer layer of a single particle. Both cases lower stability as bridging within the polymer layer decreases osmotic repulsion, while interparticle bridging will lead to formation of aggregates. In the case of poly(AMPS-co-AA) grafted particles, the AMPS unit has very low affinity for Ca^{2+} , thus enabling solvation of the polyelectrolyte layer. PAMPS is a much more acidic polyelectrolyte ($\text{pK}_a = 1$) than PAA and thus interacts more weakly with divalent cations. Na NMR spectroscopy revealed that the coupling constant for Na-PAMPS was maintained with added Ca^{2+} even at a Ca^{2+} /PAMPS molar ratio of 1.4 (0.4 mM monomer and 0.6 mM Ca^{2+}), suggesting relatively weak binding to Ca^{2+} . In addition to the high acidity of the PAMPS sulfonate group, the hydrophilic amide group favors hydration, to further weaken Ca^{2+} binding. Additionally, only 25% of the polymer units are composed of AA, many of which are consumed towards amide bond formation. Thus, the small amount of residual AA, if any, did not destabilize polymer grafted IONPs [34].

3.4. Transport properties of polymer grafted IONPs through porous media

3.4.1. Unconsolidated Porous Media

To investigate the mobility of IONPs through porous media in the presence of API brine, a series of column studies were conducted using IONPs (input concentration of 2.4 mg/mL) in crushed Berea sandstone or Ottawa sand (Table 3). The Ottawa sand column studies were carried out in the presence and absence of IsoparTM-L (IsoparTM L is clear isoparaffin fluid, typically containing less than 1 ppm benzene and less than 1 ppm Sulphur), to evaluate the impact of residual oil saturation (which is expected to be present in subsurface reservoirs) on nanoparticle transport. In the case of Ottawa sand, nearly 100% breakthrough was achieved in both the presence and absence of residual oil as the breakthrough curves (BTCs) essentially overlap that of an inert tracer (Figure 5). The average retention values in Ottawa sand in the absence and presence of residual oil were 2.5 and 3.1 $\mu\text{g/g}$ (0.13 and 0.17 mg/m^2 on a surface

area basis), respectively (Table 3). Xue et al. measured IONP retention in a flow experiment in a 40-50 mesh Ottawa sand column and a background electrolyte of 2.04 M NaCl or 0.68 M CaCl₂ (equivalent ionic strengths), and obtained values of 17.5 and 27.5 µg/g (1.4 and 2.2 mg/m²), respectively [35]. The order of magnitude lower adsorption of the IONPs in Ottawa sand column experiments in the present study (2.5-3.1 µg/g or 0.13-0.17 mg/m²) may be attributed to more uniform and dense amine and polymer coating on the IONP surfaces as well as the smaller NP size, which weakens the VDW forces.

For the crushed Berea sandstone, which is an extremely retentive media due to the presence of clay fines, 82% mass breakthrough was achieved with an average retention of 452 µg Fe₃O₄/g sand (0.02 mg/m² on a surface area basis). Although a greater mass percentage of IONPs was retained in the crushed Berea sandstone compared to Ottawa sand, the retention on a surface area basis was an order of magnitude lower in the crushed sandstone due to the much higher surface area of crushed sandstone vs. 80-100 mesh Ottawa sand (22.54 m²/g and 0.01875 m²/g, respectively). For this reason, it is important to also consider the µg/g retention values when comparing nanoparticle mobility between different types of porous media.

A comparison of the mobility of different generations of polymer-grafted IONPs in crushed Berea sandstone is presented in Table 3 and Figure 6. The IONP mass breakthrough of two previous batches (referred to as A (polymer grafting on IONPs done by catalyst) [35] and B (polymer grafting done by thermal approach) [36] and the current batch were: 0.01%, 55%, and 82%, respectively. The nanoparticle retention in crushed Berea sandstone was reduced 10-fold from 4083, 1234, and 452 µg Fe₃O₄/g sand retention for batches A, B, and the current batch, respectively). A primary difference between the current and batch B versus batch A is the use of a silica shell to obtain a high and uniform amine density in the current batch, which in turn laid the foundation for more uniform polymer grafting. Additionally, EDC was used as a catalyst for polymer grafting in both batch A and the current batch, while batch B was synthesized by thermal grafting approach. The low adsorption of the NPs on the mineral surfaces results from the strong steric repulsion as a consequence of the extension of the polyelectrolyte chains from the surface even in the high salinity brine [34]. It was shown that poly(AMPS-co-AA) grafted NPs retain about half of their electrophoretic mobility even with 380 mM Na⁺ and 50 mM Ca²⁺. This is the same copolymer as the one in the present study. Furthermore, the pure polymer poly(AMPS-co-AA) is only partially collapsed at high ionic strength as was shown by DLS

[34]. Thus, the polymer chains provided a significant degree of electrosteric as well as steric repulsion. The high acidity of the AMPS groups and their resistance to Ca^{2+} binding were essential for avoiding polymer chain collapse [34, 35, 55]. Finally, the lower retention is also favored by the smaller size of the IONP relative to previous studies, which lowers the amount of filtration and also weakens the VDW interactions with the mineral surfaces.

3.4.2. Intact (Consolidated) Core Flood

To evaluate the mobility of poly(AMPS-co-AA) IONPs under harsher conditions with a lower permeability substrate, three experiments with consolidated Berea sandstone were carried out at elevated temperature (65 °C) and pressure (1000 psi net confining stress). Poly(AMPS-co-AA) IONPs were injected at two concentrations (1000 and 2400 mg/L), and a sacrificial polymer pre-flood was also evaluated for the 1000 mg/L IONP injection, based on a previous study that demonstrated an 8-fold reduction in IONPs retention on crushed sandstone using a HEC-10 pre-flood [56]. HEC-10, a non-ionic cellulosic polymer, is often used to enhance viscosity in petroleum industry. After an HEC-10 pre-flood or with HEC-10 coinjection, the van der Waals, hydrogen bonding, polar and/or hydrophobic interactions between HEC-10 and sandstone or clay preferentially block the adsorption sites, thus allowing further propagation of nanoparticles [56]. In addition, the preferential adsorption of HEC-10 onto positively charged sites in the subsurface media will help mitigate interactions with anionic coated IONPs [57].

The mass breakthrough values for the 2400 mg/L, 1000 mg/L, and HEC-10 pre-flood + 1000 mg/L IONPs experiments were 43%, 9%, and 44%, respectively, corresponding to retention values of 519, 433, and 253 $\mu\text{g/g}$ (0.35, 0.29, and 0.17 mg/m^2), shown in Figure 7. Although the IONP retention on a surface area basis (mg/m^2) was larger for the intact core experiment compared to the one with the crushed Berea sandstone, when compared on a nanoparticle to media mass basis ($\mu\text{g/g}$), the retention was similar between the two experiments (e.g., 519 $\mu\text{g/g}$ for the intact sandstone core vs. 452 $\mu\text{g/g}$ for the crushed Berea sandstone). Here the smaller values for the crushed Berea sandstone (mg/m^2 basis) suggests that the NPs were too large to interact with all of the surface area of the extremely fine crushed clay particles (Figure S1). A pre-flood with 1000 mg/L HEC-10 resulted in earlier IONP breakthrough (at 2 PVs compared to 3.5 PVs) and improved the IONP mobility substantially, with a two-fold decrease in retention compared to 1000 mg/L IONP alone. This result suggests that the use of HEC-10

could further improve nanoparticle mobility under representative reservoir conditions (high temperature, pressure, salinity).

Conclusions

The IONPs grafted with the random copolymer poly(AMPS-co-AA) were colloidally stable at 120 °C in standard API brine for one month with a hydrodynamic diameter less than 100 nm and exhibited very low adsorption in porous media in API brine (0.02 mg/m² in crushed Berea sandstone and 0.13-0.17 mg/m² in Ottawa sand), three to ten-fold lower than in previous studies [35, 36]. The uniform and high polymer grafting density was achieved by providing sufficient amine density on the IONP@SiO₂ NPs and by using EDC catalyzed amide bond formation between the amine molecules and the AA groups of the polymer chains. The improved grafting procedures provided a larger polymer content of 33% on the magnetite nanoparticles as compared to 15±3 % obtained with the earlier methods. Another reason for the smaller sub 100 nm particles was the minimization of aggregation with tangential flow filtration, for both diafiltration and concentration, relative to magnetic separation and centrifugation that formed highly concentrated dispersions and pellets in earlier studies. The high concentration of a monolayer of solvated poly (AMPS-co-AA) chains on the NP surfaces provided electrosteric stabilization between the NPs and weak interactions of the NPs with anionic silica and sandstone surfaces. This behavior was enabled by low affinity of Ca²⁺ towards the highly acidic AMPS monomers resulting in strong solvation in API brine. In crushed Berea sandstone, the retention was reduced by three fold [36] and nine fold [35] relative to our earlier studies, given the more uniform grafted polymer layer and the smaller particle size. For intact core Berea sandstone experiments carried out at elevated temperature (65°C) and pressure (1000 psi net confining stress) at 2380 mg/ml, the retention was 519 µg/g, comparable to the value for crushed Berea sandstone. Furthermore, the addition of a relatively small amount (0.1% v/v) of commercially available sacrificial polymer (e.g., HEC-10) further reduced IONP retention to 252 µg/g or 0.17 mg/m² by blocking retentive sites.

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List of Figure and Tables

Figure 1: (a) Schematic of poly (AMPS-Co-AA) functionalized IONP synthesis and TEM images of (b) Citrate IONPs (c) TEOS IONPs and (d) poly(AMPS-co-AA) IONPs. Scale bar 50 nm for all images.

Table 1: Characterization of IONPs synthesized in DI water at ambient temperature.

Property	Citrate IONPs	TEOS IONPs	APTES IONPs	Poly(AMPS-co-AA) IONPs (in brine)
Hydrodynamic Diameter of a Representative Sample (nm) (%V Cumulant)	19-26(90) ^a 67-77(10)	22-26(78) 76-90(22)	50-59(79) 132-166(21)	54-79(74) 159-190(26)
Zeta Potential at pH 5 (mV)		-34.5 ± 6	28.6 ± 3	-53.6 ± 1
Organic content (wt. %)		8 ± 1.0	19.5 ± 1.0	47.9 ± 4.5
Amine content (μmol/mg IO)		---	3.6 ± 0.5	---

^a volume average data obtained by fitting the data using NNLS algorithm. The number in parentheses represent % volume cumulant.

Figure 2: Zeta Potential of IONPs at each stage of functionalization. The zeta potential measurements were carried out in filtered 10 mM KCl solutions while the IONPs concentration was ~0.1 mg/mL. The Smoluchowski equation was used to convert measured electrophoretic mobility to zeta potential.

Figure 3: Thermal gravimetric analysis (TGA) after each stage of functionalization. The TGA was carried out at a heating rate of 10 °C/min under N₂. The samples were heated from 25 to 900 °C.

Figure 4: Conductometric titration of amine coated Iron oxide nanoparticles. The conductivity and pH of the suspension was measured as it was titrated with 0.01 N HCl.

Table 2: Stability of IONPs at 120 °C as characterized by the volume average distribution *via* dynamic light scattering (DLS).

Batch	Hydrodynamic Diameter(nm), (Cumulative, %V)									
	0 days		7 days		15 days		21 days		30 days	
	DI	API	DI	API	DI	API	DI	API	DI	API
1	153-177 (54) 410-453 (46)	34.5-48.6 (58) 140-185 (42)	152.9 (92)	45-56 (64) 179-195 (36)	34-45.9 (59) 150-175 (41)	60-73 (68) 165-195 (32)	38-63.9 (54) 165-182 (46)	60-85 (70) 185-210 (30)	61-70 (48) 193-235 (52)	65-97 (74) 200-267 (26)
2	167-180 (42) 357-401 (58)	36.6-42.4 (74) 159-198 (26)	157.5 (93)	33-48 (73) 160-210 (27)	30-43 (76) 163-181 (24)	43-65 (77) 165-225 (23)	34-55 (76) 155-195 (24)	55-75 (68) 190-223 (32)	42-68 (55) 183-245 (45)	54-100 (65) 210-280 (35)

Both batches were synthesized using the approach presented in the manuscript and long term stability was investigated on both batches to ensure reproducibility. No corrections were made for brine viscosity.

DI = deionized water; API = American Petroleum Institute brine (8% wt. NaCl + 2% wt. CaCl₂).

Table 3: Experimental conditions and results for unconsolidated porous media and intact Berea sandstone core tests with poly(AMPS-co-AA) IONPs.

Media*	IONP batch	IONP pulse width (PV)	C ₀ IONP (mg/L as Fe ₃ O ₄)	HEC-10 pre-flood (mg/L)	Residual Oil Saturation (%)	IONP Mass breakthrough (%)	Retention	
							µg/g	mg/m ²
Ottawa Sand	Current	4.0	2,450	NA	NA	99.9%	2.5	0.13
Ottawa Sand	Current	4.1	2,430	NA	17%	99.9%	3.1	0.17
Crushed sandstone	Current	3.8	2,430	NA	NA	81.7%	452	0.02
Crushed sandstone	Previous (Batch B)	3.9	2,510	NA	NA	55.0%	1234	0.06
Crushed sandstone	Previous (Batch A)	5.9	2,440	NA	NA	0.10%	4084	0.18
Intact sandstone core	Current	4.1	2,380	NA	NA	42.9%	519	0.35
Intact sandstone core	Current	4.0	1,240	NA	NA	8.7%	433	0.29
Intact sandstone core	Current	4.0	1,230	1000 mg/L	NA	44.3%	252	0.17

*Ottawa sand = washed 80-100 mesh, specific surface area, SSA = 0.01875 m²/g; Crushed sandstone = 60-170 mesh crushed Berea sandstone, SSA = 22.54 m²/g; Intact core = Berea sandstone core, SSA = 1.6 m²/g.[58]

Batch A refers to IONPs from [35] while Batch B refers to the IONPs from [36]. Complete characterization data is available from the references cited.

Figure 5: Transport of current poly(AMPS-co-AA)-grafted IONPs in columns packed with Ottawa sand (80-100 mesh washed) or crushed Berea sandstone (60-170 mesh, unwashed). Input concentration = 2,400 mg/L (as Fe_3O_4) IONPs in API brine at room temperature (23 ± 1 °C) at pH 7. The Isopar-L residual saturation was 17%.

Figure 6: Improved transport of successive batches of poly(AMPS-co-AA)-grafted IONPs in columns packed with crushed Berea sandstone (60-170 mesh, unwashed). Input concentration = 2,400 mg/L (as Fe_3O_4) IONPs in API brine at room temperature (23 ± 1 °C) at pH 7. Batch A and Batch B

Figure 7: Breakthrough curves for Berea sandstone core flood experiments with current batch of poly (AMPS-co-AA)-grafted IONPs, performed at 65 °C in API brine at pH 7, with and without 1000 mg/L HEC-10 pre-flood.