

# Cationic polymeric chemical inhibitors and multifunctional blends for the control of silica scale in process waters

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## Abstract

Water is used globally for cooling purposes in industry. During its re-use, scaling and deposition can develop due to the high content of dissolved species. Among the toughest to combat is silica scale, or amorphous silicon dioxide. In this paper, we present how certain chemical interventions in the water chemistry can be beneficial for inhibiting silica polycondensation. Specifically, we have used chemical additives known as dendrimers. These are dendrimeric molecules based on polyaminoamide backbones that possess amine moieties as surface groups. These become protonated at circumneutral pH, hence charging the dendrimer molecules cationically. Their blends with anionic polymers such as polyvinylphosphonic acid are also studied for their silica scale inhibition efficiency.

**Key words:** *silica scale, deposits, water systems, silica inhibitors, dendrimers, polyvinyl phosphonic acid.*

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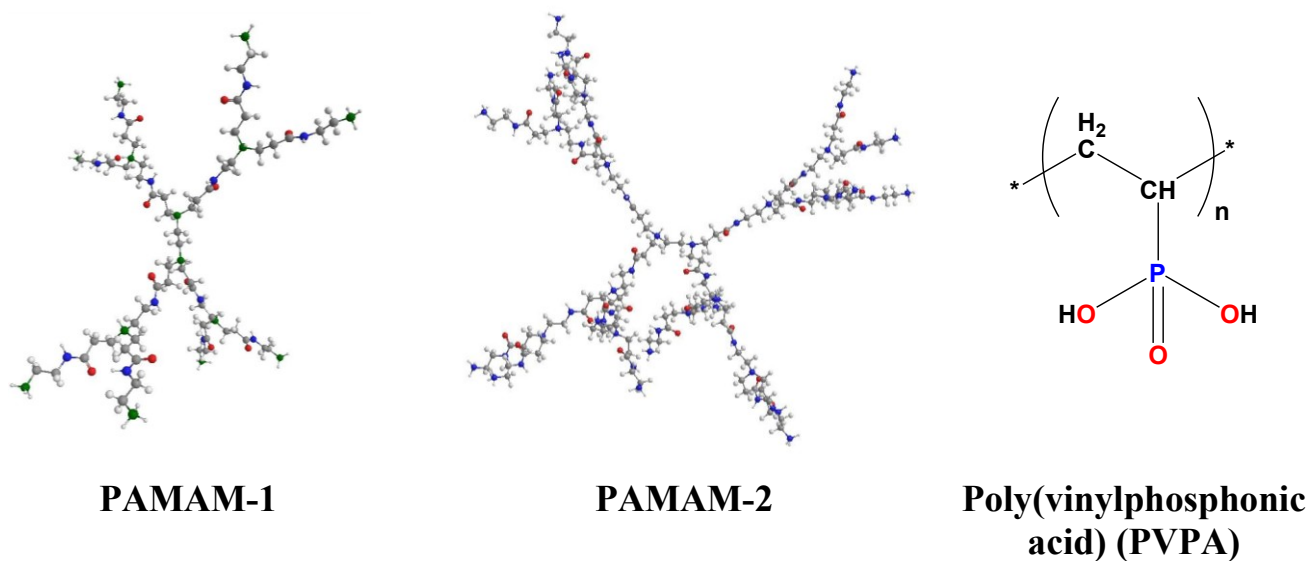
## Introduction

Among water-formed deposits colloidal silica ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ,  $n$  is variable and dependent on hydration) is especially troublesome because it can cause serious materials failure and operational shut-downs, Fig. 1. Silica scale prevention, in principle, can be achieved by use of scale inhibitors, significant components of a well-thought chemical water treatment strategy [1]. Unfortunately, traditional scale control methods (inhibition and crystal modification) applied to crystalline mineral salt precipitates [2], do not apply to silica because of its amorphous state [3]. Therefore, much more well-designed inhibition approaches have to be applied for controlling silica deposition. Increasing environmental concerns and discharge limitations have imposed additional challenges in treating process waters. Therefore, the discovery and successful application of chemical additives that have mild environmental impact has been the focus of several researchers [4, 5]. In this paper we also focus on use of “green” inhibitors for silica scale inhibition. This research is part of our on-going investigation on the discovery and application of scale inhibitors, with an emphasis on “green” additives, in industrial process waters [6–14].



**Figure 1.** Amorphous silica deposits on industrial equipment.

In this work, we present the inhibiting effect of chemical additives known as dendrimers on the formation of amorphous silica. These dendrimeric molecules are based on polyaminoamide (PAMAM) backbone that possesses amine moieties as surface groups, see Fig. 2. These amine moieties become protonated at circumneutral pH, hence charging the dendrimer molecules cationically. Multifunctional blends with anionic polymers such as polyvinylphosphonic acid (see Fig. 2) are also studied for their silica scale inhibition efficiency.



**Figure 2.** Structures of the silica scale inhibitors used in this work.

## Experimental Section

**Instruments:** IR spectra were recorded on an FT-IR Perkin-Elmer FT 1760. The measurements of soluble silicic acid were carried out with a HACH 890 spectrophotometer from the Hach Co., Loveland, CO, U.S.A.

**Reagents and chemicals.** The dendrimer inhibitors PAMAM-1 and PAMAM-2 and the polymer poly(vinylphosphonic acid) (PVPA) were from Aldrich Chemical Co., USA. The structures of these molecules are shown in Fig. 2. Sodium silicate  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  was from EM Science (Merck). Ammonium molybdate  $((\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O})$  and oxalic acid

( $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) were from EM Science (Merck). Sodium hydroxide (NaOH) was from Merck, hydrochloric acid 37% was from Riedel de Haen. Potassium bromide (KBr) for preparation of the IR discs was from Fluka. Acrodisc filters (0.45  $\mu\text{m}$  pore size) were from Pall-Gelman Corporation. In-house, nanopure water was used for all experiments. This water was tested for soluble silica and was found to contain negligible amounts.

**Preparation of supersaturated silicate solutions.** A solution containing silicate, 500 ppm as  $\text{SiO}_2$ , was prepared by dissolving 4.4 g of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  in 2.5 L nanopure water. Stock solutions of the additives in water were 1% (10,000 ppm). The following solutions were prepared for the silicate spectrophotometric detection test. (a) 10 g of ammonium molybdate were dissolved in 100 mL water and its pH was adjusted between 7–8 with NaOH to avoid precipitation of ammonium molybdate. (b) HCl 1+1 is prepared by mixing one volume 37% HCl with equal volume water. (c) 8.75 g of oxalic acid was dissolved in 100 mL water. All solutions were kept in PET containers (glass containers must be avoided in order to minimize silica dissolution and silicate leaching into the test solutions).

**Silicate polymerization protocol. “Control” protocol.** 100 mL from the 500 ppm silicate stock solution was placed in a PET beaker which contained a teflon-covered magnetic stir bar. The pH of this solution was initially  $\sim 11$  and adjusted to  $7.00 \pm 0.1$  by addition of HCl and NaOH (the change in the resulting volume was about 3%). Then the beaker was covered with plastic membrane and set aside without stirring. The solution were checked for the soluble silica by the silicomolybdate method every two hours for the first twelve hours or after 24, 48, 72 h time intervals after the pH reduction.

**Inhibitor protocol.** 100 mL portions of the 500 ppm  $\text{SiO}_2$  stock solution were placed in PET containers charged with teflon-covered magnetic stir bars. In each container different volumes of inhibitor (10,000 ppm stock solution) were added to achieve desirable inhibitor concentration. These ranged from 20–40–60–80 ppm and the volumes where added were 200–400–600–800  $\mu\text{L}$ . After that the same procedure as the control test was followed.

**Determination of soluble (reactive) silica.** Frequently there is a misconception on the use of the terms “soluble silica”, “silicic acid” and “silicate”. In this paper the term “silica” indicates the product of silicate polymerization. The terms “soluble silica”, “silicic acid” and “silicate” indicate all the forms of the species  $\text{Si}(\text{OH})_4$  at various deprotonated states, which are molybdate-reactive. According to this method, 2 mL filtered sample, with 0.45  $\mu\text{m}$  syringe filter, from the test solution is diluted to 25 mL in the cell, with light path 1 cm. 1 mL ammonium molybdate stock solution and 0.5 mL 1+1 HCl are added to the sample cell, the solution is mixed well and left undisturbed for 10 min. Then 1 mL oxalic acid solution is added and mixed again. The solution is set aside for 2 min. After the second time period the photometer is set at zero absorbance with water. Finally the sample absorbance is measured at 452 nm as “ppm soluble silicate”. The detectable concentrations range is 0–75.0 ppm. In order to calculate the concentration in the original solution a dilution factor is applied.

The silicomolybdate method is based on the principle that ammonium molybdate reacts only with “reactive” silicate and any phosphate present at low pH (about 1.2) and yields heteropoly acids, yellow in color. Oxalic acid is added to destroy the molybdophosphoric acid leaving silicomolybdate intact, and thus eliminating any color interference from phosphates. It should be emphasized that molybdate reacts only with soluble silicate forms, but is totally unreactive to colloidal silica species. This was verified experimentally in our laboratory.

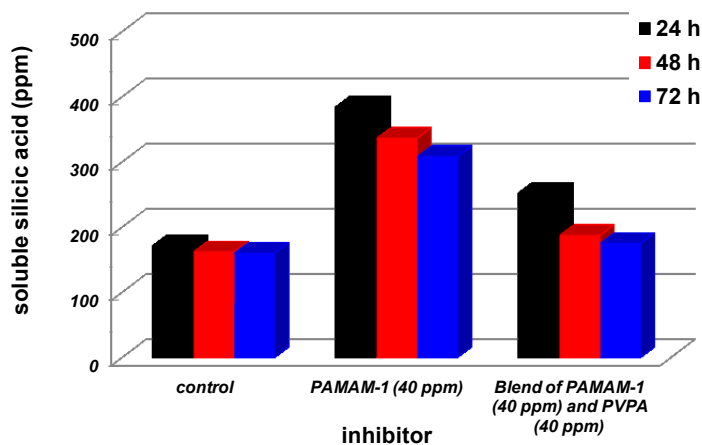
## Results and Discussion

We have already reported extensive silica inhibition studies with the two dendrimeric inhibitors, PAMAM-1 and PAMAM-2 [5, 6, 7, 8, 10, 15–19]. Some of these results will be mentioned here for comparison reasons.

Inhibitory activity results of PAMAM-1 and its blend with poly(vinylphosphonic acid) (PVPA) are presented in Table 1 and Fig. 3.

**Table 1.** Silica inhibition measurements with PAMAM-1 (40 ppm) and PAMAM-1/PVPA (40/40 ppm) blends.

Time (hours)	Soluble silicic acid (ppm)		
	control	PAMAM-1 (40 ppm)	Blend of PAMAM-1 (40 ppm) and PVPA (40 ppm)
24	171	384	252
48	162	336	187
72	160	308	175



**Figure 3.** Silica inhibitory activity of PAMAM-1 and its blend with poly(vinylphosphonic acid) (PVPA).

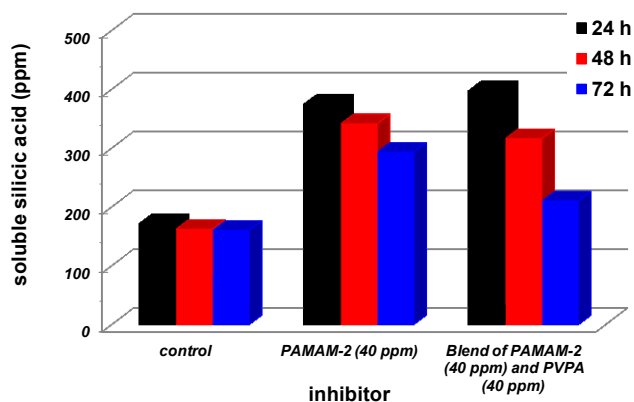
Silicic acid polymerizes to yield amorphous silica at pH=7 at a fairly fast rate. In the absence of inhibitors, 171 ppm remain soluble after 24 h, 162 ppm after 48 h, and 160 ppm after 72 h. PAMAM-1 has been studied before at various dosages (at pH=7) ranging from 10 ppm up to 100 ppm, and it was discovered that the dosage of 40 ppm was the optimum. At this dosage it substantially increases the levels of soluble silicic acid: 384 ppm (after 24 h), 336 ppm (after 48 h) and 308 ppm (after 72 h), see Fig. 3.

However, in the presence of PAMAM-1 some amorphous silica precipitates are noted. These form due to the ability of the cationic PAMAM-1 to coagulate the formed silica that is unable to inhibit. In order to “relieve” the excessive cationic charge, we thought of using a second anionic polymer, in hope that it will partially neutralize the positively charged amine groups on the PAMAM-1 backbone. However, upon testing blends of PAMAM-1 (40 ppm) and PVPA (40 ppm) we observed that the inhibitory activity of PAMAM-1 is dramatically affected, but it still is slightly above the “control”, see Fig. 3. These results prove unequivocally that the amine cationic groups on the PAMAM-1 periphery are essential for silica scale inhibition.

Inhibitory activity results of PAMAM-2 and its blend with poly(vinylphosphonic acid) (PVPA) are presented in Table 2 and Fig. 4.

**Table 2.** Silica inhibition measurements with PAMAM-2 (40 ppm) and PAMAM-2/PVPA (40/40 ppm) blends.

Time (hours)	Soluble silicic acid (ppm)		
	control	PAMAM-2 (40 ppm)	Blend of PAMAM-2 (40 ppm) and PVPA (40 ppm)
24	171	374	397
48	162	341	316
72	160	293	210



**Figure 4.** Silica inhibitory activity of PAMAM-2 and its blend with poly(vinylphosphonic acid) (PVPA).

PAMAM-2 is a comparable silica scale inhibitor to PAMAM-1 (compare Tables 1 and 2 and Figures 3 and 4). However, the effect of PVPA is entirely different on PAMAM-2 than it is on PAMAM-1. No substantial loss of PAMAM-2 inhibitory activity is observed, at least for the first 24 hours. In fact there is a ~ 25 ppm silicic acid solubility enhancement when PAMAM-2 is “blended” with PVPA, as compared to PAMAM-1/PVPA blend. However, there is a slight loss of soluble silicic acid after 48 h (~ 25 ppm) and a more substantial reduction after 72 h (83 ppm).

The variability in the results with the two different blends of PVPA with either PAMAM-1 or PAMAM-2 can be explained when some structural arguments are invoked. PAMAM-1 is a much “smaller” dendrimer (Molecular Weight = 1,430, measured diameter = 22 Å) than PAMAM-2 (Molecular Weight = 3,256, measured diameter = 29 Å) [20]. It also possesses only eight surface amine groups, compared to PAMAM-2, which has 16. Therefore, PVPA interacts with PAMAM-2 to a lesser extent, thus neutralizing a smaller number of amine groups. The smaller enhancement of silicic acid solubility (in the first 24 h) in the case of the PAMAM-2/PVPA blend may be assigned to the fact that a possible PAMAM-2/PVPA “complex” in solution prohibits PAMAM-2 from coagulating amorphous silica.

## Conclusions

In this paper we reported the inhibitory efficiency of dendrimer/poly(vinyl phosphonic acid) multifunctional synergistic mixtures in silica scale formation. The extensive cationic charge on the dendrimer backbone may be detrimental to its inhibitory activity, and this may, in part, be corrected and improved by the use of secondary, anionic polymer add-ons. In this case, PVPA was proven to be beneficial for PAMAM-2, but not for PAMAM-1.

## References

1. K. D. Demadis, in *Compact Heat Exchangers and Enhancement Technology for the Process Industries*, Ed. R. K. Shah, Begell House Inc., New York, 2003. pp. 483–490.
2. E. Barouda, K. D. Demadis, S. Freeman, F. Jones and M. I. Ogden, *Cryst. Growth Des.*, 2007, **7**, 321.
3. H. Ehrlich, K. D. Demadis, P. G. Koutsoukos and O. Pokrovsky, *Chem. Rev.*, 2010, **110**, 4656.
4. M. A. Quraishi, I. H. Farooqi and P. A. Saini, *Corrosion*, 1999, **55**, 493.
5. K. D. Demadis, E. Neofotistou, E. Mavredaki, M. Tsiknakis, E.-M. Sarigiannidou and S. D. Katarachia, *Desalination*, 2005, **179**, 281.
6. K. D. Demadis and E. Neofotistou, *Mater. Performance*, 2004, **43**, 4, 38.
7. E. Neofotistou and K. D. Demadis, *Coll. Surf. A: Physicochem. Eng. Asp.*, 2004, **242**, 213.
8. E. Neofotistou and K. D. Demadis, *Desalination*, 2004, **167**, 257.
9. K. D. Demadis, *Power*, 2004, **148**, 6, 19.

10. K. D. Demadis, *J. Chem. Technol. Biotechnol.*, 2005, **80**, 630.
11. E. Mavredaki, E. Neofotistou and K. D. Demadis, *Ind. Engin. Chem. Res.*, 2005, **44**, 7019.
12. K. D. Demadis and E. Mavredaki, *Env. Chem. Lett.*, 2005, **3**, 127.
13. K. D. Demadis and A. Stathoulopoulou, *Mater. Performance*, 2005, **45**, 1, 40.
14. K. D. Demadis, E. Mavredaki, A. Stathoulopoulou, E. Neofotistou and C. Mantzaridis, *Desalination*, 2007, **213**, 38.
15. K. D. Demadis and A. Stathoulopoulou, *Ind. Engin. Chem. Res.*, 2006, **45**, 4436.
16. K. D. Demadis and E. Neofotistou, *Chem. Mater.*, 2007, **19**, 581.
17. K. D. Demadis, in *Desalination Research Progress*, Eds. D. J. Delgado and P. Moreno, Nova Science Publishers, Inc., New York, 2008, Ch. 6, pp. 249–259.
18. K. D. Demadis and M. Öner, in *Green Chemistry Research Trends*, Ed. J. T. Pearlman, Nova Science Publishers, New York, 2009, Ch. 8, pp. 265–287.
19. M. Preari, A. Tsistraki and K. D. Demadis, in *Mineral Scales in Biological and Industrial Systems*, Taylor and Francis, New York, 2013, Ch. 12, pp. 215–226.
20. D. A. Tomalia, *Aldrichimica Acta*, 2004, **37**, 2, 39.

