

Increasing solubility of metal silicates by mixed polymeric antiscalants

Gokhan Topcu^a, Aslı Çelik^a, Ali Kandemir^a, Alper Baba^b, Hasan Sahin^{c,d}, Mustafa M. Demir^{a,*}

^a Department of Materials Science and Engineering, İzmir Institute of Technology, 35430, Gülbahçe, Urla, İzmir, Turkey

^b Department of Civil Engineering, İzmir Institute of Technology, 35430, Gülbahçe, Urla, İzmir, Turkey

^c ICTP-ECAR Eurasian Centre for Advanced Research, İzmir Institute of Technology, 35430, Gülbahçe, Urla, İzmir, Turkey

^d Department of Photonics, İzmir Institute of Technology, 35430, Gülbahçe, Urla, İzmir, Turkey



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ABSTRACT

The increase of silicate solubility is a big challenge for both hot and cold water because it reduces the deposition of metal silicates frequently observed in such systems and causes operational obstacles. The deposition of silicate coats the inner surface of the pipelines in an uncontrolled manner and reduces the harvesting of energy from brines. In this work, the solubility performance of two commercial water-soluble polymeric agents (poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA)) of various molecular weights employing dosage from 25 to 100 mg/L was examined. Along with dispersant-type antiscalant, poly(acrylamide) (PAM), poly(vinylsulfonic acid, sodium salt) (PVSA), and poly(vinylphosphonic acid) (PVPA) having chelating acidic groups were employed. Metal silicate deposits were obtained artificially in the lab-scale pressurized reactor. The experimental conditions employed were quite similar to a model power plant located in Çanakkale, Turkey. The concentration of dissolved silica was increased from 130 to 420 mg/L when 100 mg/L PEG 1500 and 25 mg/L PVSA were employed as a mixture. For the atomic-level understanding of the interaction of chelating groups with metal cations, DFT calculations were performed too.

1. Introduction

Metal silicate scaling is a frequently observed obstacle to the utilization of hot geothermal/petroleum fields and cold industrial water systems. Metal silicates are formed by the polymerization of silicate ions in the presence of metal cations via condensation polymerization. The accumulation of metal silicates on the surface of parts such as pipes, separating vessels and heat exchangers interferes with the flow of the system, hence reducing the efficiency of the plants (Gallup, 2002; Potapov et al., 2001). Since silicate scaling is dense and mechanically resistant, strong acids particularly HF are often employed to disintegrate the Si–O bond and eventually the silicate deposit (Demadis et al., 2011a, b). However, working in an acidic environment is risky because it may lead to serious corrosion or health issues unless the concentration and chemical structure of the acid are selected meticulously (Demir et al., 2014; Zhang et al., 2011). Increasing the solubility of silicates by soft antiscalants appears to be a promising remedy to minimize of scaling (Gallup, 2002; Gallup and Barcelon, 2005).

A limited number of studies on increasing the solubility of metal silicates exists (Corsi, 1986; Demadis et al., 2012a, b; Gallup, 1998, 2002, 2009; Gallup and Barcelon, 2005; Spinde et al., 2011), and which focus on mitigating the scaling via stabilization of the silicic acid by

dispersion and/or chelation. The working principle is based on the stabilization of silica colloids, which are considered to be the main component of the metal silicate deposits. Polymeric molecules stabilize the colloids (van der Waals forces or hydrogen bonding) so that they are prevented from aggregating/agglomerating of the colloids. For instance, Preari et al. (2014) employed PEG, which is mostly known as a non-ionic surfactant, with various molecular weights (from 1.55 to 20 kg/mol) and revealed that PEG interacts with silica species via H bonding at neutral conditions. On the other hand, another study focused on the removal of an ionic substance from the medium by electrostatic interaction (Palencia et al., 2009; Porcelli and Judd, 2010). Organic compounds containing positively charged groups have often been preferred as ligands. These compounds include protonated primary, secondary or tertiary amines (Danilovtseva et al., 2011; Demadis et al., 2008; Spinde et al., 2011); amide moieties (Demadis and Neofotistou, 2007); and phosphonium (Demadis et al., 2012a, b), while the functional groups are reactive silica species. The polymers reported so far are molecules intended merely for the improvement of silica solubility; however, similar attempts for the metal-silicates aiming at metal solubility have not been examined (Topçu et al., 2017). The effect of metal cations, known as catalysts for silica polycondensation (Demadis et al., 2012a, b), on metal-silicate formation was reduced by

* Corresponding author.

E-mail address: mdemir@iyte.edu.tr (M.M. Demir).

using polymers with pendant groups that are capable of chelating metals.

The Tuzla Geothermal Power Plant (TGPP) in Çanakkale, Turkey, was chosen as a model binary system to study metal silicate scaling. This geothermal site is located in the volcanic zone and allows the generation of 7.5 MWe from a connate water reservoir. Iron-magnesium silicate (Fe, Mg silicate) is a deposit heavily formed in this plant. The level of silica concentration is ~200 mg/L; note that some organic acids are used for pH modification (Baba et al., 2015). A Fe, Mg silicate deposit can be prepared synthetically in the lab using a pressurized autoclave, starting from chloride-rich precursors in the presence of silicate and carbonate salts.

In this study, poly(ethylene glycol) (PEG) and poly(vinyl alcohol) (PVA), with various molecular weights, are employed as silica-targeted metal-silicate antiscalants in several dosages. The solubility performance of PEG and PVA (at 25, 50, and 100 mg/L) was investigated from the concentration of leftover silica species in liquid phase after centrifugation of the reaction mixture. To enhance the antiscaling efficiency by eliminating metal cations, additional polymeric co-antiscalants containing acidic chelating groups were used, such as poly(acrylamide) (PAM) (Girma et al., 2005, 2006), sodium salt of poly(vinylsulfonic acid) (PVSA) (Palencia et al., 2009), and poly(vinylphosphonic acid) (PVPA) (Rivas et al., 2004). Since metal-silicate scaling is more common in hot/cold water systems, experiments were carried out in a closed reactor system as an operational system to simulate the real field conditions in terms of salinity of brine, pressure, and temperature of the plants.

2. Experimental

2.1. Materials

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Merck (Kenilworth, NJ, USA), CaCl_2 and Na_2CO_3 were obtained from Sigma-Aldrich (St. Louis, MO, USA). Na_2SiO_3 (35.5 wt.% in H_2O) was employed (Carl Roth, Karlsruhe, Germany) as a silica source. The various molecular weights of PEG (M_w : 0.4, 1.5, and 6.0 kg/mol) and PVA (M_w : 40, 50, and 92 kg/mol) were supplied by Sigma-Aldrich. PAM, PVSA, and PVPA were synthesized in our lab to employ as co-antiscalants and detailed information regarding the synthesis was given in a previous study (Topcu et al., 2017). All the antiscalants were dissolved in 50 mL dH_2O and their dosage was fixed to 25, 50, and 100 mg/L. The molecular structure of inhibitors is presented in Fig. 1. The deionized water

Table 1

The concentration (mg/L) of the components in artificial brine for the control experiment before and after the reaction.

	[Fe ²⁺]	[Mg ²⁺]	[Ca ²⁺]	[Na ⁺]	[SiO ₂]
Before Reaction	927	404	1330	1912	598
After Reaction	3.5*	48	270	332	135

Temperature (°C): 137.6 – Pressure (bar): 3.2, * $\Sigma[\text{Fe}^{2+}/^{3+}]$.

(18.2 $\text{M}\Omega \text{ cm}^{-1}$ at 25 °C) used in all experiments was produced by a Milli-Q Advantage Water Purification System (Merck).

2.2. Methods

Metal-silicate deposits were synthesized in an autoclave reactor system (Büchi Glas Uster, mini clave 075 model, Switzerland). First, a synthetic brine solution was prepared in 200 mL deionized water using 132 mg $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 135 mg $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 240 mg CaCl_2 , 70 mg Na_2CO_3 , and 440 μL Na_2SiO_3 (Table 1). The solution was loaded into the reactor under ambient conditions. Subsequently, the mixture was heated to 137.6 °C at 3.2 bar pressure. The technical drawing of the reactor is shown in Fig. 2. After a heat and pressure treatment for ≈ 45 min, an antiscalant solution was added to the brine solution. The mixture was ejected to plastic vessel through a Teflon pipe to cool down in ice bath. A sudden decrease in the pressure and temperature of the reaction causes the precipitation of an artificial deposit. The resulting reaction mixture is centrifuged at 6000 rpm. The deposit is isolated for analysis. The leftover decantate solution was analyzed using UV-spectrophotometry (Hach DR 5000, Loveland, CO, USA) for molybdate reactive silica and an Inductively Coupled Plasma Mass Spectroscopy (ICP-MS, Agilent 7500 CE Octopole, Santa Clara, CA, USA) for metal cation concentrations. The pH regime of the solution was examined at room temperature by using a multiparameter (pHEnomenal MU 6100 L, VWR International, Vienna, Austria)

Spectrometric methods are utilized on the liquid phase for precise examination of the performance of the polymers in silica formation. For instance, the silicomolybdate method is a facile way used in UV spectroscopy to detect reactive silica species, including monomeric, dimeric, and perhaps trimeric forms of silica (Coradin et al., 2004; Iler, 1979). This method is based on the principle that ammonium molybdate reacts with reactive silica (especially monomer form) and any phosphate group at low pH resulting in yellow products. The molybdophosphoric

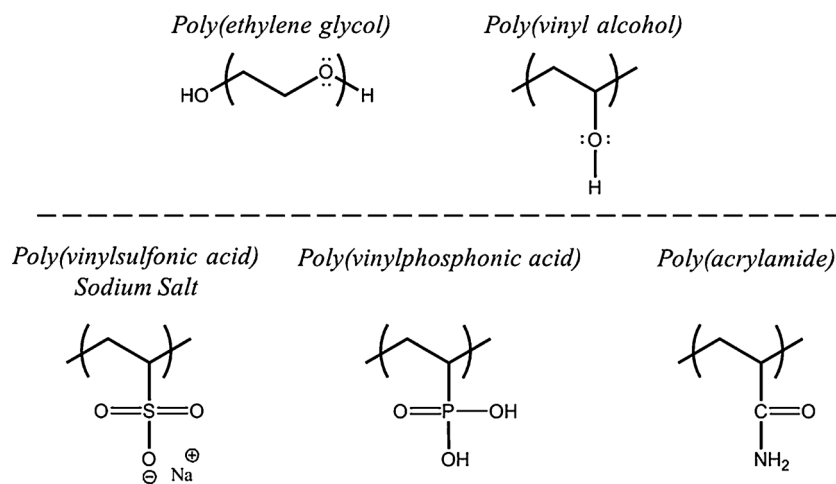


Fig. 1. Molecular structures of polymeric antiscalants.

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