

RECENT ADVANCES IN ENHANCED POLYAMIDOAMINE INHIBITORS FOR SILICATE SCALES IN THE PETROLEUM UPSTREAM

BEE CHEA TAN^{1,2*}, ISMAIL MOHD SAAID^{1,2}, SHIFERAW REGASSA JUFAR^{1,2},
SUZALINA ZAINAL³, ABDELAZIM ABBAS AHMED AWADELSEED⁴

¹*Petroleum Engineering Department, Universiti Teknologi PETRONAS, Seri Iskandar, Malaysia*

²*Centre of Research in Enhanced Oil Recovery, Institute of Hydrocarbon Recovery, Universiti Teknologi PETRONAS, Seri Iskandar, Malaysia*

³*PETRONAS Research Sdn Bhd, Bangi, Malaysia*

⁴*Wood PLC Group, Scotland, United Kingdom*

*Corresponding author: tan_22000121@utp.edu.my

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ABSTRACT: Chemical flooding is regarded as a promising enhanced oil recovery technique to recover more hydrocarbon from reservoirs. However, the dissolution of quartz minerals in a highly alkaline environment poses the risk of silicate scaling near the production well region from the mixing of two different waters. Commercial scale inhibitors are effective, but they are also harmful to the environment. This paper aims to provide insights into current advances in environment-friendly or “green” scale inhibitors for petroleum upstream. Previous research works have demonstrated that green chemicals are effective in mitigating silicate, carbonate, and sulfide scales. Polyamidoamine or amide-based inhibitors have been widely investigated in recent literature due to several advantages. The addition of anionic compounds in these inhibitors enhanced scale inhibition efficiency by roughly 10%. Nevertheless, the reported findings were deliberated for industrial wastewater treatment. Meanwhile, understanding the performance of polyamidoamine or amide-based scale inhibitors in petroleum upstream is inadequate to a certain extent. The formation process of silicate scales inside a reservoir is rather complicated by looking at the influence of water salinity, composition of brine, temperature, pressure, and rock type. Hence, it is essential to study and develop green scale inhibitors that are effective and environmentally friendly to meet increasingly stringent disposal regulations in the petroleum industry.

ABSTRAK: Pembanjiran kimia merupakan teknik pemulihan minyak. Ia berpotensi dalam memperoleh lebih banyak hidrokarbon dari takungan. Namun, pelarut mineral kuarza dalam persekitaran beralkali tinggi memberi risiko penumpukan silikat berhampiran kawasan takungan pengeluaran. Ia disebabkan oleh pencampuran dua jenis cecair berbeza. Perencat penumpukan silikat komersial adalah berkesan, tetapi sangat berbahaya pada alam sekitar. Kajian ini bertujuan bagi menambahbaik kemajuan perencat silikat mesra alam terkini atau perencat silikat hijau bagi bidang saluran petroleum. Kajian terdahulu telah membuktikan bahawa bahan kimia mesra alam adalah berkesan dalam pengurangan penumpukan silikat, karbonat dan sulfida. Perencat poliamidoamina atau perencat bersumber amida telah dikaji secara meluas dalam beberapa kajian sejak kebelakangan ini kerana kelebihannya yang banyak. Penambahan sebatian anionik dalam perencat ini mampu meningkatkan keberkesanan perencat silikat sebanyak 10%. Namun, laporan kajian terdahulu adalah khusus bagi rawatan sisa air industri. Sementara itu, pemahaman tentang prestasi perencat silikat bersumberkan poliamidoamina atau perencat bersumber amida dalam saluran petroleum masih tidak mencukupi. Proses pembentukan penumpukan silikat dalam takungan

adalah agak rumit berdasarkan faktor saliniti air, komposisi air garam, suhu, tekanan dan jenis batuan. Oleh itu, kajian dan pembangunan berkesan tentang perencat silikat mesra alam adalah penting bagi memenuhi peraturan pelupusan sisa yang semakin ketat dalam industri petroleum.

KEYWORDS: *Green Scale Inhibitor, PAMAM, Silicate, Formation Damage, and ASP Flooding.*

1. INTRODUCTION

Global oil demand is projected to rise and is expected to reach its peak either in the year 2024 at 98.1 million barrels per day or 103.2 million barrels per day in the year 2035 [1]. In addition, conventional oilfields are maturing, and the impact of waterflooding will wear off eventually. This could result in the rise of field implementation of tertiary oil recovery in the coming years. Tertiary recovery is the stage where advanced techniques are used to recover the remaining hydrocarbons from a reservoir. It is commonly known as enhanced oil recovery (EOR) in the petroleum upstream sector. These techniques include microbial injection, steam injection, gas flooding, chemical flooding, and even hybrid methods.

Chemical flooding is of special interest for its success in cost-effectively recovering significant amounts of residual hydrocarbon from matured oilfields. The common chemicals used are polymers, surfactants, and alkalis. They can be injected either singly or in combination according to the reservoir's characteristics and limitations [2, 3]. The combination of all three chemicals is referred to as alkaline surfactant polymer (ASP) flooding. The combination of alkali and surfactant in a chemical injection slug is to achieve overall interfacial tension reduction of fluids, meanwhile, the polymer is used to achieve better sweep efficiency in the reservoir. Compared to other chemical EOR types, ASP flooding could improve oil recovery as much as 45% in laboratory experiments and up to 28% in oilfield tests [4].

Although ASP flooding is deemed as a promising EOR technique, it has raised concern for silicate scaling. This could cause problems in terms of formation damage and flow assurance, thus hindering the productivity of a well. Scale can be deposited at any point of the petroleum production system, from near the wellbore region up to the surface facilities [5]. Several oilfields have reported the presence of silicate scale in their production systems. For instance, the silicate content in one of the Daqing's production wells was reported to be about 70% in scaling peak stage due to ASP flooding [6]. Meanwhile in Alberta, silicate scale was found inside pumps, pipelines, and facilities after one year of ASP injection [7]. Hence, it is important to manage oilfield scales when adopting an alkaline-based chemical flooding.

Chemical treatment using scale inhibitors is an effective approach to maintain well productivity by retarding or minimizing the risk of scaling at the production wellbore and its proximity region [5, 8]. For oilfield operations, phosphonates and phosphino-polyacrylates are the two commonly used scale inhibitors due to good thermal stability. Unfortunately, they are not intended to treat silicate scales. In fact, they are primarily used to inhibit carbonate, sulfate, and phosphate scales [9,10]. Besides that, the inherent biodegradability of phosphonates were reported to be less than 40% in 28 days, while phosphino-polyacrylates were reported as non-biodegradable [11].

Owing to rising environmental concerns and discharge restrictions, environment-friendly or "green" scale inhibitors were developed for sustainable alternatives. Carboxymethyl inulin (CMI), polyaspartic acid (PASP), polyepoxysuccinic acid (PESA), and chitosan are some

examples of well-accepted green inhibitors in the industry. This paper provides an insight into the current state of green scale inhibitors and their challenges. Special attention is given to highlight the limitations of polyamidoamine-based formulations and alternative components for their enhancement in mitigating silicate scales. The formation of silicate scales due to ASP flooding and the mechanism of chemical scale inhibition are also described in this paper. The green chemicals used for scale inhibition are reviewed according to their effectiveness and mechanisms in reported laboratory works. The effectiveness of amine-based chemicals such as polyamidoamine dendrimers is also discussed accordingly.

2. FORMATION OF SILICATE SCALE

The alkaline slug in ASP injectant is often at pH 11 and above [12]. The excessive aqueous alkali would dissolve the quartz mineral of sandstone rock surface when they are in contact for sufficient time at elevated temperature and pressure, such as reservoir conditions [13]. Unfortunately, the dissolution of quartz is an irreversible chemical reaction at high pH environment. The dissolved quartz mineral is present in the form of monomeric silica in solution ($\text{Si}(\text{OH})_3\text{O}^- \text{Na}^+$) that is usually soluble and stable at high pH reservoir conditions [14].

As the alkaline solution (pH ≥ 11) that contains monomeric silica flows towards the production well, the solubility of monomeric silica decreases due to pH reduction when gradually mixing with formation water or connate water that is usually in the range of pH 6 to pH 8 [15]. The soluble monomeric silica begins to polymerize and form colloidal silica when pH drops below 10.5. When the pH drops further to 8.5, the colloidal silica polymerizes further and forms insoluble amorphous silicate scale [16, 17]. In addition, the monomeric silica also tends to form metallic silicates in the presence of excessive divalent cations in connate water, such as magnesium (Mg^{2+}) and calcium (Ca^{2+}) ions [18, 19]. As such, Fig. 1 illustrates the mixing of two different waters in a production well.

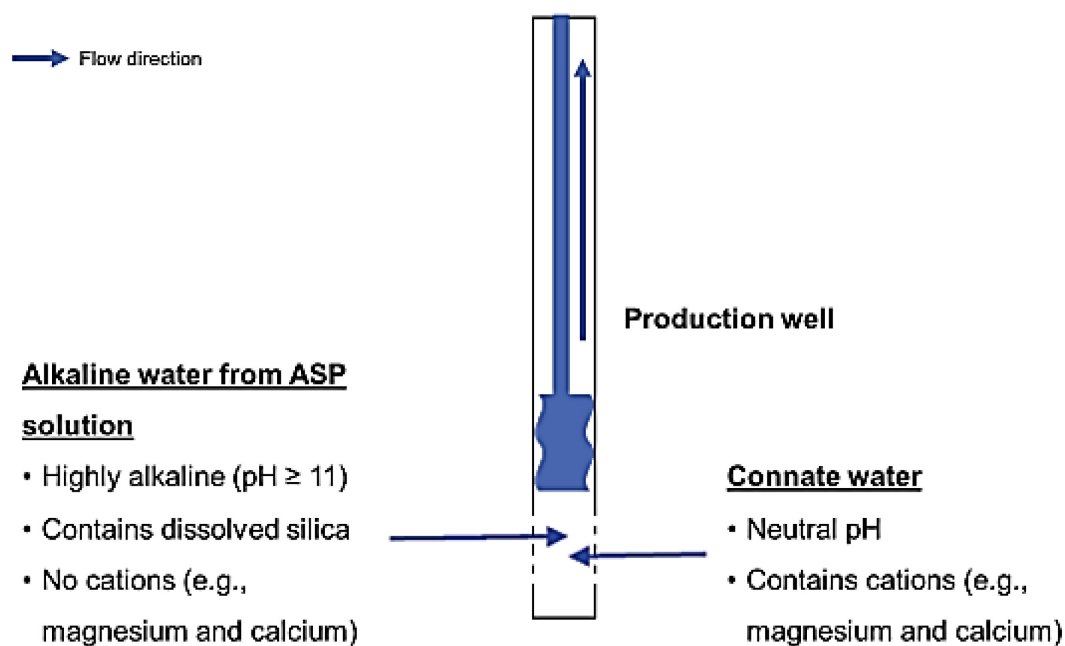


Fig. 1. Mixing of ASP solution and connate water in a production well, modified from Arensdorf et al. [20].

Based on the process described above, the pH change in alkaline water and divalent cations in connate water are the two important factors that influence the final form of the silicates at constant temperature and pressure. The research findings on the effects of pH and divalent cations that contribute to silicate scale formation are summarized in Table 1.

Table 1: Experimental findings of factors that influence the final form of silicate scales

Factor	Main Findings	Reference
pH	The experiment was carried out using fixed concentration of magnesium and silicon ions by varying the final mixture's pH. Amorphous silica and magnesium silicate were identified in the beginning at pH 8.5. Infrared spectrum revealed the tendency of magnesium silicate scale formation increased with increasing pH. However, the reduction of pH on silicate scale formation is not conducted in this study.	[17]
	This review article mentioned that silica scale formation usually takes place at pH less than 8.5 whereas magnesium silicate scale forms at pH 8.5 and above if water contained significant magnesium cations.	[16]
Divalent Cations	Test brine is composed of monovalent ions, divalent ions, and silicon. The ScaleSoftPitzer™ software predicts that calcium silicate and calcium/magnesium silicate are the two dominant scales with saturation index of 17.51 and 10.35, respectively. The environment conditions were set at 95°C temperature, 14.7 psia pressure, and brine with pH 10.3.	[18]
	Different concentrations of silicon, magnesium, and calcium ions in the final brine mixture were studied. Pure silicon brine of pH 5 turned cloudy and polymerized after 22 hours. At the same pH condition, severe white precipitates were formed in the beginning when magnesium and calcium ions were added in silicon brines. The same reaction occurred when the final mixture was adjusted to pH 8.5 and pH 11. Imaging showed that these precipitates were amorphous solid silicate scales with traces of microcrystals.	[19]

3. MECHANISMS OF CHEMICAL SCALE INHIBITION

In comparison to mechanical scale removal, chemical scale inhibitors are preferred in oilfield practice due to several advantages. The chemicals are usually added upstream of the problematic region and must be constantly present in the scaling water to inhibit scales from precipitating and growing [21]. A scale inhibitor can work in one or several ways in accordance with different stages of scale formation. With the aid of Fig. 2, the following five mechanisms of scale inhibition are disseminated [5, 8]:

- Chelating, whereby the inhibitor ions control water hardness and scaling ion deposits.
- Interfering nucleation process, whereby the inhibitor ions reach and to disrupt scaling ion clusters, thus preventing further growth of the existing clusters.
- Retarding crystal growth, whereby the inhibitor ions diffuse over the crystal surface and active sites through strong affinity, thus promoting the formation of small crystals to reduce supersaturation of the solution. It would be an advantage if the inhibitor ions

are absorbed into the crystal to make the crystal become soft, friable, and easy to remove.

- Modifying crystal surface, whereby the inhibitor ions adsorb strongly onto the crystal surface and prevent attachment of crystals.
- Dispersing flocculation, whereby the inhibitor ions modify the kinetics of nucleation and growth of scale on surfaces.

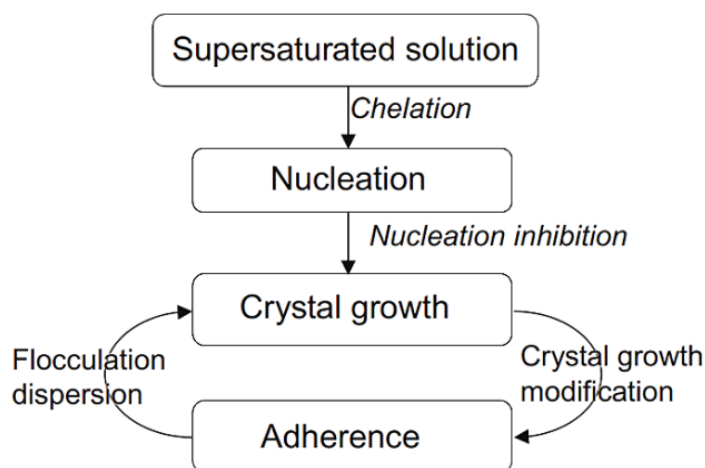


Fig. 2. Scale inhibition mechanisms (on arrow) at different stages of scale formation (in boxes), adapted from Wu [5].

It is essential to determine the inhibition mechanisms for successful application. This will allow the chemical inhibitors to work more efficiently for specific scale types, hence leading to optimum industrial operations. Nonetheless, there are some challenges in determining the precise mechanisms. In reality, scales can exhibit diverse mechanisms and evolve over time due to variation in operational conditions. This may degrade the performance of inhibitors in comparison to laboratory work. As a result, bridging the knowledge gap between research studies and practical application could benefit the formulation and development of existing inhibitors for sophisticated scales.

4. GREEN SCALE INHIBITORS FOR SILICATES

Fink (2021) suggested that an ideal scale inhibitor should possess low toxicity and be highly biodegradable [12]. Because of the increasing environmental awareness and stringent disposal regulations, environment-friendly or “green” scale inhibitors are continuously developed and improvised according to scale types and reservoir conditions. Over the past 10 years, research on green scale inhibitor is drawing the interest of stakeholders. As provided in Fig. 3, the number of research articles on green scale inhibitor has increased four-fold in Scopus and six-fold in Web of Science databases.

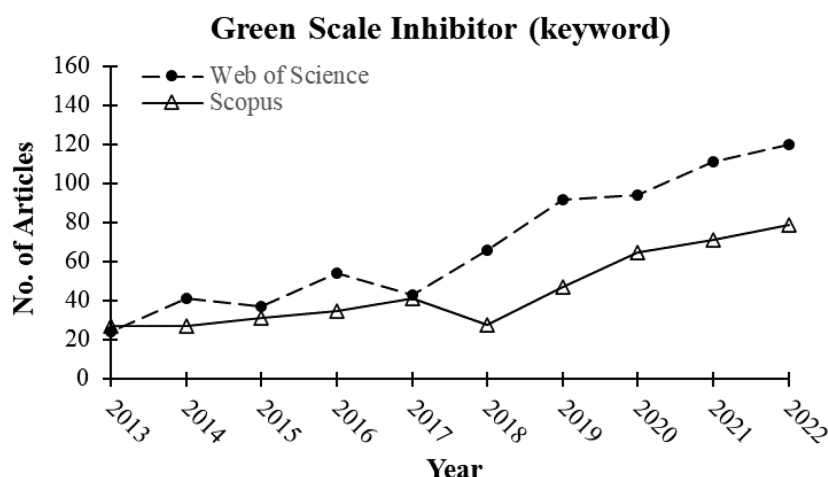


Fig. 3. Number of research articles on green scale inhibitor from year 2013 to 2022, reproduced from databases of Scopus [22] and Web of Science [23].

Numerous polymeric inhibitors have been investigated for their effectiveness against silicate scaling. Among others, cationic polymers and neutral polymers were found effective for silicate scale inhibition [24]. Green scale inhibitors such as amine-based polymers [25-28], modified resin [29], and grafted polymethacrylates [30, 31] were tested in the recent works. The performance and mechanism of these green scale inhibitors are summarized in Table 2.

Table 2: Summary of the performance and mechanism of green scale inhibitors from reported laboratory experiments

Green Chemicals	Max. Scale Inhibition	Parameters	Mechanism	Reference
PER-PAMAM G1	Silicate: ~ 85% Carbonate: ~ 85%	Conc.: 5–120 ppm pH: 5–9	Crystal surface modification	[25]
PER-PAMAM G2	Silicate: ~ 79% Carbonate: ~ 79%	Base: Pure water Temp.: 30–80°C Time: 10–30 hrs		
PER-PAMAM G1 + PAPEMP	Silicate: ~ 95% Carbonate: ~ 96%	Conc.: 80 + (5–45) ppm pH: 7 Base: Pure water Temp.: 40°C, 80°C Time: 10–30 hrs	N/A	
PAMAM-0 G-Eth	Silicate: 80%	Conc.: 10–80 ppm pH: 5–9	Crystal growth retardation	
PAMAM-0 G-Prop	Silicate: 83%	Base: Pure water		
PAMAM-0 G-But	Silicate: ~ 81%	Temp.: 30°C		
PAMAM-0 G-Hex	Silicate: 77%	Time: 12–24 hrs		
AA/AT/DE + PESA	Silicate: ~ 90%	Conc.: (20–70) + (5–50) ppm pH: 7 Base: Pure water Temp.: Ambient Time: 24–96 hrs	Nucleation interference and crystal growth retardation	[27]

Green Chemicals	Max. Scale Inhibition	Parameters	Mechanism	Reference
CPEG + TOMAC	Silicate: N/A	Conc.: 2000 ppm + (1–5)% pH: 3–9 Base: N/A Temp.: 90°C Time: 1 hr	Nucleation interference	[28]
GA-type resin	Silicate: 80%	Conc.: ~1440 ppm pH: 4–10 Base: Pure water Temp.: 25°C Time: 2–130 hrs	Nucleation interference	[29]
OH-type resin	Silicate: 5%			
PEGPHOS-LOW	Silicate: ~ 84% Carbonate: ~ 98% Sulfide: ~ 95%	Conc.: 500–5000 ppm pH: 8.5 Base: Pure water Temp.: Ambient Time: 3 hrs	Chelation and flocculation dispersion	[30]
HOMOPEG	Silicates: ~ 12% Sulfides: < 5% Carbonate: ~ 5%		Inactive	
HOMOPHOS	Silicates: ~ 15% Sulfides: ~ 20% Carbonate: ~ 95%	Conc.: 100–400 ppm pH: 8.5 Base: Pure water Temp.: Ambient Time: 3 hrs		[31]
PEGPHOS-LOW	Silicates: 81% Sulfides: ~ 75% Carbonate: < 10%		Chelation	
PEGPHOS-HIGH	Silicates: 69% Sulfides: ~ 30% Carbonate: ~ 30%			

PER-PAMAM G1 = first generation polyamidoamine dendrimer with pentaerythritol-acrylonitrile adduct initiator core; PER-PAMAM G2 = second generation polyamidoamine dendrimer with pentaerythritol-acrylonitrile adduct initiator core; PAPEMP = polyamine polyether methylene phosphonic acid; PAMAM-0 G-Eth = zeroth generation amine-terminated dendrimer synthesized with 1,2-ethylenediamine; PAMAM-0 G-Prop = zeroth generation amine-terminated dendrimer synthesized with 1,3-diaminopropane; PAMAM-0 G-But = zeroth generation amine-terminated dendrimer synthesized with 1,4-butanediamine; PAMAM-0 G-Hex = zeroth generation amine-terminated dendrimer synthesized with 1,6-diaminohexane; AA = polycation adipic acid; AT = amine-terminated polyether D230; DE = diethylenetriamine copolymer; PESA = polyepoxysuccinic acid; CPEG = chitosan-polyethylene glycol composite; TOMAC = tri octyl methyl ammonium chloride; GA= gallic acid; OH = hydroxide; HOMOPEG = polyethylene glycol grafted polymethacrylate; HOMOPHOS = methyl phosphonic acid grafted polymethacrylate; PEGPHOS-LOW = polymethacrylate grafted with methyl phosphonic acid and lower short-chain polyethylene glycol ratio; and PEGPHOS-HIGH = polymethacrylate grafted with methyl phosphonic acid and higher short-chain polyethylene glycol ratio.

It can be inferred from Table 2 that effective scale inhibition can be achieved with low concentrations of green chemicals. They also showed good thermal stability which is also suggested in terms of ideal scale inhibitor [12]. On top of that, scale inhibition was improved further with the chemical additive of polyamine polyether methylene phosphonic acid (PAPEMP) and polyepoxysuccinic acid (PESA). Other than silicate scales, these green scale inhibitors were also examined for their effectiveness on carbonate and sulfide scales, which are commonly encountered in oilfields. Furthermore, it can also be deduced that several green scale inhibitors could work in two scale inhibition mechanisms. As a result, green scale inhibitors could be utilized as alternatives for phosphorous commercial chemical inhibitors, especially amine-based inhibitors.

4.1. Polyamidoamine (PAMAM) Dendrimer Inhibitors

Polyamidoamine (PAMAM) dendrimers as silicate scale inhibitors were investigated extensively in recent works. It has been demonstrated from earlier research that PAMAM inhibitors with amine group ($-NH_2$) terminal were effective in inhibiting silicate scale formation because its ammonium cations would bind with silicate anions in a solution. However, the formation of the PAMAM-silica composite was evident in the reported research. This situation has deteriorated the performance of PAMAM inhibitors over time [32-35]. Consequently, recent studies have modified the existing PAMAMs to improve their inhibition performance.

Sun et al. (2021) have synthesized the zeroth generation PAMAM with reactive cores of different carbon chain lengths to inhibit silica growth. The study was intended to investigate the inhibitory effect of PAMAM inhibitors with different carbon chain lengths. The study observed that the best scale inhibition performance was PAMAM-0 G-Prop, the synthesized PAMAM that is made up of medium carbon chain length of reaction cores. In addition, these synthesized PAMAMs also altered the morphology of the silica scale [26]. The molecular structure of the PAMAM-0 G-Prop is illustrated in Fig. 4. It has eight amine groups, $-NH_2$ and $-NH$, which are distributed evenly in the carbon chains.

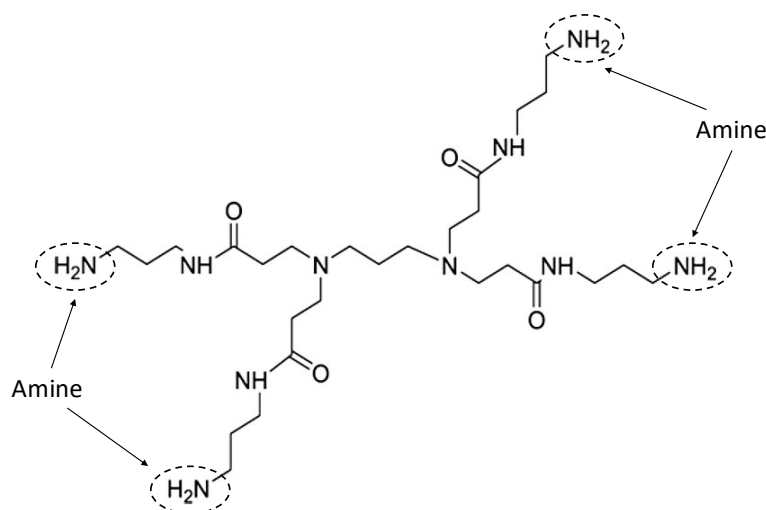


Fig. 4. Synthesized zeroth generation polyamidoamine dendrimer with 1,3-diaminopropane (PAMAM-0 G-Prop), reproduced from Sun et al. [26].

Furthermore, Shi et al. (2022) modified the initiator core of first and second-generation PAMAMs from ethylenediamine to pentaerythritol-acrylonitrile adduct (PER-PAMAMs). The study aimed to diversify the existing PAMAM scale inhibitors. The study found that PER-PAMAM G1 exhibited better silicate scale inhibition and yielded the best inhibition performance when 15 ppm of PPEMP was added at the tested conditions. Likewise, the morphology of the silicate scale was also altered due to PER-PAMAM inhibitors [25]. The molecular structures of PER-PAMAM G1 are provided in Fig. 5. It also consists of eight amine groups but with pentaerythritol-acrylonitrile adduct initiator core, such that four oxygen atoms are in the molecule's core.

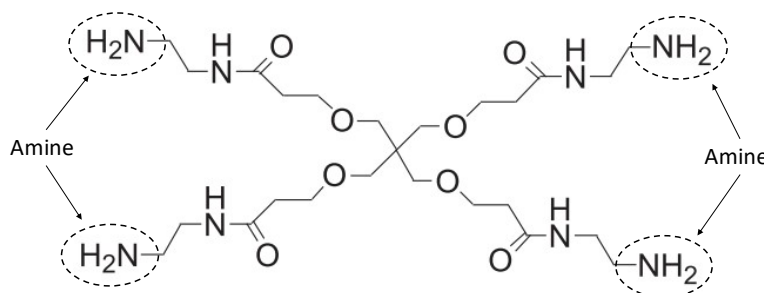


Fig. 5. Synthesized first-generation polyamidoamine dendrimer with pentaerythritol-acrylonitrile adduct initiator core (PER-PAMAM G1), reproduced from Shi et al. [25].

Based on both studies, the length of the carbon chain has more influence than the molecular core itself. Apparently, PAMAM dendrimer with medium carbon chain length is the optimum inhibitor for industrial water systems. The silicate scale inhibition test was conducted using distilled water at neutral pH and temperature up to 40°C. Unfortunately, this condition does not represent the typical oil reservoir. Thus, it is uncertain regarding the effectiveness of these inhibitors if they were undertaken for saline water, a wider range of pH, as well as greater temperatures and pressures. Moreover, PAMAM chemicals are expensive due to their specialty. Consequently, other amine-terminated polymeric chemicals shall also be assessed and improvised for silicate scale inhibition.

4.2. Amine-terminated AA/AT/DE Inhibitor

Another amine-based inhibitor, AA/AT/DE, was also tested for silicate scale inhibition. It is made up of adipic acid (AA), amine-terminated polyether D230 (AT), and diethylenetriamine (DE) at a molar ratio of 4:1:3, respectively. In the study, 50 ppm of AA/AT/DE inhibitor stabilized 500-ppm silicate at the tested conditions. Similar to the PAMAM inhibitor, a small amount of polymer floc appeared in the solution because the AA/AT/DE inhibitor was cationic at pH 7. The addition of polyepoxysuccinic acid (PESA) into the AA/AT/DE inhibitor has prevented floc formation and improved inhibition as well. For the same silicate concentration, 40-ppm AA/AT/DE added with 40-ppm PESA was the most optimal inhibitor formulation [27].

The chemical structures of AA/AT/DE inhibitor and PESA are provided in Fig. 6 (a) and Fig. 6 (b). The figure shows that AA/AT/DE inhibitor carries $-NH_2$ functional groups, while PESA carries carboxyl ($-COOH$) as well as hydroxyl ($-OH$) functional groups. Previous work also revealed that PESA alone was not effective towards silica scale formation under the tested conditions [27].

Based on the previous work, this inhibitor was tested to inhibit silica for a reverse osmosis membrane at room temperature and in distilled water [27]. Therefore, it remains uncertain whether AA/AT/DE inhibitors could perform similarly under reservoir conditions that have higher temperatures and pressures. The compatibility of formation water and AA/AT/DE inhibitor is not known either. Besides that, the study has not reported whether this inhibitor is feasible above neutral pH, which may be useful in treating magnesium silicate or aluminum silicate.

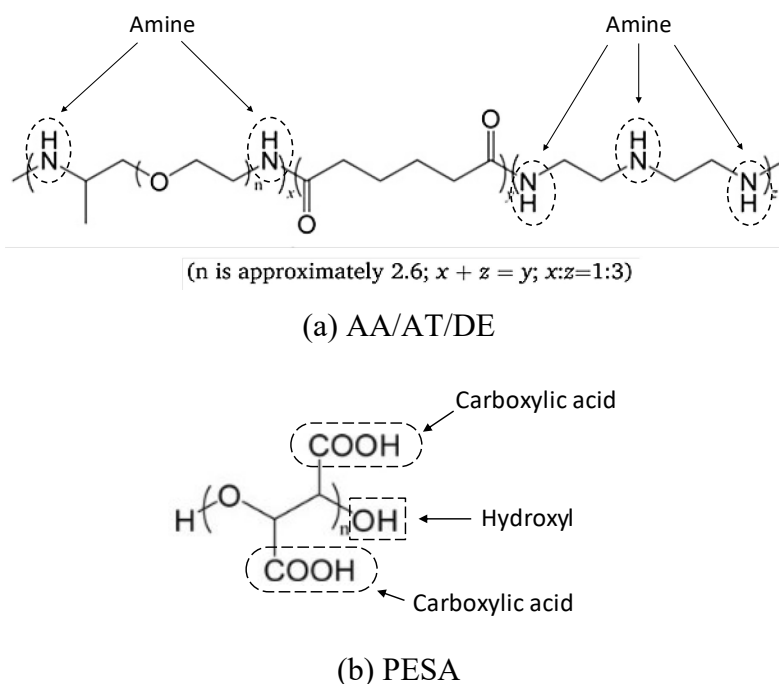


Fig. 6. Chemical structures of (a) adipic acid/ amine-terminated polyether D230/ diethylenetriamine copolymer (AA/AT/DE) inhibitor and (b) polyepoxysuccinic acid (PESA), reproduced from Tan et al. [27].

4.2. Chitosan-Polyethylene Glycol Composite (CPEG) Inhibitor

Chitosan is a biopolymer that carries both -NH_2 and -OH functional groups, meanwhile, polyethylene glycol (PEG) is a neutral polymer that carries -OH groups only. The amine group in chitosan possesses adsorption capacity to eliminate anions from aqueous solutions, and the addition of PEG is believed to improve the adsorption capacity of chitosan [36]. The change in chitosan's structure due to PEG addition is illustrated in Fig. 7 below. The addition of PEG polymer, represented in shaded circles, seems to strengthen chitosan's structure without changing its number of functional groups.

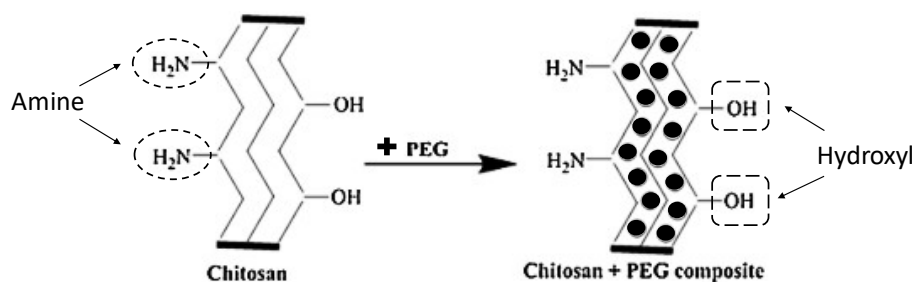


Fig. 7. Structural change in chitosan due to polyethylene glycol (PEG), reproduced from Rajeswari et al. [36].

This composite of chitosan and polyethylene glycol (CPEG) was studied in silicate scale inhibition. Hayati et al. (2021) reported that the highest adsorption capacity of CPEG was achieved at pH 6 with approximately 7.5 mg/g. Moreover, the additive of 1% tri octyl methyl ammonium chloride (TOMAC) emulsifier in CPEG has significantly increased the adsorption capacity of CPEG to 72.6 mg/g [28].

Nevertheless, the effectiveness of CPEG and CPEG-TOMAC inhibitors on silicate scale inhibition was not measured, and a mere 20 ppm of silicate was tested in the mentioned work. Moreover, the paper is focused on the elimination of silicic acid (H_2SiO_4^-) in geothermal fluid from the Dieng Geo Dipa Power Plant in Indonesia. Hence, these polymeric inhibitors are yet to be examined in the petroleum industry in which the composition of the formation water can be different from the geothermal fluid. Sodium chloride is a dominant compound in most formation water. However, the composition of the geothermal fluid is not revealed in the paper for comparison.

5. ENHANCED POLYAMIDOAMINE SCALE INHIBITORS

The advantages of polyamidoamine (PAMAM) dendrimers have gained interest in the research field. They have relatively large surface functional groups, exhibit greater biocompatibility due to amine groups, and exhibit decent solubility in water. These characteristics have positioned PAMAMs as environment-friendly or “green” scale inhibitors. Besides that, they also have good adsorption and encapsulation functions for metallic cations, such as cadmium and nickel [37, 38]. Even though they are effective in inhibiting amorphous silica scale at low concentrations, they tend to produce insoluble PAMAM-silica composite in water because of the incomplete interaction of anionic silica and cationic inhibitor.

Table 3: Summary of investigated anionic compounds for PAMAM scale inhibitor’s enhancement before the year 2018

Anionic Compound	Best Formulation	Max. Scale Inhibition	Condition	Reference
PGLU	5000 ppm (+ 10 ppm of PAMAM-2) with volume ratio of 2:3	Silicate: ~70%	pH: N/A Base: Synthetic brine Temp.: N/A Time: 12–24 hrs	[39]
SAA	Synthesized PAMAM G4.0 with mass ratio 1.0	Carbonate: 92.8%	pH: 7 Base: N/A Temp.: 40–80°C Time: 10 hrs	[40]
PAM-co-AA		Silicate: 6.28 ^a		
PAA (low molecular weight)	20 ppm (+ 40 ppm of PAMAM-2)		pH: 7 Base: Pure water Temp.: N/A Time: 12–72 hrs	[41]
PAA (high molecular weight)		Silicate: 6.16 ^a		
CMI		Silicate: 6.75 ^a		

^a Defined as the number of silicate molecules stabilized as found experimentally divided by the estimated silicate molecules stabilized per molecule of dendrimer.

PGLU = pteroyl-L-glutamic acid; SAA = sodium acrylate; PAM-co-AA = poly(acrylamide-co-acrylate); PAA = polyacrylate; CMI = carboxymethyl inulin; PAMAM-2 = second generation polyamidoamine dendrimer; and PAMAM G4.0 = fourth generation polyamidoamine dendrimers.

It remains controversial whether more sophisticated scale types could be produced and deposited at any point in time. Subsequently, an anionic compound is added to the cationic PAMAM inhibitor to enhance the inhibition performance. Apart from the aforementioned PAPEMP and PESA, Table 3 sets out other anionic compounds that have been investigated for PAMAM inhibitor enhancement in the last decade. These include pteroyl-L-glutamic acid [39], polyacrylates [40], carboxymethyl inulin, and poly(acrylamide-co-acrylate) [41]. In the case of distilled water, a small volume of anionic compounds was sufficient to enhance PAMAM inhibitors. The mass ratios of cationic to anionic compounds were found to be 1:1, 2:1, and 1:018 in the reported works. In contrast, a greater concentration of anionic compounds may be needed for reservoir conditions. For instance, 5000 ppm of anionic pteroyl-L-glutamic acid was added with a small volume of cationic PAMAM inhibitors [39]. Its inhibitory mechanism was briefly described; however, the characteristics of the formulation itself are not presented in the paper. It is apparent from Table 2 and Table 3 that not much literature employed PAMAM in silicate scale inhibition studies. This may hold back eventual pilot testing due to insufficient data.

6. SUMMARY AND FUTURE DIRECTIONS

Silica or silicate ions are negatively charged upon dissolution in water. Thus, polymeric inhibitors with positive charge are believed to be effective in impeding scale formation by attracting negatively charged scaling ions. Many positively charged or cationic inhibitors usually carry at least an amine functional group in their chemical structures. Polyamidoamine (PAMAM) dendrimers have gained popularity in scale inhibition studies due to larger surface areas of active sites, good water solubility, and better biocompatibility. Research works also reveal that PAMAM dendrimers inhibit many types of scale such as silica, silicate, as well as carbonate. Unfortunately, it has been observed in some works that PAMAM dendrimers tend to form insoluble composites with silica in water. This has called for the addition of anionic compounds in PAMAM inhibitors and their effectiveness in scale inhibition has also been enhanced because of this. Nevertheless, the enhanced PAMAM inhibitors are yet to be adopted in oilfields and treatment plants. Other than cost, the working mechanism of these enhanced PAMAM inhibitors is still not comprehensive. The optimum mass ratio and type of anionic compound are also important to the effectiveness of PAMAM dendrimers. For future oilfield applications, it is essential to research further the development of “green” scale inhibitors that have a balanced cationic-anionic property and performance on par with commercial scale inhibitors, such as phosphonates and phosphine-polyacrylates.

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