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REVIEW PAPER - EXPLORATION ENGINEERING

Green silica scale inhibitors for Alkaline-Surfactant-Polymer flooding: a review

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Abstract Alkaline-Surfactant-Polymer flooding is a tertiary enhanced oil recovery (EOR) method designed to lower interfacial tension (IFT), water wet the formation, and decrease water mobility to produce residual oil. The ASP flood uses a combination of alkali, surfactant, and polymer to achieve these results. The use of these three fluid injection additives offers great synergistic effects in terms of oil recovery and sweep efficiency. Despite its popularity as a potentially cost-effective chemical flooding method, it is not without (its) problems, one of which is the excessive formation of silicate scales. Silicate scale is a very serious problem in the oil and gas industry; which forms in perforation holes, casing surface, tubing, and surface facilities. This study reviewed and assessed some of the inhibition techniques used in the industry with regard to handling oilfield scales in general and silicates scales in particular. Besides, the inhibitors with enhanced functionality in mitigating silicate scale also have been discussed. However, the conventional scale inhibitors used are facing restrictions world over, due to their ecotoxicity and non-biodegradability, which, therefore, has led to the call for green scale inhibition in the oil and industry. Green scale inhibitors are considered as alternative scale inhibitors due to their value-added benefits to the environment with respect to the methods of treating oilfield scales.

Introduction

Alkaline-Surfactant-Polymer flooding (ASP) is a tertiary recovery method designed to lower interfacial tension (IFT) and decrease water mobility to produce residual oil (Wyatt et al. 2002). ASP flood uses a combination of alkali, surfactant, and polymer to achieve these results. The purpose of the surfactant in an ASP flood is to lower the IFT between the residual oil and the injected fluids. However, the alkali reacts with acidic components of the oil to form additional surfactant within the formation to further lower the IFT. The use of alkali is much less costly than equivalent levels of surfactant, allowing for a more cost-efficient flood (Demin et al. 1997). The polymer is used for better sweep of the reservoir due to its ability to increase the viscosity of the fluids. This allows for better mobility control. The use of these three fluid injection additives offers great synergistic effects in terms of oil recovery and sweep efficiency (Huang and Dong 2004).

The ASP flood has high pH of 11 or above. As it moves through the reservoir, quartz silica is dissolved (Arensdorf et al. 2010) and the dissolved silica becomes stable in the high pH alkaline flood. However, the ASP flood encounters neutral pH connate water either near the wellbore or in the well as it flows to the production well. This, therefore, neutralizes the high pH alkaline water. The decreased pH of the mixed waters dramatically lowers the solubility of the monomeric silica. Besides, silicate ions complex with metal ions in the formation water pose a scale mitigation challenge. Systems with pH levels greater than 8.5 and

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increasing temperature may experience magnesium silicate scaling. Magnesium have been shown to aggravate the scaling tendency by complexing silica and providing the hydroxide ion in which silica precipitation is catalyzed (Demadis et al. 2007). Other metal hydroxides such as calcium hydroxide may also interact with silica, but these metal silicates have higher solubility than magnesium silicate (Amjad and Zuhl 2008). Furthermore, silica deposition may also be affected by the formation of calcium carbonate. Calcium carbonate scale does not provide nucleation sites, but it provides a matrix in which silica may be entrapped (Gill 1998). In accordance with this theory, co-precipitation and deposition of silica and silicate may also occur in this manner. The presence of both silica and magnesium creates a predicament, due to the converse solubilities of colloidal silica and magnesium silicate. Both scale species tend to form concurrently in ASP flood production systems.

Scale prevention, in principle, can be achieved by use of scale inhibitors. Scale inhibitors are chemicals that delay, reduce, or prevent scale formation when added into scaling water. Most of the scale inhibitors work by absorbing onto the crystal surface to prevent further growth of precipitate or by preventing the precipitate from adhering to solid surfaces such as pipes and vessels. The most common scale inhibitors used in the oil industry are inorganic phosphates, organophosphorous compounds, and organic polymers. Unfortunately, these "traditional" scale control methods applied to crystalline mineral salt precipitates do not apply to silica because it is amorphous (Ehrlich et al. 2010). In addition, the inherent and consequent environmental hazards of using toxic and non-biodegradable scale inhibitors have hindered the use of phosphonates due to their poor ecotoxicity. Moreover, many polymers fail to meet minimum biodegradation requirements (Holt et al. 2009). Therefore, the call for going green with scale inhibitors has become necessary. Though the use of green scale inhibitors to inhibit scale in oil and gas wells is relatively an unexplored area (Kumar et al. 2010), there have been several works on this "promising alternative" (Kohler et al. 2004).

Silicate scale formation

Solubility of silica depends upon several factors including pH, temperature, other ions present, and the silica form(s) present. The solubility of silica increases with pH varying from 120 mg/L at pH 6–140 mg/L at pH 9 and increases rapidly as pH is increased from 9.5 to 10.5 (Iler 1979). This could suggest that adjusting the pH may solve the problem of silica scale deposition. Also, solubility of silica increases with increasing solution temperature (Iler 1979). Because silica solubility increases with increasing

pH, operating systems at high pH may potentially reduce silica scaling problems; the presence of various multivalent ions also influences the solubility of amorphous silica in aqueous solution (Chan 1989).

Summary of the silicate scale formation.

1. *Silica dissolution* The alkaline flood typically has pH 11 or higher as it sweeps the reservoir. The high pH water dissolves quartz in the formation, which results in dissolved monomeric silica $(Si(OH)_3O^- \; Na^+)$ flowing with the water flood.

2. *Silica polymerization* As the ASP water flows to the production well, it encounters neutral pH connate water near the wellbore or in the well. As the high pH ASP water is partially neutralized by the connate water, dissolved silica begins to polymerize and forms colloidal silica nanoparticles. Colloidal silica forms when the solubility level of monomeric silica is exceeded. The solubility of monomeric silica is pH dependent and decreases significantly below pH 10.5 (Amjad and Zuhl 2008).

3. *Silica scale formation* Magnesium, if present, can bridge the colloidal silicate particles and form an amorphous magnesium silicate scale. The ASP water is typically softened, and any residual magnesium would precipitate as $Mg(OH)_2$ in the ASP. Magnesium is introduced in the neutral pH connate water. Magnesium silicate scale typically has non-stoichiometric ratios of magnesium to silicate. Similar interactions are possible with other polyvalent metal ions (iron, aluminum, and calcium), but magnesium silicate has a higher scaling index than the other metal silicates. In the absence of divalent cations, the polymerized silicate may continue to grow and form an amorphous "silica scale." In the oilfield, different ratios of the two scales are likely forming in various wells as pH and cation concentrations differ.

4. *Co-precipitation of silicate scale with other mineral scales, e.g., calcium carbonate* If calcium is introduced in the connate water, the high pH of the ASP water mixing in the well will promote calcium carbonate scale. Calcium carbonate may provide nuclei for the development of silicate scales (Gill 1998). In industrial water, it has been observed that if carbonate scale is prevented, then silica can be tolerated at higher levels without generating scale.
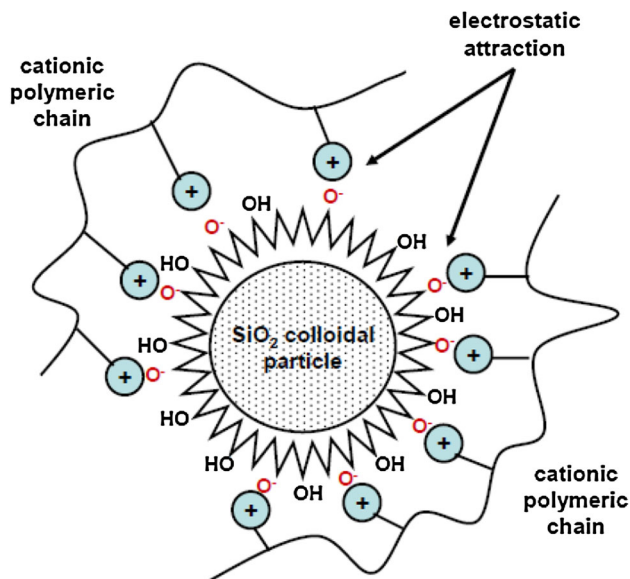
Handling of silicate scale

The inhibition program using calcium carbonate inhibitor such as phosphonates or phosphates-based was put in place in early 2008, and was very successful for the first

6 months (Hunter et al. 2013). The program significantly increased pump run life and resulted in minimal or no scale buildup in pipelines or facilities. In late 2008 serious scale problems returned, indicated by numerous well failures and significant buildup of scale on downhole equipment. It was clear that the calcite inhibitor used was no longer effective. Wohlever et al. (2001) found that under stressed conditions (i.e., high pH, high temperature, high hardness, etc.), these phosphorus-containing inhibitors frequently react stoichiometrically with calcium ions leading to calcium-polyphosphate/phosphonate precipitation (Wohlever et al. 2001). This is because the amorphous nature of silica renders crystal modifiers phosphonates or mixed phosphonates/carboxylates ineffective (Agnihotri et al. 1999). Therefore, to overcome this problem, Arensdorf et al. (2010) and (2011) have developed new scale inhibitors in mitigating silicate scale during ASP flooding (Arensdorf et al. 2010, 2011). Even though the developed scale inhibitors could not completely prevent the silicate scale formation, they could delay it. After initial trials, the primary conclusion was that the same scale inhibitor had significantly different levels of effectiveness, depending on the inhibitor concentration and water chemistry of the individual wells. From the study, none of the silicate inhibitors acted as threshold inhibitors and completely prevented scaling at low doses. It was found that the effective delay process of scaling required high doses of inhibitors about 500 ppm (Arensdorf et al. 2010, 2011).

Therefore, much more well-thought inhibition approaches have to be utilized for controlling silica scale. Increasing environmental concerns and discharge limitations have imposed additional challenges. Therefore, the discovery and successful application of low doses chemical additives that have mild environmental impact has been the focus of several researchers (Quraishi et al. 1999; Demadis et al. 2007, 2005, 2004; Neofotistou and Demadis 2004a, b; Mavredaki et al. 2005). Recently, the use of cationic polymer as silica polymerization inhibitors has been the subject of numerous investigations. Amjad and Yorke in their evaluation of polymers reported that cationic-based copolymers are effective silica polymerization inhibitors (Amjad and Yorke 1985). Similar conclusions were also reported by Harrar et al. (1982) in their investigation on the use of cationic polymers and surfactants in inhibiting silica polymerization under geothermal conditions (Harrar et al. 1982). It is now certain that effective silica scale inhibition is dependent on the cationic charge on the polymer backbone (Demadis 2004a, b, 2005; Mavredaki et al. 2005; Demadis and Mavredaki 2005; Demadis and Stathoulopoulou 2006; Demadis and Neofotistou 2004; Neofotistou and Demadis 2004a, b).

Aside from that, extensive silica inhibition also have been done using two dendrimer inhibitors, Poly(amido amine)-1 and Poly(amido amine)-2 (Demadis and Oner 2009; Demadis 2005, 2008; Demadis and Neofotistou 2007, 2004a, b; Demadis and Stathoulopoulou 2006; Demadis et al. 2005; Neofotistou and Demadis 2004a, b). Poly(amido amine) dendrimers (PAMAM) backbone are composed of amide bonds rendering them biodegradable. Therefore, they are undoubtedly benign molecules. The dendrimer generation number indicates its degree of growth and branching. More specifically, PAMAM dendrimers of generations 0.5, 1.5, 2.5 possess –COOH termini, and those of generations 1 and 2 have –NH$_2$ termini. From the previous studies, it was reported that the –COOH terminated dendrimers (generations 0.5, 1.5, and 2.5) showed virtually no activity as silica inhibitors (Neofotistou and Demadis 2004a, b; Demadis 2005). In contrast, the –NH$_2$ terminated analogs (generations 1 and 2) are potent SiO$_2$ scale inhibitors (Fig. 1).

Schematic structures of PAMAM-1 and 2 dendrimers are shown in Fig. 2.

Despite the excellent performance of PAMAM-1 and 2 as colloidal silica growth inhibitors, these dendrimers suffer from a serious disadvantage: the silicates that are not inhibited lead to formation of large colloidal silica particles that entrap the dendrimers (Demadis 2008). This also leads to inhibitor depletion from solution, resulting in drop of inhibitory activity in the bulk. Formation of SiO$_2$-PAMAM precipitates occurs due to association of anionic silica particles and cationic dendrimers as illustrated in Fig. 3.

Additionally, from the literature it was found that scale inhibition can be achieved by use of scale inhibitors in combination with dispersant polymers (Barouda et al.

Fig. 1 Cationic polymer attachment on a single silica nanoparticle (Demadis 2008)

Fig. 2 Structures of PAMAM-1 and PAMAM-2 (Mavredaki et al. 2007)
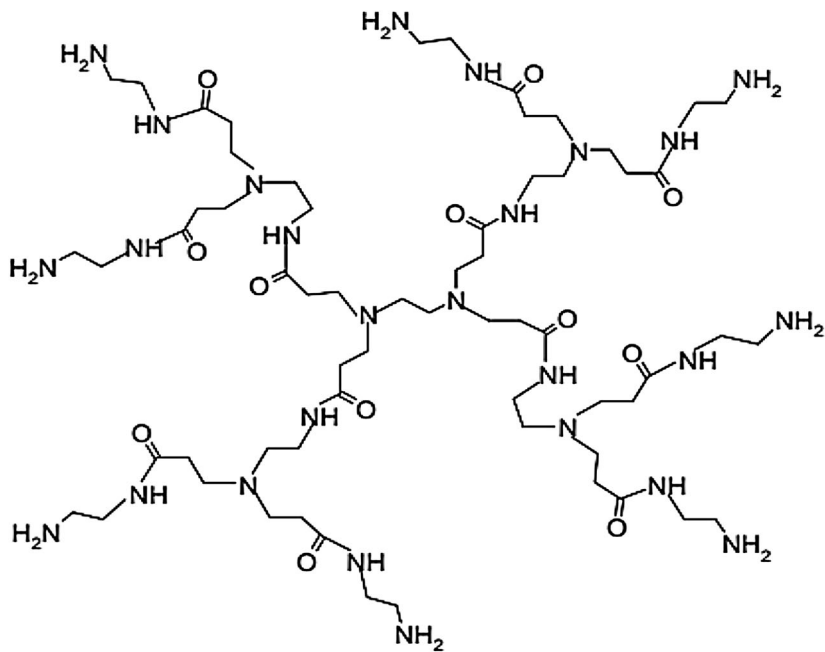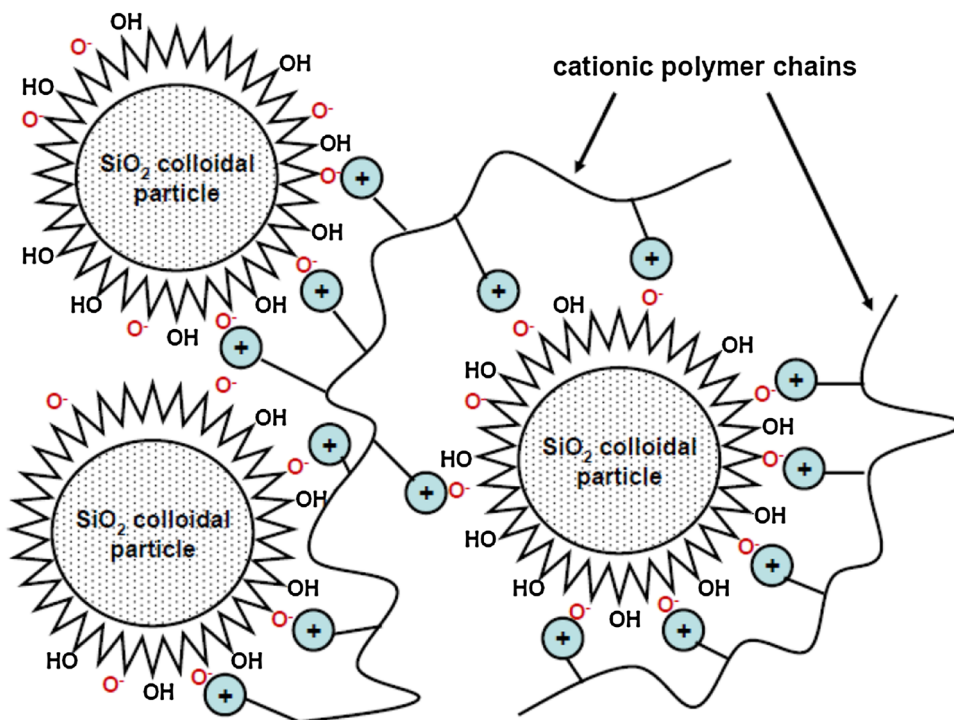

PAMAM-1
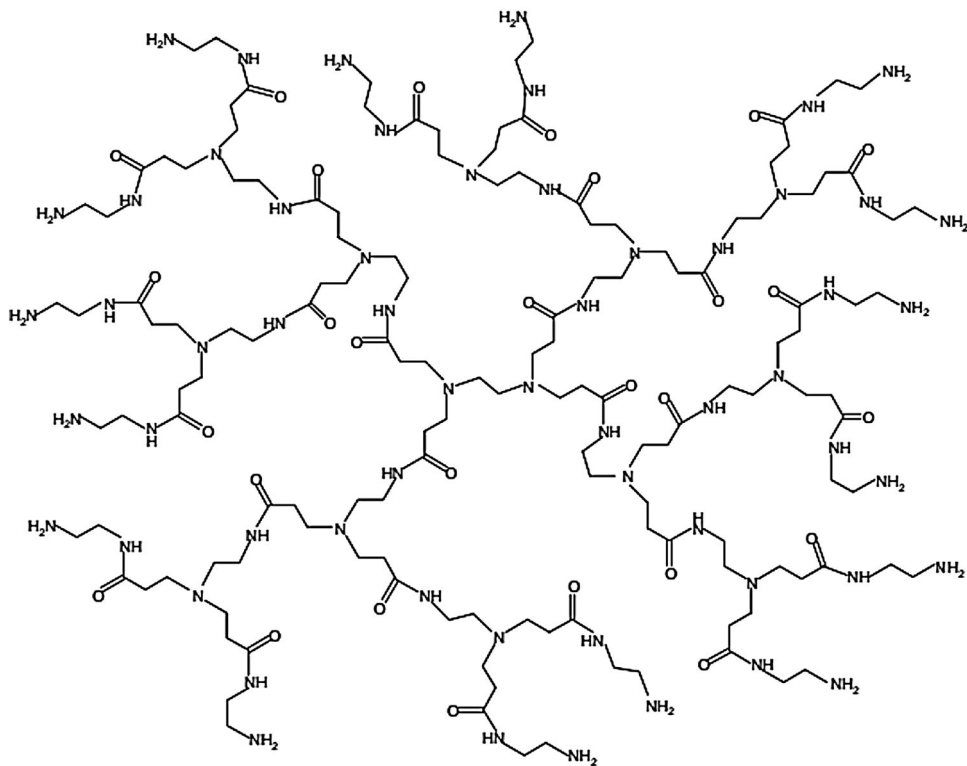
PAMAM-2

Fig. 3 Inhibitor entrapment within the colloidal silica matrix because of polycation (polymer)-polyanion (silica) interactions (Demadis 2008)

2007). Therefore, to combat this problem some researchers resorted to use anionic polymer additives that could work with the dendrimer inhibitors (Neofotistou and Demadis 2014; Mavredaki et al. 2005, 2007). However, if the dosage of anionic polymer used is high, the activity of the dendrimers drops dramatically. It was found that the negative charge of polymer "overwhelms" the dendrimer and poisons its inhibitory ability (Demadis 2008; Mavredaki et al. 2005). Plus, most anionic polymers used are not green and/or have mild environmental impact. Based on the previous study, Mavredaki et al. 2005 have proposed a possible mechanism for the dissolution of colloidal silica by such zwitterions (Mavredaki et al. 2005). It is believed that an effective silica inhibition should be based on a delicate balance structure of cationic–anionic charges. In the study, a zwitterion compound that contains a positive and a negative charge on its backbone is used in synergistic action with cationic polymer. The possible mechanism of the dissolution of colloidal silica with zwitterions is shown below:

From the Fig. 4, it can be seen that the first silica–zwitterion additive interaction is an electrostatic association between the negatively charged silica particle and the cationic moiety of the zwitterion additives. This cationic group would minimize the effect of "overwhelms" on the cationic polymer and thus maintain its inhibitory ability. The positioning of the zwitterion additives in such way cause deprotonated and negatively charged carboxylate
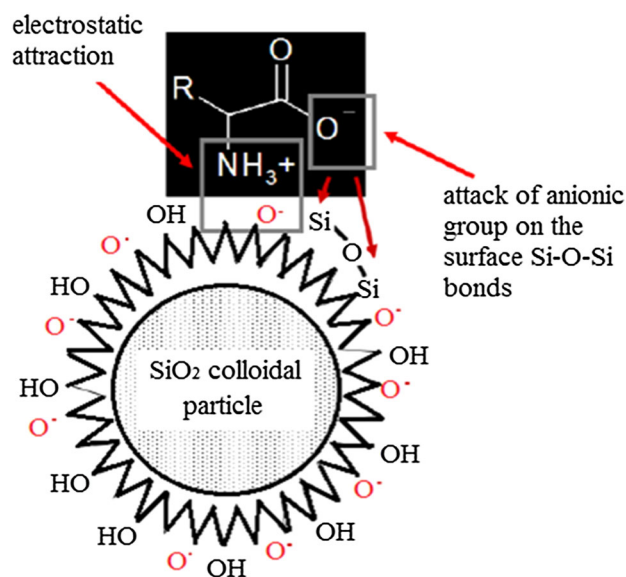
Fig. 4 Possible mechanism of dissolution enhancement of colloidal SiO_2 in the presence of zwitterion additives (Mavredaki et al. 2007)

group can "swing" and attach to surface of Si center. Once OH^- forms a Si–OH bond with surface Si, the Si–O network that connects the surface Si atoms with internal Si centers starts to collapse, thus exposing additional Si sites that become susceptible to attack. This function is in a way "mimicking" the action of HO^- anions in the hydrolysis of the Si–O–Si network.

Conclusion and future directions

Despite the excellent performance cationic polymer as colloidal silica growth inhibitors, these polymers have some limitations which require improvement. Cationic charge on the polymer backbone, although necessary for inhibition, can cause inhibitor entrapment within the colloidal silica matrix because of polycation–polyanion interactions. Inhibitor entrapment causes its depletion from solution and its deactivation. Therefore, some researchers resorted to use anionic polymer additives that could work together with the cationic inhibitors. Nevertheless, increase of anionic polymer dosage above a certain threshold "overwhelms" the cationic charge of the inhibitor and poisons its inhibition ability. Therefore, an effective silica inhibition is based on a delicate balance of cationic–anionic charges on the polymer backbone. Thus, a green zwitterion compound that contains a positive and a negative charge on its backbone is proposed. This zwitterion compound would assist the inhibitors to operate more effectively. However, the details of such a dissolution mechanism are still under study and required further investigation. Besides, these dendrimers are widely used in water treatment and do not yet apply in mitigating silicate scales during ASP flooding. This previous fundamental research will be used as a guideline to improve our knowledge on the state of the anionic–cationic charges in the optimized inhibitor toward the presence of silica colloidal particles. This added knowledge would be a new information for developing and enhancing new and improved chemical additives for silicate scale inhibition during ASP flooding. Besides, it is anticipated that the results ensuing from this study will assist the oil and gas service industry in applying the optimized inhibitor at reservoir conditions. Moreover, green formulations have become the goal of most inhibitor developers. The diversified use of green scale inhibitors has been sporadic and evolutionary, and the trend seems to adopt a rather reactionary response to the present and potential environmental regulations and to support economic activities of oil and gas industry in the future.

References

Agnihotri R, Mahuli SK, Chauk SS, Fan LS (1999) Influence of surface modifiers on the structure of precipitated calcium carbonate. Ind Eng Chem Res 38:2283

Amjad Z, Yorke MA (1985) Carboxylic functional polyampholytes as silica polymerization retardants and dispersants. US Patent No. 4,510,059

Amjad Z, Zuhl RW (2008) An evaluation of silica scale control additives. In: Proceedings of the CORROSION, New Orleans

Arensdorf JJ, Hoster D, McDougall D, Yuan M (2010) Static and dynamic testing of silicate scale inhibitors.In: Proceedings of the SPE International Symposium on Oilfield Scale, Bejing, China

Arensdorf JJ, Kerr S, Miner K, Ellis-Toddington TT (2011) Mitigating silicate scale in production wells in an oilfield in Alberta. In: Proceeding of the SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas

Barouda E, Demadis KD, Freeman S, Jones F, Ogden MI (2007) Barium sulfate crystallization in the presence of variable chain length aminomethylenetraphosphonates and cations (Na$^+$ or Zn^{2+}). Cryst Growth Des 7:321

Chan SH (1989) A review on solubility and polymerization of silica. Geothermics 18:49–56

Demadis KD (2004a) Focus on operation and maintenance: scale formation and removal. Power 148(6):19–23

Demadis KD (2004b) Focus on operation and maintenance: scale formation and removal. Power 148(6):19–23

Demadis KD (2005) A structure/function study of polyaminoamide (PAMAM) dendrimers as silica scale growth inhibitors. J Chem Technol Biotechnol 80:630–640

Demadis KD (2008) Silica scale inhibition relevant to desalination technologies: progress and recent developments. In: Delgado DJ, Moreno P (eds) Desalination research progress. Nova Science Publishers Inc., New York, pp 249–259

Demadis KD, Mavredaki E (2005) dissolution enhancement of colloidal silica by environmentally benign additives. potential applications in silica-laden water systems. Env Chem Lett 3:127–131

Demadis KD, Neofotistou E (2004) Inhibition and growth control of colloidal silica: designed chemical approaches. Mater Perform 43(4):38–42

Demadis KD, Neofotistou E (2007) Synergistic effects of combinations of cationic polyaminoamidedendrimers/anionic polyelectrolytes on amorphous silica formation: a bioinspired approach. Chem Mater 19:581–587

Demadis KD, Öner M (2009) In: Pearlman JT (ed) Green chemistry research trends, Nova Science Publishers, New York, Ch. 8, pp 265–287

Demadis KD, Stathoulopoulou A (2006) Novel, multifunctional, environmentally friendly additives for effective control of inorganic foulants in industrial water and process applications. Mater Perform 45(1):40–44

Demadis KD, Neofotistou E, Mavredaki E, Tsiknakis M, Sarigiannidou EM, Katarachia SD (2005) Inorganic foulants in membrane systems: chemical control strategies and the contribution of green chemistry. Desalination 179:281–295

Demadis KD, Mavredaki E, Stathoulopoulou A, Neofotistou E, Mantzaridis C (2007a) Industrial water systems: problems, challenges and solutions for the process industries. Desalination 213:38

Demadis KD, Stathoulopoulou A, Ketsetzi A (2007) Inhibition and control of colloidal silica: can chemical additives untie the knot of scale formation? In: Proceeding of the NACE International Corrosion Conference and Expo, Nashville, Tennessee

Demin W, Zhenhua Z, Jiecheng C, Jingchun Y, Shutang G, Lin L (1997) Pilot test of alkaline/surfactant/polymer flooding in daqing oil field. SPE Res Eng 12(4):229–233

Ehrlich H, Demadis KD, Koutsoukos PG, Pokrovsky O (2010) Modern views on desilicification: biosilica and abiotic silica dissolution in natural and artificial environments. Chem Rev 110:4656–4689

Gill JS (1998) Silica scale control. Mater Perform 37(11):38

Harrar JE, Lorensen LE, Locke FE (1982) Method for inhibiting silica precipitation and scaling in geothermal flow systems. US Patent No. 4,328,106

Holt SPR, Sanders J, Rodrigues KA, Vanderhoof M (2009) Biodegradable alternatives for scale control in oil field applications. In: Proceeding of the SPE International Symposium on Oilfield Chemistry, The Woodlands, Texas

Huang S, Dong M (2004) Alkaline/surfactant/polymer (asp) flood potential in southwest saskatchewan oil reservoirs. J Can Pet Technol 43(12):56–61

Hunter KD, Kerr SH, Ellis-Toddington TT, McInnis LE (2013) The use of modeling and monitoring to control scale in Alberta ASP floods. In: Proceeding of the SPE Enhanced Oil Recovery Conference, Kuala Lumpur, Malaysia

Iler RK (1979) The chemistry of silica. Wiley, New York

Kohler N, Bazin B, Zaitoun A, Johnson T (2004) green inhibitors for squeeze treatments: a promising alternative. In: Proceeding of the CORROSION 2004, New Orleans

Kumar T, Vishwanatham S, Kundu SS (2010) A laboratory study on Pteroyl-L-Glutamic acid as a scale prevention inhibitor of calcium carbonate in aqueous solution of synthetic produced water. J Pet Sci Eng 71(1–2):1–7

Mavredaki E, Neofotistou E, Demadis KD (2005) Inhibition and dissolution as dual mitigation approaches for colloidal silica fouling and deposition in process water systems: functional synergies. Ind Engin Chem Res 44:2019–7026

Mavredaki E, Neofotistou E, Stathoulopoulou A, Demadis KD (2007) Environmentally benign chemical additives in the treatment and chemical cleaning of process water systems: implications for green chemical technology. Desalination 210:257

Neofotistou E, Demadis KD (2004a) Use of antiscalants for mitigation of silica (SiO_2) fouling and deposition: fundamentals and applications in desalination systems. Desalination 167:257

Neofotistou E, Demadis KD (2004b) Silica scale growth inhibition by polyaminoamide STARBURST dendrimers. Coll Surf A Physicochem Eng Asp 242:213–216

Neofotistou E, Demadis KD (2014) Cationic polymeric chemical inhibitors and multifunctional blends for the control of silica scale in process waters. Int J Corros Scale Inhib 3(1):28–34

Quraishi MA, Farooqi IH, Saini PA (1999) Investigation of some green compounds as corrosion and scale inhibitors for cooling systems. Corrosion 55:493–497

Wohlever JA, Amjad Z, Zuhl RW (2001) Performance of anionic polymers as precipitation inhibitors for calcium phosphonates, In: Advances in Crystal Growth Inhibition Technologies, Kluwer Academic Publishers, New York

Wyatt K, Pitts MJ, Surkalo H (2002) Mature waterfloods renew oil production by alkaline-surfactant-polymer flooding. In: Proceeding of the SPE Eastern Regional Meeting, Lexington, Kentucky