

# Unlocking the Potential of Polyaspartic Acid (PASP) and Its Enhanced Derivative PASP-SEA-ASP: Advancements in Antiscalant Chemistry for Water Treatment

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## Introduction

Polyaspartic acid (PASP) and its derivative Polyaspartic acid-Sulfonic acid-Ethylenediamine-Aspartic acid (PASP-SEA-ASP) were subjected to comprehensive laboratory-scale testing as environmentally friendly scale inhibitors for a polyamide reverse osmosis (RO) membrane employed in the desalination of synthetic brackish water containing diverse scale-forming ions. In comparison with a commercially available RO antiscalant containing phosphonic acid, these inhibitors showcased notable enhancements. The introduction of these scaling inhibitors into the feedwater resulted in a marked increase in water recovery and removal efficiency of inorganic matter within the RO unit, which operated under a constant transmembrane pressure. Notably, PASP-SEA-ASP exhibited superior performance, achieving a remarkable water recovery rate of 90%, surpassing PASP (87%) and the commercial antiscalant (85%). Its efficacy extended to superior scaling inhibitor/fouling reduction attributed to a notable decrease in the deposition of scale-forming ions on the membrane surface. Microscopic analysis using scanning electron microscopy and X-ray diffraction revealed distinct effects of the antiscalants on the resultant crystalline morphology of the membrane surface. PASP and its derivative demonstrated cost-effectiveness in maintaining permeate flux and inhibiting the formation of a dense scale layer. This study underscores the significant potential of these non-phosphorus-containing agents for effective scale inhibition, particularly in domestic and industrial wastewater reclamation as well as brackish water desalination applications.

## Why PASP and PASP-SEA-ASP?

Polyaspartic acid (PASP) emerges as a promising and eco-friendly antiscalant in freshwater environments, thanks to its lack of phosphorus and biodegradable nature. Its scale inhibition effect, attributed to functional groups formed through aminolysis reactions, has been acknowledged in previous studies. Gao et al. took this a step further by synthesizing a derivative, PASP-ASP, aiming to enhance chelating performance. Their experimental findings supported improved scale inhibition in

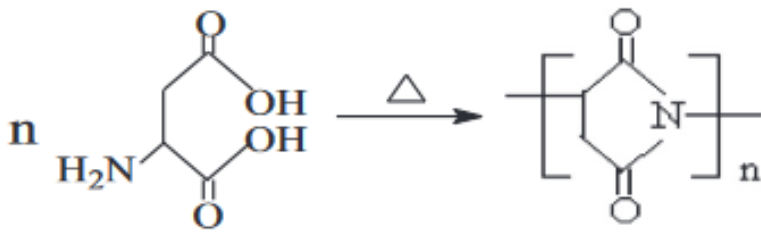
freshwater applications. The ionization ability of PASP, forming water-soluble complexes with ions like  $\text{Ca}^{2+}$ , contributed to reducing scale-causing ion deposition on membrane surfaces. In the pursuit of inhibiting scale formation in saline environments, a derivative, PASP-SEA-ASP, was created with added sulfonic and carboxylic acids. The sulfonic acid group altered the charge state of crystal particles, enhancing dispersion in water. While PASP and its derivatives showed promise in preventing scaling on carbon steel in freshwater and seawater, their impact on polymeric reverse osmosis (RO) membranes for wastewater and brackish water desalination had yet to be explored.

This study seeks to fill that gap by examining the antiscaling effects of PASP and its derivative, PASP-SEA-ASP, on polyamide RO membranes used for desalination. The focus is on a synthetic saline water containing various scale-forming ions. A comparison with a phosphorus-containing commercial RO antiscalant is also included. The assessment involves determining filtration performance in terms of water recovery and removal efficiency of inorganic matter, analyzing the quantity and chemical composition of scale on membranes, and examining scale crystals using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

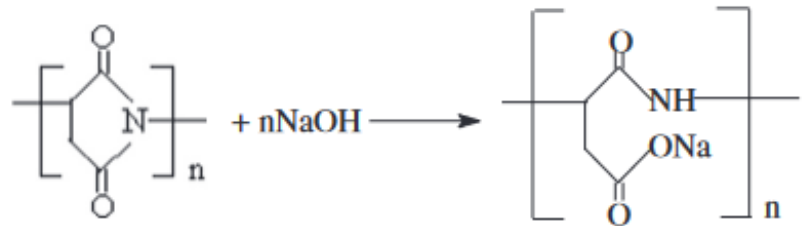
# Chemistry and Synthesis of Antiscalants

## 1. *PASP (Polyaspartic acid)*

The synthesis of Polyaspartic acid (PASP) involved a two-step process. In the initial step, polysuccinimide was synthesized by subjecting L-aspartic acid monomer (Industrial grade, Sigma Aldrich) to pyro-condensation at 240 °C for 4 hours in an electric thermostatic drying oven. The subsequent step comprised the synthesis of PASP. Initially, the polysuccinimide was suspended in water at three times its weight. The aqueous polysuccinimide suspension was stirred at 12 °C, and a solution of NaOH (15%, industrial grade) was added. The reaction occurred for 4 hours at 12 °C, maintaining a pH of 8–9. The solid PASP was obtained through a separation process involving the addition of double the volume of absolute alcohol, followed by washing the resulting precipitates with deionized water. The solid was then dried at 80 °C for 48 hours. To prepare a PASP stock solution (36%), the solid PASP was dissolved in deionized water. The entire synthetic process is illustrated in Schemes 1 and 2.



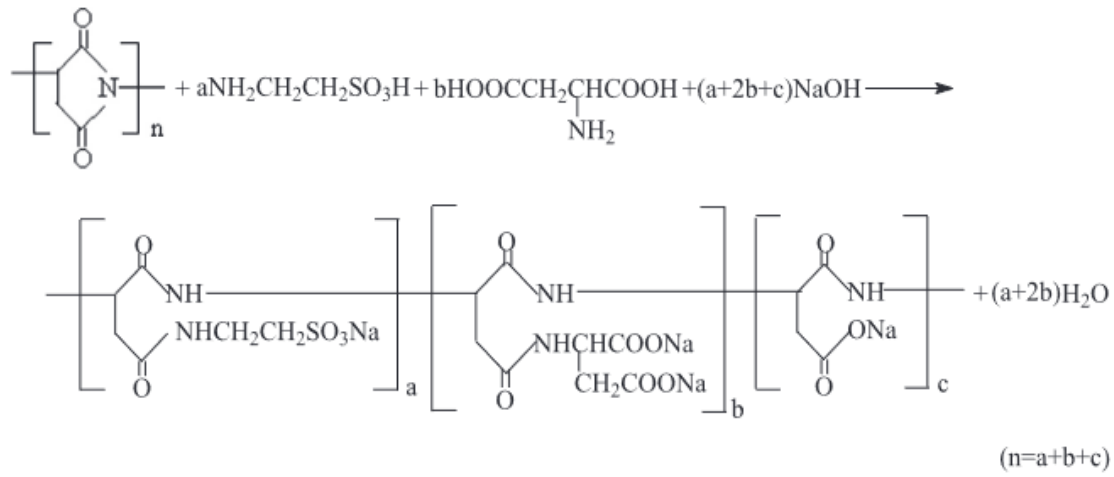
**Scheme 1.** Synthesis route of polysuccinimide.



**Scheme 2.** Synthesis route of polyaspartic acid.

## 2. *PASP-SEA-ASP (Polyaspartic acid-Sulfonic acid-Ethylenediamine-Aspartic acid)*

The synthesis of PASP-SEA-ASP occurred in two sequential steps. In the initial step, polysuccinimide was synthesized according to the procedure outlined in Section 2.3.1. The subsequent step involved the synthesis of PASP-SEA-ASP. Initially, polysuccinimide was suspended in water at three times its weight. This suspension was stirred at 25 °C. Subsequently, a mixture of aspartic acid and 2-aminoethanesulfonic acid (both Industrial grade, Sigma Aldrich), dissolved in NaOH solutions (15%), was added. The reaction took place over 24 hours at 25 °C and maintained a pH of 8–9. Following this, the pH of the mixture was lowered to 5.2 by introducing 2 N HCl to eliminate any unreacted 2-aminoethane sulfonic acid through filtration. Further pH adjustment to 2.8 and subsequent filtration were performed to remove any remaining unreacted aspartic acid. The resulting solid PASP-SEA-ASP was obtained through a separation process. This involved adding a double volume of absolute alcohol to the filtrate, rinsing the precipitate with deionized water, and then drying it at 80 °C for 48 hours. A stock solution of PASP-SEA-ASP (30%) was prepared by dissolving the obtained solid in deionized water. The synthetic reaction is depicted in Scheme 3.



**Scheme 3.** Synthesis route of PASP-SEA-ASP.

# Impact of scale inhibitors on RO permeate water quality

The investigation into metal ion concentrations in feedwater, permeate, and concentrate aimed to assess scale formation conditions. The presence of antiscalant in the feedwater notably enhanced the membrane's removal efficiency of ions, with PASP-SEA-ASP demonstrating superior ion removal compared to PASP, which, in turn, outperformed the commercial antiscalant (refer to Table 2). The higher concentration of metal ions in the concentrate stream for PASP-SEA-ASP and PASP suggested less salt attachment to the membrane surface when compared to the commercial antiscalant. Subsequent analyses and quantification of deposits extracted from the membrane surface confirmed that the application of antiscalants resulted in reduced scale formation, with the antiscalating effectiveness following the order of PASP-SEA-ASP > PASP > commercial antiscalant (see below Fig and table).

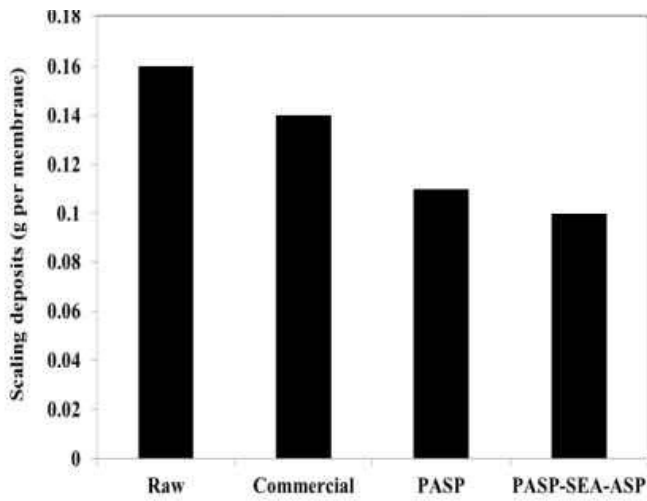


Fig. 2. Scale deposits per membrane surface area for RO tests without and with addition of antiscalant.

Concentration of ions in RO feedwater, permeate, concentrate and the solutions containing deposits extracted from the used membranes.

		Without antiscalant	Commercial antiscalant	PASP	PASP-SEA-ASP
Feed (mg/L)	Na <sup>+</sup>	5842			
	Mg <sup>2+</sup>	184			
	Si <sup>4+</sup>	624			
	Ca <sup>2+</sup>	2338			
Permeate (mg/L)	Na <sup>+</sup>	176	148	132	112
	Mg <sup>2+</sup>	16	12	6	10
	Si <sup>4+</sup>	46	38	26	28
	Ca <sup>2+</sup>	94	82	68	62
Concentrate (mg/L)	Na <sup>+</sup>	17,540	18,960	20,448	23,376
	Mg <sup>2+</sup>	388	456	524	676
	Si <sup>4+</sup>	1376	1584	1640	1842
	Ca <sup>2+</sup>	4560	5176	5872	6284
Solution containing the extract of membrane scaling layer (mg/L)	Na <sup>+</sup>	3640	2942	1492	856
	Mg <sup>2+</sup>	98	112	66	28
	Si <sup>4+</sup>	396	342	312	186
	Ca <sup>2+</sup>	1536	1448	1224	972

It is likely that the antiscalants facilitated the formation of chelated structures with metal ions, thereby reducing the passage of salt through the RO membrane and resulting in a lower ion concentration in the permeate. The higher ion concentration in the RO concentrate stream can be attributed to the good solubility of the chelates. However, it's important to note that antiscalants have limitations, and they cannot infinitely increase the solubility of inorganic compounds. Once the solubility reaches a certain value, carbonate scale may start to form. Considering that PASP-SEA-ASP possesses both carboxylic acid and sulfonic acid groups, while PASP has only carboxylic acid groups, it was expected that PASP-SEA-ASP would exhibit greater inhibition of scale-forming ion deposition on the membrane compared to PASP. Further investigations are needed to explore the chelation function of the antiscalants and examine the solubility of calcium carbonate as influenced by the antiscalants to confirm the suggested mechanism. The assessment of water recovery revealed a rate of 83% for the RO test without using antiscalant, 85% for the commercial antiscalant, 87% for PASP, and 90% for PASP-SEA-ASP. These results align with the anticipation that the antiscalant with a more pronounced scale inhibiting effect would lead to less inorganic fouling on the membrane and, consequently, higher water productivity.

# Conclusion

PASP and its derivative PASP-SEA-ASP underwent testing as potential environmentally friendly antiscalants to mitigate scaling in a reverse osmosis (RO) membrane. The experiments involved filtering a synthetic saline feedwater containing various scale-forming ions and comparing the results with a commercially available antiscalant. All scale inhibitors demonstrated an enhancement in RO performance, leading to improved water recovery and the rejection of inorganic matter. Notably, PASP-SEA-ASP outperformed PASP, which, in turn, showed better performance than the commercial antiscalant. Scanning electron microscopy (SEM) analysis confirmed the formation of larger crystals and a less dense scale layer on the membrane surface when PASP-SEA-ASP was added to the feedwater, indicating effective chelation of scale-forming ions.

This study underscores the potential of polyaspartic acid and its derivative as effective scale inhibitors, particularly for applications in wastewater and brackish water desalination. Considering the cost-effectiveness aspect, with the chemical cost per unit of water treated being  $\$4.5 \times 10^{-6}/\text{m}^3$  for the commercial antiscalant,  $\$2.1 \times 10^{-6}/\text{m}^3$  for PASP-SEA-ASP, and  $\$1.5 \times 10^{-6}/\text{m}^3$  for PASP, both PASP and its derivative demonstrate an advantage.

It is recommended that further investigations explore the impact of process variables such as pH, inorganic species, the presence of organic matter in feedwater, and membrane materials on their scale inhibition effect. These investigations should be conducted at lab and pilot scales before considering full-scale applications.