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EXPLORING SPECIAL PROPERTIES AND VERSATILE APPLICATIONS OF DENDRIMERS IN MEMBRANE-BASED WATER-TREATMENT SYSTEMS

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Abstract

Dendrimers are well-defined three-dimensional hyper-branched macromolecules whose physiochemical properties provide distinct advantages in their use as scale inhibitors in reverse osmosis applications. Dendrimers and dendritic structures are ubiquitous in nature, however, their implementation in commercial and industrial applications is growing and providing an exciting avenue to explore new opportunities and challenge conventional chemistries. This paper will study the unique chemical and physical properties of dendrimers and explore diverse membrane-based applications that the dendrimer can be used for.

The dendrimers discussed in this paper are synthetically engineered to allow their functionality to be tailored to two complex mechanisms required for scale inhibition: chelation and dispersion. Laboratory studies were conducted to provide an objective measure of the dendrimer's chelation and dispersion capabilities for various organic and inorganic compounds. Different case studies in different parts, with complete different qualities of feed water, from a waste water reuse plant working at high recovery and also an industrial water treatment plant, will also be presented highlighting the inherent performance, logistical, and economic benefits associated with implementing Dendrimer-based technologies in full-scale systems.

Dendrimer molecules can be generated specific to this application, minimizing the harsh chemical nature present in other conventional scale inhibitors. Dendrimer based scale inhibitors are naturally phosphate-free, non-hazardous chemicals with exceedingly low toxicity properties in this class of products. Such properties, performance and otherwise, make dendrimer-based technology advantageous in current and emerging global water treatment systems.

The unique molecular structure of dendrimer-based antiscalant provides a greater surface area and thus a higher loading capacity. With this higher loading capacity, dendrimer-based antiscalants can control a wider range of foulants. Reviewing the performance and cleaning regimen data of a reverse osmosis system that changed its scale-inhibitor chemical from a homopolymer-based antiscalant to a dendrimer-based antiscalant, one can observe this advantage. Switching to a phosphorus-free technology has also eliminated the inherent environmental impacts of phosphorus-based antiscalants.

Keywords: Dendrimer, Water Treatment, Membrane Systems, Wastewater reuse, Industrial water, performance, antiscalant.

1.1 General Background

TFC membrane-based separation systems operate in a continuous process, as ultrapure water is produced, the brine stream will increase in the concentration of sparingly soluble salt ions. At the conditions generated towards the tail-end of this process the ion concentrations reach supersaturation and mineral scaling becomes favorable. The formation of scale can be modeled by a complex thermodynamic model interdependent of the activity of all constituents present in the water source making the implications of seemingly minor changes in operating conditions (recovery, pH adjustment, feed-water quality, temperature) significant to the behavior of the system. As such, attention to the type of scale inhibitor and dosage is paramount.

Scale formation in supersaturated solutions can occur due to both homogeneous crystallization directly onto the membrane surface and the deposition of crystals formed in a bulk solution. The type of scale forming compounds and their favourability to precipitate over other compounds will vary given the make-up of the water and operating conditions and can vary significantly depending on application: seawater desalination, brackish, wastewater reuse, etc. Although the onset of fairly common sulfate and carbonate scales on a membrane surface is often reversible through routine Clean-in-Place (CIP) implementation, recurrent cleaning incurs additional costs and can have prolonged negative effects on the system and membrane life due to harsh cleaning conditions. Additionally, the onset of less commonly encountered scale forming/fouling compounds such as barium, strontium, fluoride, and organic/biological complexes or infrequent/improper CIP's, can have severe consequences leading to irreversible fouling events and membrane damage.

1.2 Introduction to Dendrimers

Dendrimers are synthetically engineered three dimensional hyper-branched polymers whose unique intrinsic physicochemical properties provide exciting opportunities to generate substances specifically tailored to one or more functionalities. Dendrimer is derived from the Greek 'dendron' which translates to 'tree', a reference to the highly branched nature characteristic of these molecules. Such dendritic structures are ubiquitous in nature due to the abundance of surface sites coupled with mechanical integrity associated with their symmetrical and spherical structure. Examples of dendritic structures in nature include trees who rely on the branched structure for photosynthesis and vascular systems in living organisms. On a molecular level dendrimer rely on precise step-by-step convergent or divergent synthesis from repeat monomer units to generate a macromolecule of the desired structure with typical size ranges between 1 – 100 nm. This ability to control the size, charge, and functional groups makes dendrimers very desirable in several fields including targeted drug delivery, consumer products, bio-mimics, and scale inhibitors [1]. Unlike more traditional linear, cross-linked, or branched polymers, the repeat units in a dendrimer polymer branch outward in a defined and consistent manner making them the most ordered subcategory of hyper-branched polymers (Figure 1).

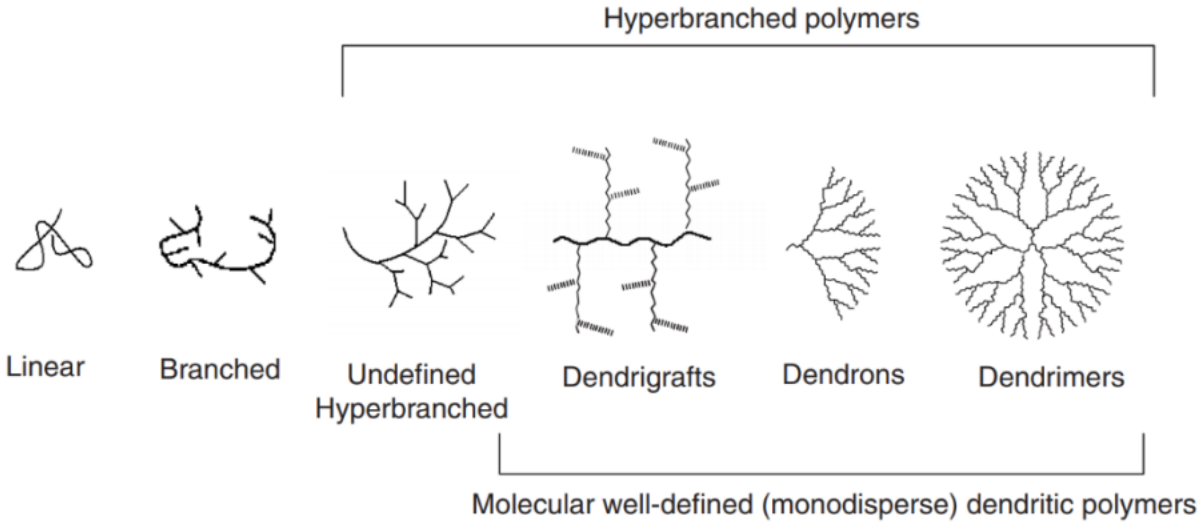

Figure 1. Diagram of various polymer sub-categories [2].

Dendrimers consist of three basic parts: the core unit, end group, and branching units (Figure 2). The linking of these monomer units forms the supramolecular structure with the number of branching points going from the core unit to the outer shell referred to as the *generation* [2]. When synthesizing higher generation dendrimer molecules there is a cubic relationship with respect to occupied space with an exponential increase in mass, the result of which is a high-density solution with enhanced solubility and reactivity. In the context of generating a commercial scale inhibitor, the ability to have high reactivity with small dense molecules results in concentrated solutions, in turn significantly lower dosage rates which carries logistical benefits in terms of shipping, handling, reduced CAPEX/OPEX costs, etc., compared to conventional linear alternatives.

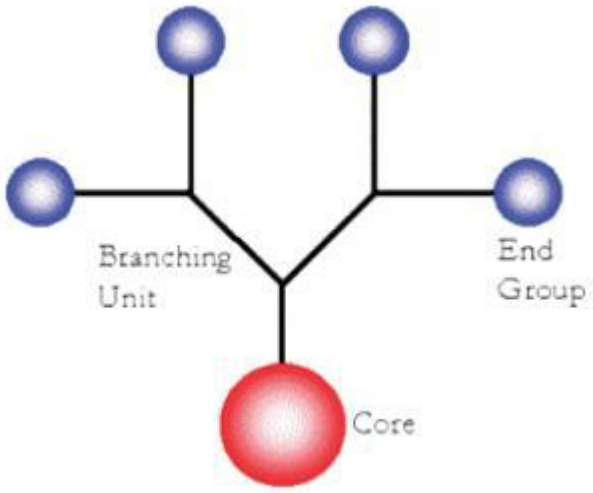

Figure 2. Structural representation of dendrimer section

An additional benefit of utilizing dendrimer technology is the ability to generate molecules with low polydispersity, the ratio between the weight average molecular weight to the number average molecular weight. The stepwise synthesis and ordered conformation of these structures allows for predictability and repeatability of composition. Dendrimers commonly have a polydispersity ratio on the order of 1.002 compared to a polydispersity ratio of 1.2 or greater for a linear equivalent [3]. Optimal scale inhibition requires a precise concentration of scale inhibitor present in solution, the risks of using a molecule with high polydispersity is ineffective dispersion of active sites and destabilization which could lead to premature crystal formation and higher dosage requirements. Dendrimers have active sites that are more easily accessible in comparison with a liner polymer with the same molecular weight which equates to higher inhibition at similar dosages.

II. EXPERIMENTAL RESEARCH CONDUCTED

2.1 Inhibition Jar Tests

The objective of inhibition jar tests is to provide a measure of relative scale inhibition capabilities of specific compounds for various scale inhibitors. Inhibition studies were carried out using standardized procedures where supersaturated solutions are generated and the inhibitors ability to prevent bulk crystallization of the isolated supersaturated species is observed. Effectiveness is marked by a % inhibition value calculated at the end of the 18-hour test period.

Two commonly encountered scale forming compounds were evaluated in these inhibition tests, calcite ($CaCO_3$) and gypsum ($CaSO_4$). In addition to the dendrimer-based scale inhibitor denoted AS-1, a linear co-polymer (AS-2) and phosphonate-based scale inhibitor (AS-3) were chosen as candidates for this comparative evaluation:

Table 1. Description of scale inhibitors used in this study.

Scale Inhibitor	Solid Content (%)	Composition
AS-1	42.0%	Dendrimer
AS-2	39.5%	Linear co-polymer
AS-3	60.0%	Phosphonate

To observe gypsum inhibition, supersaturated solutions were generated with 8,000 ppm Ca as CaCO3 and 8,000 ppm SO42- combined along with respective concentrations of scale inhibitor at a pH of 7. Solutions were stored in glass jars at 25°C for 18 hours at which the solution is passed through a 0.22 µm filter. Calcium concentration of the filtrate is determined through titration and the % inhibition is determined as the ratio of the difference in concentration of calcium in the solution with and without scale inhibitor. Calcite tests were conducted through the same method with supersaturated solutions generated with 1,500 ppm of Ca as CaCO3 and 1,300 ppm HCO3 as CaCO3 at a pH of 7.83.

2.1.1 – Experimental Jar Test Results

Figure 3 illustrates the results of the gypsum inhibition jar tests for the three scale inhibitors tested. The dendrimer-based scale inhibitor performed exceedingly well for gypsum inhibition, demonstrating 85% inhibition at 3 ppm solids content as compared to 73% for AS-2 and 66% for AS-3 at the same active solids measure. At a lower concentration of 2 ppm active solids, dendrimer AS-1 outperformed AS-2 and specially AS-3 significantly.

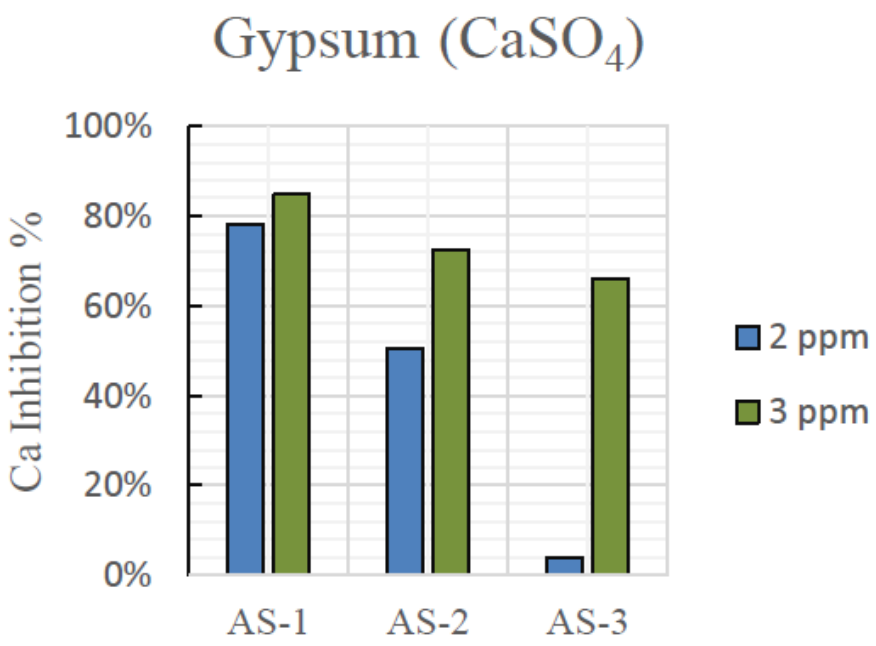

Figure 3. Results of inhibition tests for gypsum**.**

Figure 4 shows inhibition test data from calcite jar tests. Comparable inhibition % values were observed for the calcite inhibition across the board. At 3 ppm active solids the dendrimer-based scale inhibitor (AS-1) demonstrated 83% calcite inhabitation, equivalent to AS-3 and greater than AS-2 which was at 77% inhibition.

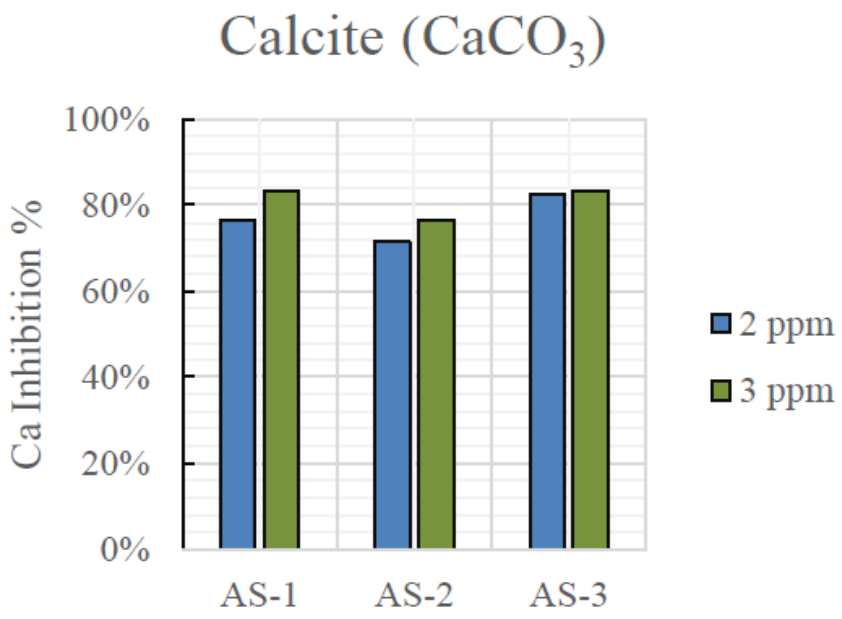

Figure 4. Results of inhibition tests for calcite.

This demonstrates the all-round versatility of a dendrimer in controlling both calcite and gypsum scale control as compared to a phosphonate based antiscalant or a linear co-polymer. It is important to note these tests are designed to provide a relative measure of performance and do not mimic real-time conditions of a typical RO/NF system. On-line application will vary significantly in ion concentrations in a dynamic environment and will require a higher dosage than that implemented in this experiment. This test does however to a degree simulate homogeneous nucleation and crystallization of mineral scale and provides an objective measure of the performance of various scale inhibitors under identical conditions. To further corroborate the benefits of dendrimer technology, a case study implementing this chemistry will be evaluated.

III. CASE STUDY

3.1 Background

A case study of a reverse osmosis site producing treated wastewater at a rate of 8.45 MGD was observed to highlight the potential benefits of dendrimer-based scale inhibitor technology compared to conventional scale inhibitors. The RO plant studied treats UF effluent from a wastewater source whose process specifications and water quality are detailed in Tables 2 & 3. Thorough evaluation of Key Performance Indicators (KPI) indicated an urgent need to reduce high differential pressures occurring in the second stage, find the root cause of fouling/scaling, and reduce CIP frequency.

Table 2: RO plant details.

Number of RO Trains	4
Total RO Capacity	8.45 MGD
Recovery	75%
Array	2:1
Vessels/Elements	28 vessels per stage – 7 elements per vessel

Table 3: RO feed water quality values.

RO Feed Water Quality					
pH	6.5 – 6.8	**Calcium Hardness**	200 – 250 ppm (as $CaCO_3$)	**Fluoride**	0.78 ppm
TDS	1500 ppm	**Chloride**	500 – 570 ppm	**Total Nitrogen**	18.8 ppm (as N)
Conductivity	3000 µS	**Manganese**	0.203 ppm	**Total Phosphate**	5.1 ppm
Turbidity	0.5 NTU	**Sulfate**	101 ppm	**Iron**	0.1 ppm
COD	25 - 100	**Silica**	33.5 ppm	**Nitrite**	16.8 ppm

Second stage differential pressure for the site reached approximately 4 times design value within only one week after CIP's. Reductions in permeate flow across all 4 trains were experienced approximately 2-3 days following CIP leading to a net loss of productivity for the plant and exhaustive CIP requirements. Membrane autopsy analysis of an element from the system indicated approximately 65-75% of foulant was due to mineral deposition of which was mostly calcium based. Evaluation of system performance indicated inadequate pre-treatment could be causing the chronic scaling issues in the second stage. The existing scale inhibitor was substituted for a dendrimer-based formula to observe the changes if any in system behavior and effects on the KPI.

3.2 Results

Transitioning to a dendrimer-based scale inhibitor addressed the key issues affecting the site. After the start of the treatment and following a thorough CIP, differential pressure remained at the design value (2 kg/cm2) for the remainder of the observed period (20 days). Figure 5 illustrates the trends in differential pressure both before and after treatment with a dendrimer-based scale inhibitor on a particular train (Train A), denoting a dramatic difference in KPI for the site following this change.

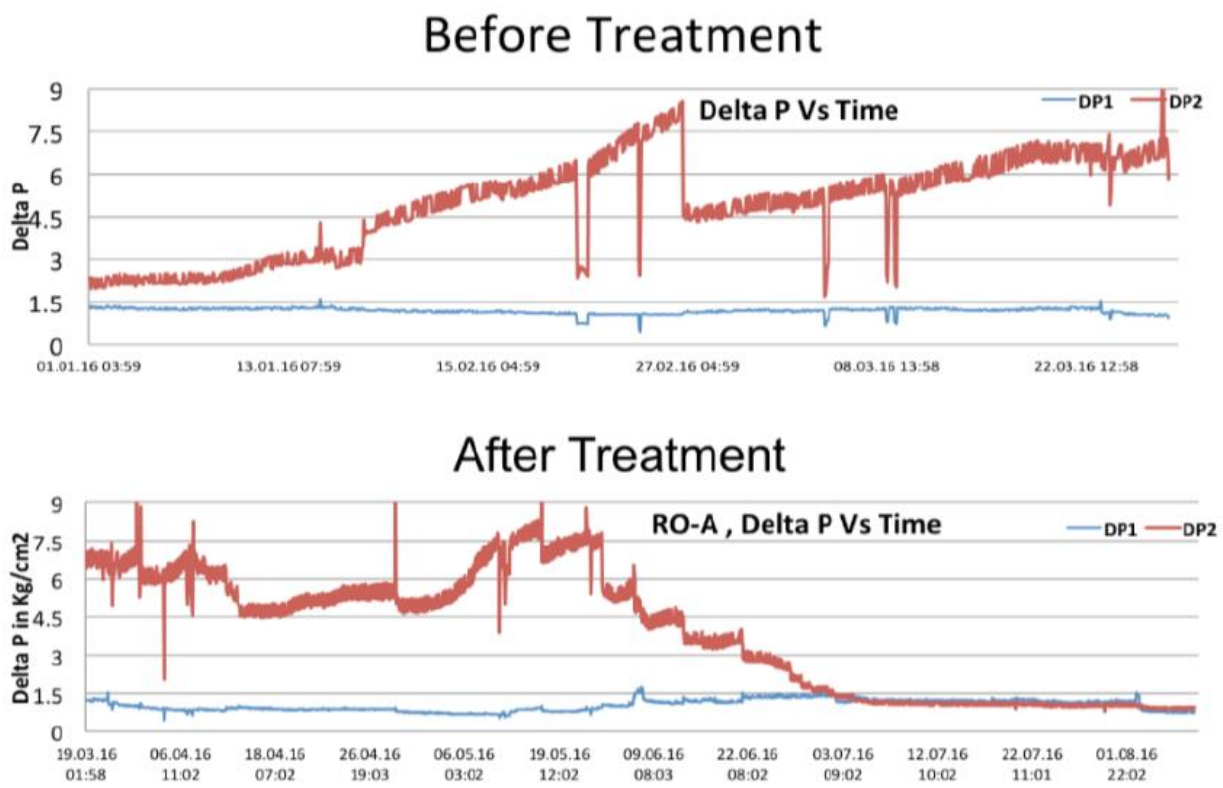

Figure 5. Differential pressures measured on an RO train before and after utilizing dendrimer-based scale inhibitor.

A reduction in CIP frequency was observed from once per week to once every three weeks. Design differential pressures in the second stage were consistent with eventual CIP requirements due to moderate organic/biological fouling in the first stage rather than scaling events in the tail end of the system as previously experienced. Evaluation of increased productivity of the system for a span of 20 days following the transition to a dendrimer-based scale inhibitor indicated a 22% increase in system productivity. Performance improvements following this implementation for the second stage of each train are highlighted in Table 4.

Table 4: KPI values for the plant before and after dendrimer application.

RO Train	2nd Stage ΔP		2nd Stage Design ΔP
	Pre-Dendrimer Treatment	Post-Dendrimer Treatment (20 days)	
RO-A	7 – 8	1.5	1 – 2
RO-B	3 – 4	1.5	1 – 2
RO-C	5 – 6	2	1 – 2
RO-D	5	2 – 2.2	1 - 2

- The use of a dendrimer-based antiscalant greatly improved the performance at the industrial RO plant.
- The effects of the change could be seen in the reduction of CIP frequency all while reducing the antiscalant consumption by 13%. which resulted in a monetary savings of 23.3% for the end-user.
- The manpower costs to perform the cleanings in addition to penalties for system downtime were also greatly reduced. In addition, the plant was able to utilize a phosphorus-free product which has minimized their impact to the environment.
- Full-scale application of Dendrimer-based technology led to significant increases in productivity and lowering of OPEX costs in modern wastewater recycle plant.
- Net 22% increase in permeate productivity following first 20 days of Dendrimer-based scale inhibitor application.
- Super-concentrated formula improved international shipping logistics, reduced costs (90%%) for the client.

CONCLUSION

The adaptation of dendrimer-based technology for scale inhibition in TFC based water system provides an interesting alternative to conventionally used scale inhibitors. The intrinsic benefits of these polymer molecules address many of the current and emerging market needs. Their unique chemical properties deliver solid performance often under lower dosage requirements as demonstrated by laboratory scale experiments. Precision step-by-step synthesis allows for reliability and predictability in production. Dendrimer molecules can be generated specific to this application, minimizing the harsh chemical nature present in other conventional scale inhibitors. Dendrimer based scale inhibitors are naturally phosphate-free, non-hazardous chemicals with exceedingly low toxicity properties in this class of products. Such properties, performance and otherwise, make dendrimer-based technology advantageous in current and emerging global water treatment systems.

VI. REFERENCES

1. Abbasi E., Aval S.F., Akbarzadeh A., Milani M., Nasrabadi H.T., Joo S.W., Hanifehnpour Y., Nejati-Koshki K., Pashaei-Asl R., Dendrimers: Synthesis, Applications, and Properties. Nanoscale Research Letters 9.1, 2014: 247.

2. Boas U., Christensen J. B., Heegaard P.M.H., Dendrimers: Design, Synthesis, and Chemical Properties. J. Mater, Chem. 38, 2006.

3. Kronmiller D.L., Special Properties and Reverse Osmosis Antiscalant Applications of Dendrimers. 1999.

4. Sankhe A., Yang L., Furukawa R., Study of Antiscalants for CaSO4 Scale Inhibition, IDA Proceedings, San Diego, CA, USA 2015.