A NOVEL CLASS OF HALITE SCALE INHIBITORS:

A SYSTEMATIC STUDY

A Thesis

by

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ABSTRACT

Halite (NaCl) scaling complicates oil and gas production from many reservoirs worldwide because of its facile and fast precipitation in well tubulars or near-wellbore areas. Current industry approaches to remove halite scales via continuous or periodic freshwater treatments are often inefficient or late measures. In this study, a new class of halite scale inhibitors is studied to identify its inhibition efficiency in halite scale with benchmark halite scale inhibitor.

A modified and improved static bottle test is used. The experimental procedure is optimized for dissolving 37.50g of NaCl in 100 mL of distilled water at 80°C. After dosing inhibitor into bottle, brine is heated in an oven to ensure complete dissolution of NaCl. Solution is then kept in a switched-off oven to gradually cool down to 23°C for the following 36 hours. Precipitated halite crystals are collected, if any, then dried, and weighed. Certain experiments are performed in duplicate to assess the reproducibility of the results.

Ten out of eighteen inhibitors tested in this study have completely inhibited halite scale growth. The inhibition efficiency of effective inhibitors is 100%. More importantly, these additives are safe for the environment since most of them are food additives. In the field, these effective inhibitors not only reduce the frequency of freshwater treatments but also increase the revenue for operators by minimizing production downtime and freshwater cost.

This study introduced a new class of inexpensive and efficient halite scale inhibitors. Field application of these products will minimize the problems associated with halite scale deposition and freshwater treatments.

DEDICATION

I would like to dedicate my research work to my late professor, Dr. Hisham Nasr-El-Din, a very honorable and beloved man.

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Finally, thanks to my mother, Nga Nguyen, my brother, Peter Le, and my relatives for their encouragement, patience, trust, and love.

NOMENCLATURE

Ba^{2+}	Barium
Ca^{2+}	Calcium
CMC-Na	Carboxymethylcellulose sodium salt
CO_2	Carbondioxide
DI water	Deionized water
DMSO	Dimethyl sulfoxide
DTPMPA	Diethylenetriamine penta(methylene phosphonic acid)
DTPA-K5	Diethylenetriaminepentaacetic acid pentapotassium
HCl	Hydrochloric acid
MIC	Minimum Inhibitor Concentration
NaHCOO	Sodium formate
Na^+	Sodium
NaCl	Sodium chloride
NTAA	Nitrilotriacetamide
P-T	Pressure - Temperature
TEPA	Tetraethylenepentamine
TREN	Tris(2-aminoethyl)amine

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1. INTRODUCTION AND LITERATURE REVIEW

1.1. Scale

Scale is known as one of the most notorious problems in the oil and gas industry. Scale deposition typically happens in near-wellbore areas. Uneven pipeline surfaces and production equipment such as pumps and valves cause scale to grow to levels that can block the pipelines (Kelland, 2014). For instance, halite (NaCl) scales form and completely deposit inside tubing within short time if water is not injected frequently to dissolve the scale. Operators not only suffer from production delays but also from the expensive cost of freshwater treatments. Thus, chemically inhibiting scale from forming and depositing not only minimizes the production setback but also prevents the damage that scale causes to the production system and downhole formation. In the oil and gas industry, scales are mainly classified into two types: organic and inorganic scales. Scales that most producers often face are asphaltenes and paraffin wax for organic scales, and calcite and barite for inorganic scales.

1.1.1. Organic scales

1.1.1.1. Asphaltenes

Asphaltenes are molecular substances that are found in crude oil, along with resins, aromatics hydrocarbon, and saturates (Mullins et al., 2007). Asphaltene precipitates due to the loss of solubility from the removal of resin fraction which causes asphaltene to form large aggregates (micelles) and precipitate out (PetroWiki). The formation of asphaltenes precipitates is mostly influenced by temperature and pressure (Al-Qasim et al., 2018). Thus, a Pressure - Temperature (P-T) phase diagram is used to assess the precipitation behavior of asphaltenes. Asphaltene

precipitation also happens due to the injection of carbon dioxide (CO_2). CO_2 helps improve oil production as it reduces the interfacial tension or the viscosity to increase the mobility. However, if CO_2 is excessively injected, asphaltenes will precipitate. Thus, CO_2 content must be estimated at the first stage of the enhance oil recovery (EOR) screening (Al-Qasim et al., 2018). For other cases when asphaltenes could not be detected or prevented earlier, a reactive solution is to use light aromatics such as benzene and toluene to dissolve asphaltene (Mitchell and Speight, 1973; Speight et al.,1984). However, this solution is not always effective. Low dissolving efficiency and high frequency of soaks result in prolonged production delays (Budd et al., 2018). Thus, asphaltene remains as one of the most troubled organic scales in the oil and gas industry.

1.1.1.2. Paraffin waxes

Petroleum waxes are complex mixtures of n-alkanes, i-alkanes, and cycloalkanes with carbon numbers ranging from 18 to 65 (Srivastava et al., 1993). There are two general classes of petroleum waxes. Waxes composed primarily of normal alkanes crystallize in large flat plates and are referred to as paraffin waxes. Waxes composed primarily of cycloalkanes and i-alkanes crystallize as small needle structures and are referred to as microcrystalline waxes (Srivastava et al., 1993). There are two main stages in wax formation: nucleation and crystal growth. (Hammami and Raines, 1999). Nucleation has two types: homogeneous and heterogeneous. Homogeneous nucleation occurs in liquids that are not contaminated with other nucleating materials (Hansen et al., 1988). Heterogeneous nucleation occurs when there is a distribution of nucleating materials throughout the liquid (Hansen et al., 1988). Wax deposits could be from a soft paste to a brittle solid (Allen and Roberts, 1982). To detect the formation and deposition of wax, wax appearance temperature (WAT) is generated to moderate the critical temperature that wax nucleic forms

(Hammami and Raines, 1997). Proactive solutions to prevent wax deposition include electric heater (to keep crude oil above a certain temperature), dispersants (to prevent wax from settling), and crystal modifiers (to deform wax crystal morphology) (Garcia et al., 1998). In some cases when wax deposits in the wellbore, it can be removed by cutting, drilling, chemical dissolution, or melting (Allen and Roberts, 1982).

1.1.2. Inorganic scales

Inorganic scales are the deposition of minerals occurring in the event of the mixing between formation water with other brines such as injection water. When two different types of water are mixed, incompatible ions would react with each other and change the thermodynamics of reservoir fluids. This change causes fluids to be supersaturated and subsequently, salt deposition occurs. The most common inorganic oilfield scales are listed in Table 1.1.

Table 1.1: Common oilfield inorganic scales.

Mineral Name	Formula
Calcite	$CaCO_3$
Barite	$BaSO_4$
Celestite	$SrSO_4$
Anhydrite	$CaSO_4$
Gypsum	$CaSO_4 . 2H_2O$
Iron sulfide	FeS
Halite	$NaCl$

1.1.2.1. Calcite

Calcite, or calcium carbonate, is formed due to the deprivation of CO_2 from the water to the hydrocarbon phase(s) as pressure drops (PetroWiki). Subsequently, carbonic acid, which keeps calcite dissolved, is removed from the water phase. This also causes calcite solubility to reduce as pressure and temperature decrease. Calcite can be removed by bullheaded hydrochloric acid (HCl) washes.

1.1.2.2. Barite

Barite, or barium sulfate, is one of the most difficult sulfate scales to remove. Barite has very high insolubility which forms very hard scale deposits. Sulfate scale forms due to the mixture of formation water and seawater. Seawater contains a high amount of sulfate ions and formation water has many Ba^{2+} and other ions. As they mix, Ba^{2+} ion and sulfate strongly attach which form into a very hard solid scale precipitate. Barite scale typically happens offshore as seawater is used to inject and recover oil (Frenier, 2008). Since sulfate scale has a low solubility in acid, chelants are used to dissolve sulfate scale by isolating the ions by their locked cage-like structures (Crabtree et al., 1999).

1.1.2.3. Halite

1.1.2.3.1. Background

One of the troublesome inorganic scales in the oil and gas industry is halite (NaCl). Halite is a type of salt, the mineralogy name for sodium chloride. Halite is mostly found in sedimentary rocks where seawater or salty lake water evaporates. Halite scale precipitation typically occurs where oil and gas wells are located over salt domes (Smith and Przybylinski, 2006). Salt domes is a mushroom-shaped diapir composed of salt, shaped due to the relative buoyancy of salt when

buried under other types of sediment (Schlumberger). Salt domes are usually predicted to have hydrocarbons adjacent because salt movement created traps for hydrocarbons to flow in and stored under evaporite minerals (Schlumberger). In the United States, halite scale precipitation is typically found in North Dakota (Bakken and Three Forks formation), and the Rockies Mountain region (Hebert et al., 2016; Lu et al., 2014; Lu et al., 2015; Spicka et al., 2012; Zhang et al., 2018). Other places such as the North Sea region, the Latin Americas, and the Middle East also suffer from halite scale precipitation (Frigo et al., 2000; Maxwell and Young, 2014; Suresh et al., 2020; Veeken et al., 2019). Halite scale is found in both oil and gas wells but mostly found in gas wells. As reservoir fluids temperature and pressure start decreasing, water starts to evaporate into gas phase and the remaining water in liquid phase eventually becomes supersaturated. At this point, an additional tiny seed crystal of salt from the fluid will initiate a recrystallization of the excess dissolved salt. The seed crystal provides a nucleation site on which the excess dissolved crystals start to grow larger and deposit within the tubing. The formation and deposition of halite scale delays and eventually stops gas flow from near-wellbore areas to the surface.

1.1.2.3.2. Problems of current approach

Frequent water injection must always be available to dissolve deposited halite scale inside tubing. Lacking frequent water injection causes scales to form and completely deposit inside the tubing within short time. Industry usually prefers to use freshwater treatment to remove halite scale. However, freshwater is very costly to use for some remote locations that must transport large volumes of freshwater from elsewhere (Spicka et al. 2012). Moreover, most of the time the dissolution is not efficient. Instead of suffering from a tough dissolution process, there is a possibility to chemically inhibit the formation of halite scale by a disturbance in crystal formation.

However, high minimum inhibitory concentration and limited performance of inhibitors discouraged operators to apply the method (Chen et al. 2009; Hebert et al. 2016).

Another gap in tackling halite scale precipitation problem is the lack of laboratory testing methodology procedures. Static bottle test is a common testing method in the industry as it is cost-effective and user-friendly setup, but it is extremely difficult to control halite precipitation and reproducibility during the test (Suresh et al. 2020). Since there is no standard testing method, the static bottle testing procedure was devised to be suitable for certain research and laboratory conditions from reports. This variation has caused difficulties to evaluate the actual inhibition efficiency of halite scale inhibitors.

1.2. Scale inhibitors

1.2.1. Class of chemistries

Scale inhibitors are specialty chemicals that are added to prevent scale deposition (Kelland, 2014). Four classes of chemistry that have been widely used to treat scale in water systems are acrylic acid, polymers, maleic acid polymers and phosphonates (Shakkativel and Vasudevan, 2006; Zahid and Petros, 2014). Other classes of scale inhibitors include inorganic phosphate, organophosphorous and organic polymer backbone (Bezemer and Bauer, 1969). Scale inhibitors are specifically designed for certain scaling conditions and biodegradability properties (Shi et al., 2013). Certain anions must be identified in the inhibitor molecular backbone structure for cations to bind in water. For instance, group (II) ions such as calcium, Ca^{2+}, are mostly sequestered by scale inhibitors with phosphonate ions ($-PO_3H^-$), phosphate ions ($-OPO_3H^-$), phosphonate ions ($-PO_2H^-$), sulfonate ions ($-SO_3^-$), and carboxylate ions ($-CO_2^-$) (Kelland, 2014). However, the

inhibition efficiency of scale inhibitors also depends on their compatibility with other production chemicals such as corrosion inhibitors (Lawless et al., 1993).

1.2.2. Halite scale inhibitors

Most developments in NaCl scale inhibition concentrates on finding new chemical inhibitors. In the late 1960s, Roland, Ralston, and Persinski generated the idea of applying a chemical inhibitor, nitrilotriacetamide (NTAA), particularly, in oil and gas wells. (Roland and Ralston, 1965; Ralston and Persinski, 1968). However, the mechanism for NTAA to inhibit NaCl was not well understood. Until 1975, Sarig and others studied the effect of NTAA on NaCl and they found that NTAA successfully prevented NaCl by altering the morphology of NaCl deposition. (Sarig et al., 1975; Sarig et al., 1975). In 1981, Earl and Nahm recognized NTAA and another inhibitor chemical, potassium ferrocyanide, as benchmark NaCl inhibitors in the industry and used to evaluate new inhibitors' effect (Earl and Nahm, 1981). Two decades later, Frigo and others introduced potassium hexacyanoferrate as a novel NaCl inhibitor (Frigo et al., 2000). In 2009, Chen and others introduced a new inhibitor that prevents NaCl scale at minimum inhibitory concentration (MIC) under dynamic conditions (Chen et al., 2009). Later in the 2010s, NaCl inhibitors was enhanced to not only inhibit NaCl scale in both static and dynamic conditions, but they also successfully inhibit other types of scale such as carbonate and sulfate. (Spicka et al. 2012; Wylde and Slayer 2013; Wang et al. 2017).

Although new halite scale inhibitors were introduced in the industry and claimed to be effective, it was difficult to evaluate the actual inhibition efficiency of new inhibitors reported from literature as there is no standard testing method. Thus, a comprehensive study of precipitating halite scale in laboratory conditions by static bottle test and a new class of halite inhibition

chemicals is introduced in this thesis. The results of this study certainly gain new insights into halite scale precipitation and inhibition laboratory testing as well as establish definitions of standard in halite scale inhibiting efficiency.

2. MATERIALS AND METHOD

2.1. Materials

2.1.1. Sodium chloride salt

Sodium chloride (NaCl) (CAS: 7647-14-5, lot number: 1446C502) is a lab-grade, white solid powder with 99.6% purity, and manufactured by BDH (VWR), USA.

2.1.2. Distilled water

Distilled water (H_2O) was purchased from Walmart, sourced from Caddo Parish, LA, USA. Water was processed by steam distillation, micron filtration, and ozonation.

2.1.3. Scale inhibitors

Chemicals used as halite scale inhibitors in the study were listed in Table 2.1 and chemical structure of some of chemicals used were shown in Figures 2.1 – 2.11.
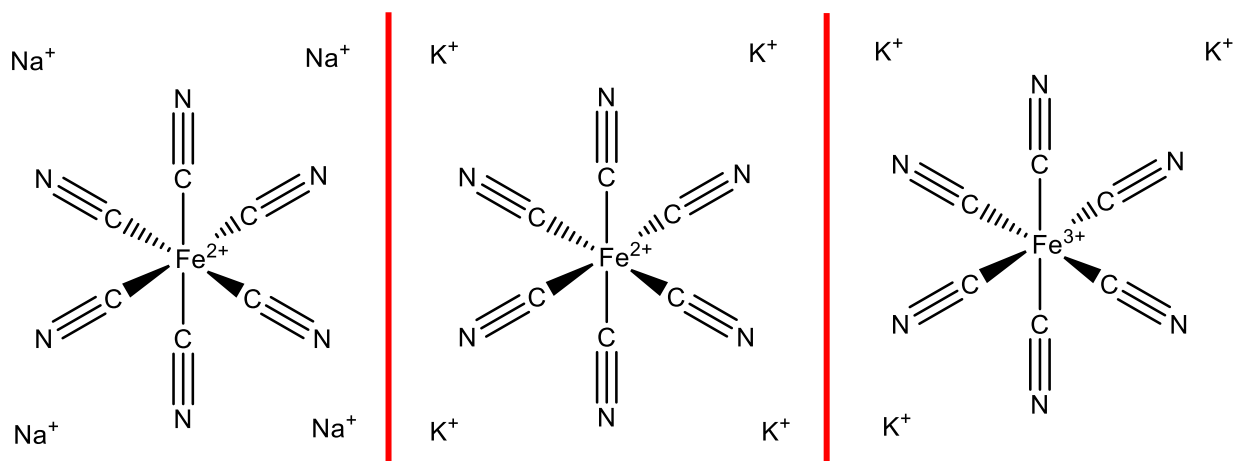
Figure 2.1: Chemical structure of sodium ferrocyanide, potassium ferrocyanide, and potassium ferricyanide.
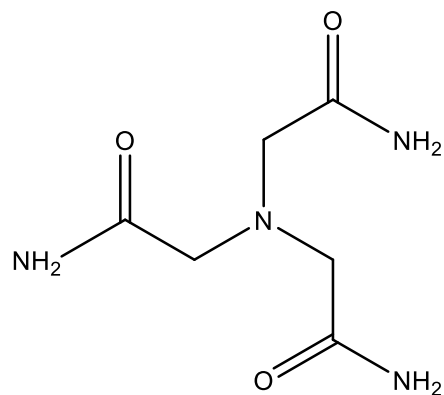
Figure 2.2: Chemical structure of NTAA.
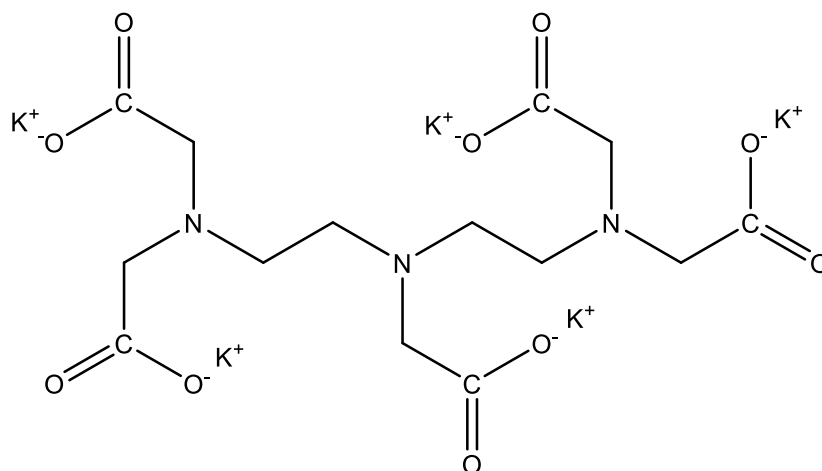
Figure 2.3: Chemical structure of DTPA-K$_5$.
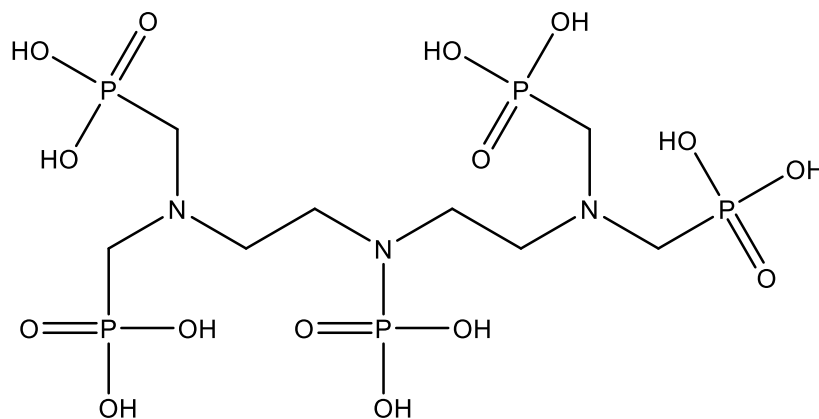
Figure 2.4: Chemical structure of DTPMPA.
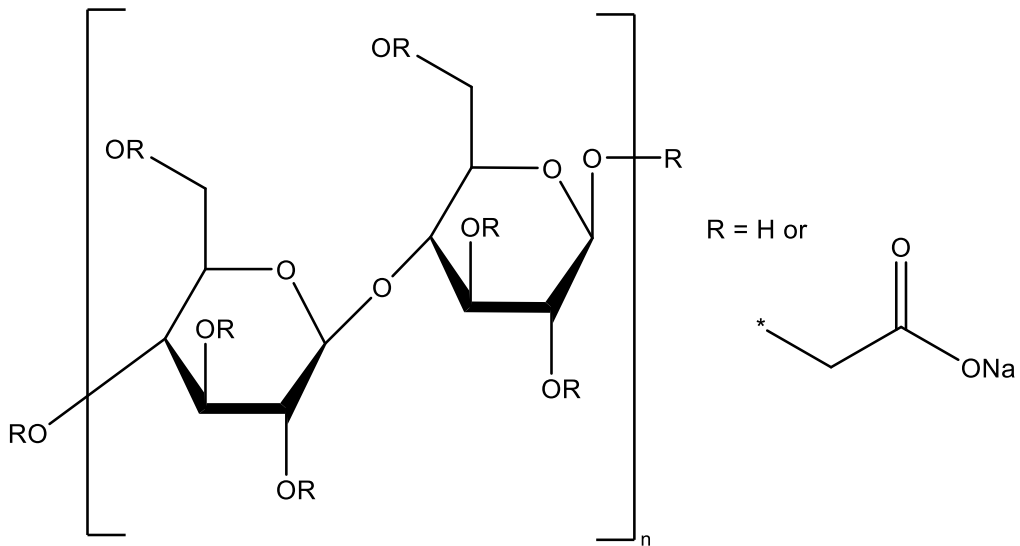
Figure 2.5: Chemical structure of CMC-Na (n = app. 500).

R = H or
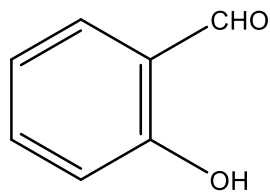
Figure 2.6: Chemical structure of salicylaldehyde.
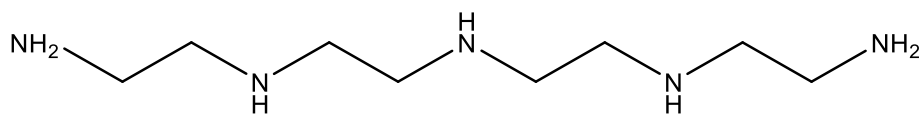
Figure 2.7: Chemical structure of TEPA.

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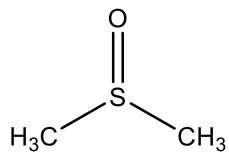
Figure 2.8: Chemical structure of DMSO.
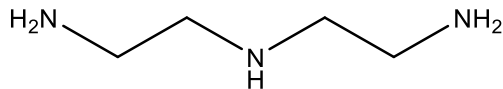
Figure 2.9: Chemical structure of Dien.
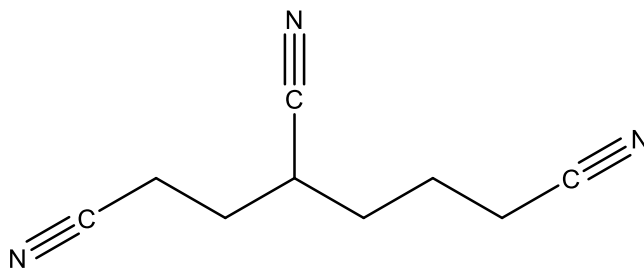
Figure 2.10: Chemical structure of 1,3,6 – hexanetricarbonitrile (Trinohex Ultra).
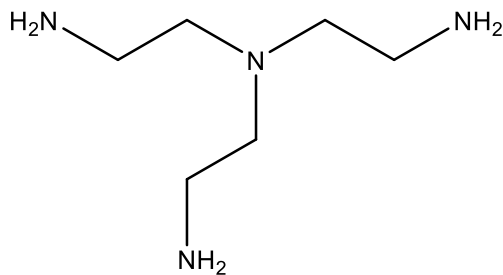
Figure 2.11: Chemical structure of TREN.

Table 2.1: Chemical name, formula, CAS number, Lot number, manufacturer, and properties of inhibitors in this study.

Name	Formula	CAS	LOT	Manufacturer	Description/Properties
Alcoflow 250	Polycarboxylate	N/A	1810364	Nouryon, Chicago, IL, USA	40% solution; Premium barium sulfate inhibitor, ultra-brine stable in acid form, high solids
Alcoflow 750	Complex multi polymer (Acrylic terpolymer)	N/A	JLJ2019070	Nouryon, Chicago, IL, USA	34.3% dark brown solution; Anionic family; Methanol soluble scale inhibitor, barium sulfate inhibition; Biodegradable
Alcoflow 920	Sulfonated polycarboxylate	N/A	1809935	Nouryon, Chicago, IL, USA	35% solution; Halite inhibitor, high brine tolerance, enhanced thermal stability

Table 2.1: Continued.

Name	Formula	CAS	LOT	Manufacturer	Description/Properties
Carboxymethylcellulose sodium salt (CMC-Na salt)	$[C_6H_7O_2(OH)_x(OCH_2COONa)_y]_n$	9004-32-4	PYV4GLR	Tokyo Chemical Industry, Tokyo, Japan	Lab-grade; Light ivory powder
Diethylenetriamine (DIEN)	$C_4H_{13}N_3$	111-40-0	N/A	Sigma Aldrich	Lab-grade; Clear $\leq$ 100% solution; Ammonia odor
Dimethyl Sulfoxide (DMSO)	$(CH_3)_2SO$	67-68-5	N/A	Sigma Aldrich	Lab-grade; Clear $\leq$ 100% solution
Diethylenetriamine penta(methylene phosphonic acid) (DTPMPA)	$C_9H_{33}N_3O_{30}P_{10}$	15827-60-8	A329794-001	AmBeed, Arlington Hts, IL, USA	Lab-grade; 50% yellow solution

Table 2.1: Continued.

Name	Formula	CAS	LOT	Manufacturer	Description/Properties
Diethylenetriaminepenta acetic acid (DTPA-K5)	$K_5.C_{14}H_{23}N_3O_{10}$	7216-95-7	N/A	Nouryon	45% solution, and sodium free; Barite scale inhibitor
Nitrilotriacetamide (NTAA)	$C_6H_{12}N_4O_3$	4862-18-4	FCC-14041	Nouryon	Lab-grade; Medium brown solution
Potassium Ferricyanide	$K_3Fe(CN)_6$	13746-66-2	AD-20045	Ward's Science	Lab-grade; Solid, yellow, crystalline powder; No odor
Potassium Ferrocyanide	$K_4Fe(CN)_6.3H_2O$	14459-95-1	AD-20241	Ward's Science	Lab-grade; Solid, red-orange, crystalline powder
Sodium Ferrocyanide	$Na_4Fe(CN)_6.10H_2O$	14434-22-1	A0401154	Acros Organics, China	Lab-grade; Solid, faint yellow crystalline powder
POLYstim PCS-252	N/A	N/A	6102-86-3	PfP Technology, TX, USA	Lab-grade; Permanent Clay Stabilizer; Solution

Table 2.1: Continued.

Name	Formula	CAS	LOT	Manufacturer	Description/Properties
Salicylaldehyde (2-Hydroxybenzaldehyde)	$C_7H_6O_2$	90-02-8	A13833	Alfa Aesar, Ward Hill, MA, USA	Lab-grade; > 98.5 weight %; Liquid, clear, colorless to pale yellow, bitter almonds odor
Silica Inhibitor	N/A	N/A	05360427	Lubrizol, Elmendorf, TX, USA	Dark yellow, viscous liquid
Tetraethylenepentamine (TEPA; Tetrene)	$C_8H_{23}N_5$	112-57-2	MKBZ4308V	Sigma Aldrich Chemistry, St. Louis, MO, USA	Technical-grade; ≤ 100% concentration; Light yellow, clear, viscous liquid
Trinohex Ultra	$C_9H_{11}N_3$	1772-25-4	N/A	Ascend	Lab-grade; ≥ 99% solution
Tris(2-aminoethyl)amine (TREN)	$C_6H_{18}N_4$	4097-89-6	N/A	Sigma Aldrich	Lab-grade; ≤ 100% solution

2.2. Equipment

2.2.1. Glass bottles

Glass bottle with heat-resistant plastic cap, which has a volume capability of 250mL, is manufactured by VWR, Czech Republic (catalog number: 10754-816). Bottle is lab-grade, made of Simax Borosilicate glass 3.3 (see Figure 2.12).

Figure 2.12: A photo showing a mixture of sodium chloride and distilled water is contained in a glass bottle.

2.2.2. Oven

Oven used in the experiment is manufactured by Ofite (model number: 173-00-1-C (230 Volt)) with a digital temperature controller that can be read directly from outside the oven. The temperature is controlled by an electronic solid-state thermostat with a high temperature automatically shut off option and operates between 38°C - 232°C.

2.2.3. Digital balances

Digital balance used to measure the weight of sodium chloride salt and distilled water was manufactured by Ohaus from China (model number PA512), has a maximum capacity of 510.00g

and readability of 0.01g. Digital balance used to measure the weight of inhibitors and collected sodium chloride precipitate crystals after test was manufactured by Mettler Toledo from Switzerland (model number: ML54/03) has a maximum capacity of 52.0000g and readability of 0.0001g.

2.2.4. Pipettes

Adjustable pipette used to measure desired volume of inhibitors was manufactured by BrandTech, USA (model: Transferpette S, catalog number: 704774), has a capacity of 10-100uL.

2.3. Static bottle test method

As a typical test, a mixture of 37.50g sodium chloride and 100.00g of distilled water is prepared in a glass bottle (see Figure 2.12 – 2.13). A desired amount of inhibitor is added to the mixture in each bottle (see Table 2.2). Oven is set at 105°C one hour before bottles are placed inside. Bottles are checked and shaken every hour to dissolve the salt completely. After 4 hours, oven temperature is set at 115°C. When salt fully dissolves, bottles are continued to heat for 2 more hours at 115°C. Then oven is switched off and bottles are stored in closed-door oven for 36 hours. After that, bottles are removed from the oven. Solutions from the bottles are decanted, and precipitated sodium chloride crystals are collected, if any, by using a laboratory spatula. Crystals are cleaned with Kim wipes, dried for 2 hours in oven at 80°C, and weighed.

1. Prepare synthetic brine

Blank | Additive A

100mL of distilled water
37.5g of NaCl
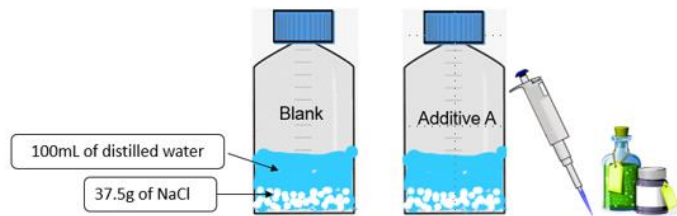
2. Dissolve the mixture

80°C
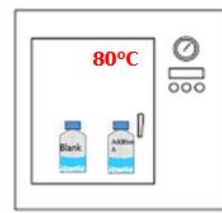
Blank | Additive A

3. Remove precipitates from each bottle

Blank | Additive A

5. Weigh precipitates and calculate efficiency

	Weight (grams)	Efficiency (%)
Blank	1.5	0%
Additive A	0.5	67%

Table 1- Example of efficiency calculation

4. Dry precipitates in oven at 80°C

80°C
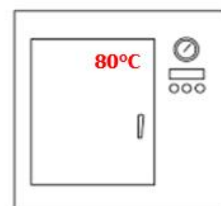
Figure 2.13: A schematic showing sample preparation and remain precipitate collection.

Table 2.2: A list of inhibitors and its concentration(s) tested in this study.

Inhibitor	Concentration(s), ppm
Alcoflow 250	500
Alcoflow 750	500
Alcoflow 920	500
CMC-Na salt	50, 200, 500
DIEN	500
DMSO	500
DTPMPA	500
DTPA-K5	500
NTAA	100, 200, 500
Potassium Ferricyanide	50, 200, 500
Potassium Ferrocyanide	500
Sodium Ferrocyanide	50, 200, 500
POLYstim PCS-252	500
Salicylaldehyde	500
Silica Inhibitor	500
Tetraethylenepentamine	500
Trinohex Ultra	500
TREN	500

3. RESULTS AND DISCUSSION

3.1. Static bottle test preparation and performance

3.1.1. Background

Static bottle test method, a commonly applied halite precipitation testing method in the oil and gas industry, was selected to use in this study (Chen et al., 2009; Goodwin & Graham 2018; Lu et al., 2014; Ruan et al., 2017; Wang et al., 2017). This test method is cost-effective and has a user-friendly setup which allows multiple trials to be performed and hence, enhances results accuracy. However, there is no standard experimental procedure in static bottle test method (Lu et al., 2014; Lu et al., 2015; Ruan et al., 2017; Suresh et al., 2020; Wylde and Slayer, 2013; Zhang et al., 2018). Experimental procedure varies from different reports has caused difficulties to reiterate the test. Lack of consistency in testing method complicated the evaluation and sometimes deviated the actual efficiency of inhibitors. For this study, to produce a consistent static bottle test procedure and reproducible results, the procedure was modified and improved (see Materials & Method section).

3.1.2. Materials specification

Sodium chloride (NaCl) salt or halite in minerology, also known as table salt, is widely used in daily food preparation. Although table salt is low-cost and ubiquitous, it could not be used in this study. Different additives, such as anticaking agents, iodine, fluoride, etc. that are added to table salt to preserve its quality and texture and enhance human well-being, could disturb the inhibition process in this study. For instance, anticaking agent is added to table salt to prevent clump formation. Commonly known anticaking agents are potassium ferrocyanide, calcium

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silicate, and sodium aluminosilicate (Luck et al., 2000). While anticaking agent is necessary for table salt, it is not appropriate for this halite scale inhibition study. Certain anticaking agent such as sodium aluminosilicate, is insoluble and precipitate itself in water. The precipitation of anticaking agent could affect to the precipitation of sodium chloride and deviate the inhibition efficiency of inhibitors. Thus, after being verified with manufacturer's certificate of analysis and its ingredients, sodium chloride salt used in this study was lab-grade, $\leq 99\%$ purity free, and most importantly, additives free.

Distilled water and deionized water (DI water) are commonly, and sometimes interchangeably, used in laboratory experiments. However, for this halite scale inhibition study, DI water is not appropriate to use as its contaminants could disturb the salt dissolution and precipitation. The deionization of DI water could only remove some of the ions such as Ca^{2+} ions and Mg^{2+} ions. Additionally, over the time, filtered ions in DI water filter cartridge could be filled up which affect the following water batch resistivity and purity. Thus, distilled water was selected to use in this study as it was purified through three stages, steam distillation, micron filtration, and ozonation. Steam distillation is a process where water is heated up into steam to separate salts. Micron filtration takes place to remove any contaminants by using a pore-size filter cartridge measured in microns. Ozonation is where organic compounds and microorganisms were attacked by oxidation process. Distilled water used in this study was processed through three stages above.

Glass bottle is commonly used in most laboratory experiment. However, in this study, certain type of glass bottle was selected. Cap is provided with the bottle to prevent water from evaporating and is heat-resistant to endure a high temperature. The bottle has a volume of 250mL to allow additional air volume contained in the bottle suppressing the solution from boiling and

preventing water from evaporating. The bottle has markings on the side to measure and detect the volume of solution before and after the heating.

3.1.3. Experimental conditions

Sodium chloride amount used in halite scale precipitation varies from literature (Chen et al., 2009; Wylde & Slayer, 2013). This variation has complicated the evaluation of halite scale inhibitor efficiency. Moreover, the amount of halite precipitation is extremely difficult to control (Hebert et al., 2016; Lu et al, 2014). The solubility of sodium chloride in water nearly does not change even when temperature dramatically changes (see Figure 3.1). The difference of sodium chloride solubility between 0°C and 100°C (3.34g) is much smaller comparing to, for example, the difference of sodium formate solubility (86.1g), which is almost 2600% difference (see Table 3.1). Thus, it is incredibly difficult to accurately predict the precipitation amount of sodium chloride. In this study, several experiments were conducted to optimize the sodium chloride amount (38.40g and 37.50g) could dissolve in 100mL distilled water. However, the precipitate weight result was not always reproducible with the dissolution of 38.40g sodium chloride in 100mL of distilled water at the boiling point (100°C). Therefore, sodium chloride amount was lowered to 37.50g and dissolved at a lower temperature (80°C) to achieve more consistent results.

Table 3.1: Solubility table of sodium chloride and sodium formate.

Temperature, °C	Solubility, g/100mL	
	Sodium chloride	Sodium formate
0	35.65	43.9
10	35.72	62.5
20	35.89	81.2
30	36.09	102
40	36.37	108
50	36.69	115
60	37.04	122
70	37.46	130
80	37.93	138
90	38.47	147
100	38.99	160
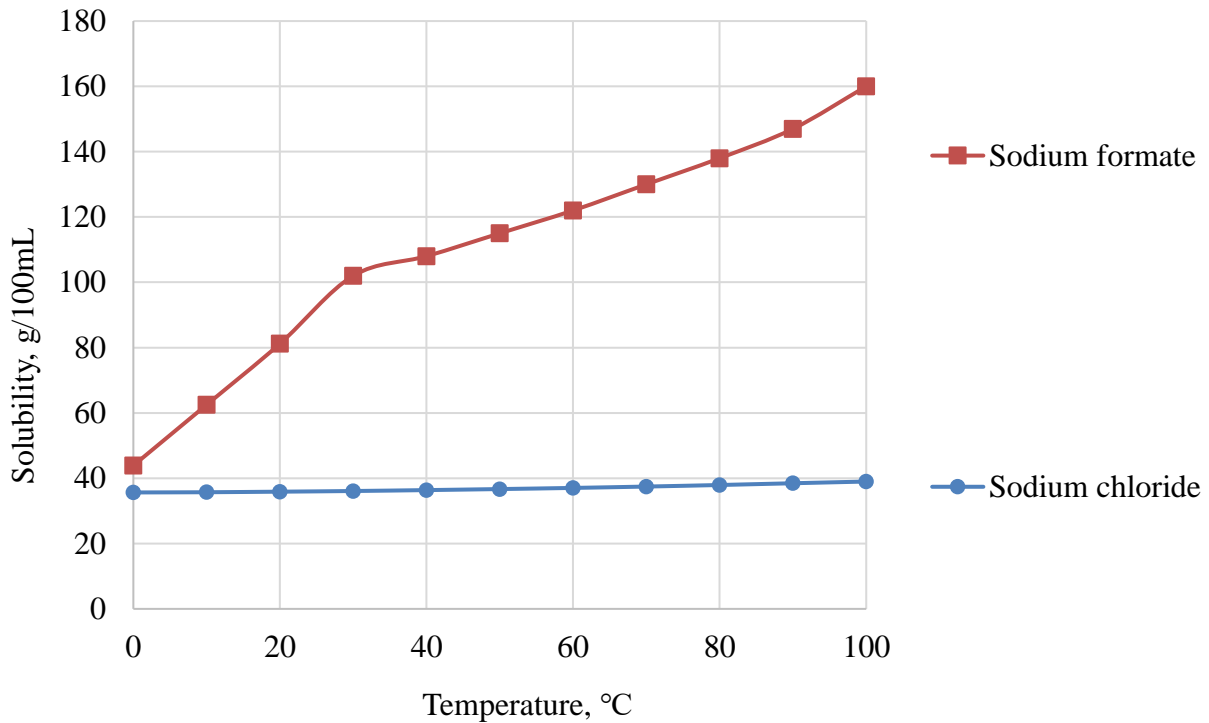
Figure 3.1: Solubility graph of sodium chloride and sodium formate.

3.1.4. Scale inhibitors

Based on the chemical properties, halite scale inhibitors in this study were categorized into three groups.

I.   Group one is the polymers, consisted of six inhibitors including carboxymethylcellulose sodium salt (CMC-Na salt), Alcoflow 250, Alcoflow 750, Alcoflow 920, POLYstim PCS-252, and silica inhibitor. Some of these polymeric chemicals were known as effective scale inhibitors other than halite scale in the industry (see Table 2.1).

II.   Group two is the iron cyanides, consisted of three inhibitors including potassium ferricyanide ($K_3Fe(CN)_6$), potassium ferrocyanide ($K_4Fe(CN)_6$), and sodium

ferrocyanide ($Na_4Fe(CN)_6$). Potassium ferrocyanide is known as halite scale inhibitor in the oil and gas industry (Guan et al., 2008; Lu et al., 2014; Hebert et al., 2016; Zhang et al., 2018; Zhang et al., 2019; Wylde and Slayer, 2013).

III. Group three is the small molecules chemicals, consisted of nine inhibitors including diethylenetriamine penta(methylene phosphonic acid) (DTPMPA), diethylenetriaminepentaacetic acid (DTPA-K5), salicylaldehyde, tetraethylenepentamine (TEPA; Tetrene), diethylenetriamine (dien); dimethyl sulfoxide (DMSO), Trinohex Ultra, Tris(2-aminoethyl)amine (TREN), and nitrilotriacetamide (NTAA). Nitrilotriacetamide (NTAA) is known as a halite scale inhibitor. NTAA's results were used as a benchmark to evaluate the inhibition efficiency results of other inhibitors.

Typical amount range inhibitors were used in previous literature was from 50ppm to 1000ppm (Chen et al., 2009). Thus, some inhibitors were tested at a 500ppm amount, about the average of 50ppm and 1000ppm, to identify their inhibition effect on halite scale precipitation. Some other inhibitors were tested at 50ppm, 200ppm, and 500ppm amount to identify the efficiency at different concentrations.

Inhibitors were typically added after salt fully dissolved in water in literature (Guan et al., 2008; Wylde and Slayer, 2013). However, this technique could disturb the salt precipitation and deviate inhibition efficiency result. As inhibitor is added after, the bottle needs to be removed from the oven. As soon as the cap is opened, the air volume is inadvertently released from the bottle. This air volume in the bottle is extremely critical to be retained since it acts as a suppressor to keep the water from evaporating into gas phase. Consequently, water would evaporate out of the bottle and leave salts dried up and precipitating. This precipitation could unintentionally depreciate the

inhibition efficiency of inhibitors. Thus, in this study, the inhibitors were added before the bottle was heated in the oven to prevent the phenomenon above from happening.

3.2. Halite scale precipitation without inhibitor

Several experiments were conducted to confirm precipitate weight accuracy and reproducibility of 37.50g NaCl solution at 80°C. Precipitate crystals were collected and weighed (see Table 3.2). The average halite precipitate weight result in Table 3.2 is consistent with the value from literature and the solubility table (1.5560g ± 0.0280g) (see Table 3.1) (Zhang et. al 2019). Precipitates of NaCl blank solution are mostly in cubic shape with sharp edges and semi-clear color (see Figure 3.2). Sizes of crystal are varying. The smaller the crystal size, the brighter and clearer the crystal color.

Table 3.2: Precipitate weight of blank solutions.

Sample	Precipitate weight, g
1	1.5500
2	1.5100
3	1.5500
4	1.5800
5	1.5900
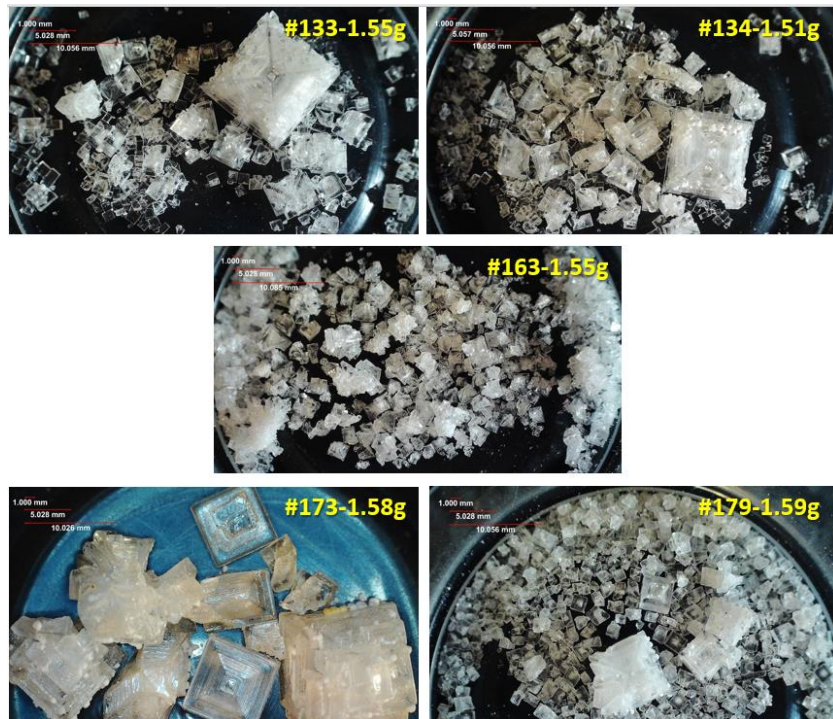
Figure 3.2: Five samples of blank solution's precipitate crystals.

3.3. Halite scale precipitation with inhibitor

3.3.1. Group one (polymers)

3.3.1.1. Carboxymethylcellulose sodium salt (CMC-Na salt)
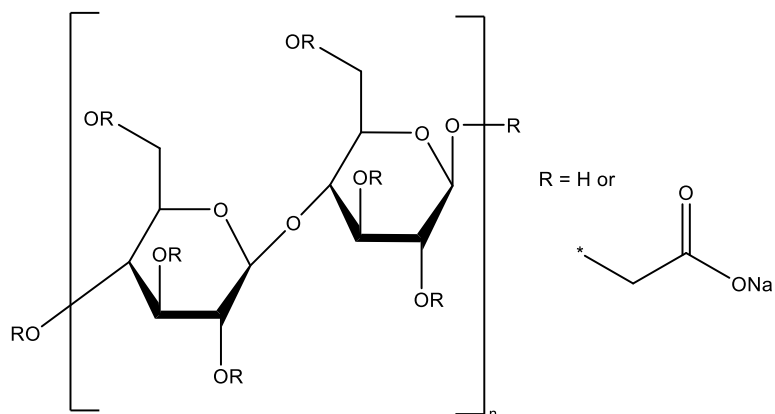
Figure 3.3: Chemical structure of CMC-Na salt.

Carboxymethylcellulose sodium salt, or CMC-Na salt, is the most frequently used form of carboxymethyl cellulose (CMC). CMC is a cellulose derivative with carboxymethyl groups (-CH_2-COOH) attached some of the hydroxyl groups of the glucopyranose monomers that construct the cellulose backbone (Santa Cruz Biotechnology) (see Figure 3.3). CMC-Na is commonly applied in many industries. In food industry, CMC-Na is a dispersant to enhance product fluidity. For instance, CMC-Na could prevent the aggregation and precipitation of milk protection in yogurt, make it uniformly dispersed (Sidley Chemicals). CMC-Na could also prevent the growth of ice crystals in ice cream (Sidley Chemicals). In cosmetics and pharmaceuticals field, CMC is used as a bulk laxative and as an emulsifier and thickener, and as a stabilizer for reagents (U.S. National Library of Medicine). CMC-Na is studied in medicals for post cataract surgery dry eye symptoms (U.S. National Library of Medicine). As these applications are important and necessary for halite scale inhibition study, CMC-Na salt was selected to test its inhibition efficiency at different concentrations in this study. There are different kinds of CMC with certain number of units (n). In this study, CMC-Na (n = app. 500) was chosen to test as its short polymer chain make CMC-Na more soluble in water. A 200ppm and 500ppm CMC-Na were added in two individual bottles. The bottles were heated in oven at 105°C in 4 hours, then at 115°C for another 4 hours, and 2 additional hours to ensure non-visible salts dissolved. The bottles were kept in switched-off oven for 36 hours to cool down to 23°C (see Materials and Method for more details). Then, the bottles were removed from the oven to check for precipitation (see Figure 3.4). For the 200ppm CMC-Na bottle, a small crystal was noticed at the bottom of the bottle (see Figure 3.5). The crystal was gently removed out of the bottle, dried in oven, and weighed. The precipitated weight of the crystal was 0.1927g which means that 12% of salt amount could not be inhibited by 200ppm CMC-Na (see Table 3.3). For the 500ppm CMC-Na bottle, there were no crystals detected (see Figure 3.6). Thus, the

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precipitate weight and the inhibition efficiency of 500ppm CMC-Na solution was resulted in Table 3.3 as 0g and 100%, respectively. Comparing to the blank solution's precipitate weight (1.5560g), the addition of CMC-Na significantly reduced the precipitate weight (0g) and improved the inhibition efficiency (100%). In this study, CMC-Na efficiently prevented halite crystals from growing. CMC-Na salt had hindered the adhesion between halite crystals and dispersed them in the solution which limited small crystals to grow larger. As 500ppm CMC-Na successfully inhibited halite scale, it is yet to know if the minimum inhibitor concentration of CMC-Na is 500ppm or could be between 200ppm and 500ppm. Thus, further studies are suggested to identify the minimum inhibitor of CMC-Na in halite scale precipitation.

Table 3.3: CMC-Na's inhibition results with and without inhibitor after 36 hours of cooling at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
200	0.1927	88%
500	0	100%

Figure 3.4: 200ppm and 500ppm CMC-Na bottles after cooling down for 36 hours at 23°C.
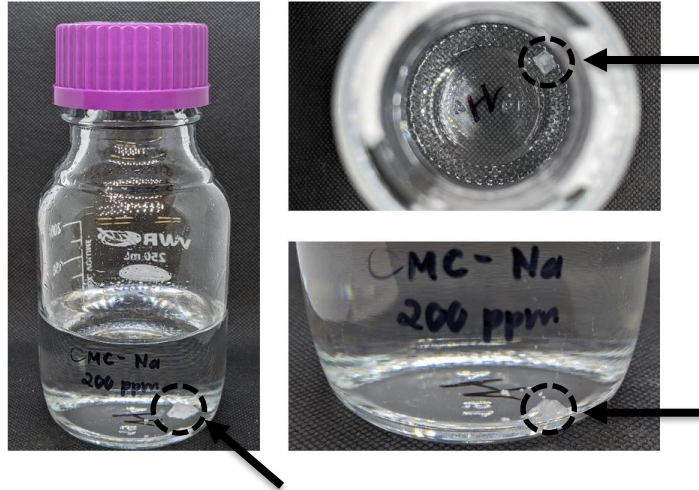
Figure 3.5: CMC-Na (200ppm) bottle cooling down for 36 hours at 23°C. Arrows show remaining crystal.
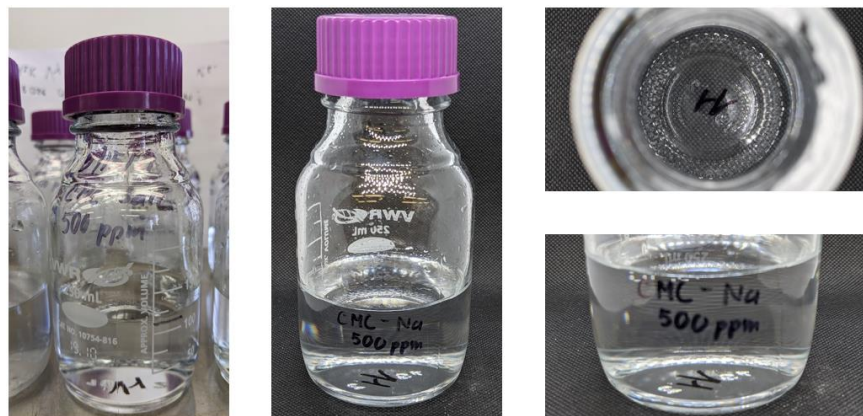
Figure 3.6: CMC-Na (500ppm) bottle cooling for 36 hours at 23°C. No precipitate crystals observed.

3.3.1.2. Alcoflow 250

Alcoflow 250 is a polycarboxylate. Polycarboxylate is used in many different applications and industry. For example, in concrete construction, polycarboxylate is included in superplasticizer, a high range water reducer for cement admixture (Yu et. al 2008). Polycarboxylate is also used in inhibiting barium sulfate and calcium carbonate scale

(AkzoNobel). As a barium sulfate inhibitor, Alcoflow 250 is used with a minimum inhibitor concentration (MIC) of $\leq$ 6ppm. The minimum inhibitor concentration of Alcoflow 250 with calcium carbonate scale is higher than with barium sulfate (10 to 15ppm). Furthermore, the stability of Alcoflow 250 polymer structure is quite significant as it can endure in high total dissolved solids (TDS) brine (25000ppm Ca^{2+}, 50000ppm Na^+) and at high temperature (95℃) for overnight. As these properties were important and necessary for halite scale inhibition study, Alcoflow 250 was selected to test its inhibition efficiency in halite scale precipitation. A 500ppm amount of Alcoflow 25 was added to a bottle of salt and water mixture. The bottle was heated in oven at 105℃ in 4 hours, then at 115℃ for another 4 hours, and 2 additional hours to ensure invisible salts completely dissolved. The bottle was kept in switched-off oven for 36 hours to cool down to 23℃ (see Materials and Method for more details). Then, it was removed from the oven to observe the precipitation. No crystal was observed in the bottle (see Figure 3.7). Thus, the precipitate weight of 500ppm Alcoflow 250 was resulted as 0g, and 100% for the inhibition efficiency. It could be seen that a significant improvement when comparing the inhibition efficiency of blank solution (0%) and Alcoflow 250 solution (100%) (see Table 3.4). The polycarboxylate of Alcoflow 250 had successfully separated and dispersed small halite crystals in the solution which hindered them to form and grow into a larger crystal with a stable structure. While 500ppm amount of Alcoflow 250 effectively prevented halite crystal growth, the minimum inhibitor concentration could probably be lower than this limit. Thus, Alcoflow 250 is suggested to have further studies as it may have a minimum inhibitor concentration that is lower than 500ppm.

Table 3.4: Alcoflow 250's inhibition results with and without inhibitor after cooling down for 36 hours at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
500	0	100%

Figure 3.7: 500ppm Alcoflow 250 bottle after cooling down for 36 hours at 23°C. No precipitate crystals observed.

3.3.1.3. Alcoflow 750

Alcoflow 750 is a multipolymer inhibitor and is a patented methanol tolerant scale inhibitor with high performance in multiscale control (AkzoNobel). Alcoflow 750 performs well in inhibiting barium sulfate scale with a minimum inhibition concentration of $\leq$ 6ppm. For calcium carbonate scale inhibition, Alcoflow 750 is comparatively effective. The minimum inhibition concentration for Alcoflow 750 to prevent calcium carbonate scale is from 7 to 9ppm. Additionally, Alcoflow 750 polymer structure is stable in brine that contains up to 2500ppm Ca^{2+}, and 25000ppm of Na^+ at high temperature (95°C) for over 24 hours. As Alcoflow 750 excellently performs in inhibiting barite and calcite scale, it was thus selected in this study to test its inhibition

efficiency in halite scale precipitation. A 500ppm amount of Alcoflow 750 was added to a bottle of salt and water mixture. The bottle was heated in oven at 105°C in 4 hours, then at 115°C for another 4 hours, and 2 additional hours to ensure invisible salts completely dissolved. The bottle was kept in switched-off oven for 36 hours to cool down to 23°C (see Materials and Method for more details). Then, it was removed from the oven to observe the precipitation. In Figure 3.8, it could be seen that Alcoflow 750 successfully prevented halite crystal growth as no crystals were observed. Hence, the precipitate weight of 500ppm Alcoflow 750 was 0g, and the inhibition efficiency was 100%. Alcoflow 750's results had outperformed the blank precipitation's results (see Table 3.5). In this study, the addition of Alcoflow 750 effectively inhibited halite scale growth. The polymer chains of Alcoflow 750 dispersed in the solution and interrupted small halite crystals from adhering to others to prevent them from growing larger. A thin fragile yellow web was noticed at the bottom bottle. It was probably a precipitate of the Alcoflow 750 polymer, but further studies are needed to confirm the hypothesis. While 500ppm Alcoflow 750 successfully inhibited halite scale, it is unknown whether 500ppm is the minimum inhibition concentration of Alcoflow 750. Therefore, further studies are suggested to identify the inhibitor concentration threshold of Alcoflow 750 in halite scale inhibition.

Table 3.5: Alcoflow 750's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
500	0	100%
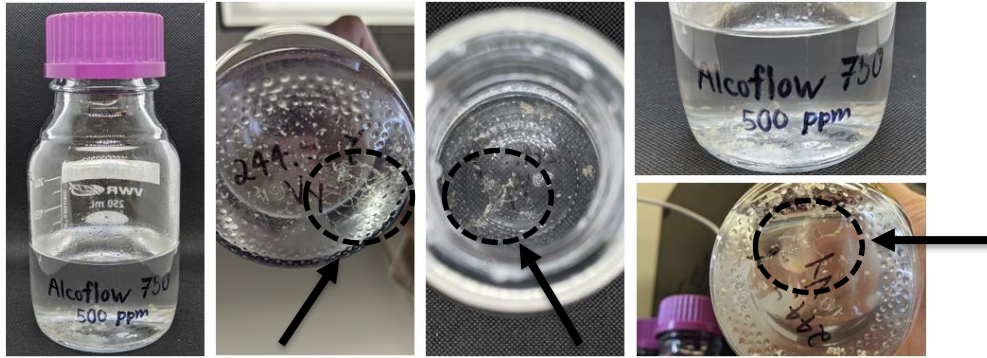
Figure 3.8: 500ppm Alcoflow 750 bottle after cooling down for 36 hours at 23°C. Arrows show a remaining thin fragile yellow web.

3.3.1.4. Alcoflow 920

Alcoflow 920 inhibitor is a sulfonated copolymer with an approximate 10000 molecular weight. Alcoflow 920 inhibitor has a high performance in inhibiting calcium carbonate scale with a minimum inhibition concentration from 7 to 9ppm. For barium sulfate scale, the minimum inhibition concentration is > 16ppm. The polymer structure of Alcoflow 920 is significantly stable at high temperature (95°C) with high solids (25000ppm Ca^{2+}, 50000ppm Na^+) for overnight. Moreover, this inhibitor is also stated in the manufacturer's brochure as a halite scale inhibitor (AkzoNobel). Therefore, Alcoflow 920 was selected to test in this study to identify its inhibition efficiency in halite scale precipitation. A 500ppm amount of Alcoflow 920 was added to a bottle of salt and water mixture. The bottle was heated in oven at 105°C in 4 hours, then at 115°C for another 4 hours, and 2 additional hours to ensure invisible salts completely dissolved. The bottle was kept in switched-off oven for 36 hours to cool down to 23°C (see Materials and Method for more details). Then, it was removed from the oven to observe the precipitation. As there were no crystals precipitated in the bottle (see Figure 3.9), the precipitate weight was 0g, and the inhibition efficiency was 100% (see Table 3.6). The addition of Alcoflow 920 in solution successfully

controlled halite scale precipitation while the blank solution could not. From the inhibition results, it could be seen that Alcoflow 920 could also inhibit halite scale besides calcium carbonate and barium sulfate scale. The sulfonated polymer of Alcoflow 920 effectively interceded between the attachment of small halite crystals to limit them growing into a larger crystal. Therefore, Alcoflow 920 could be used as a halite scale inhibitor, and further studies are suggested to identify its minimum inhibition concentration for halite scale.

Table 3.6: Alcoflow 920's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

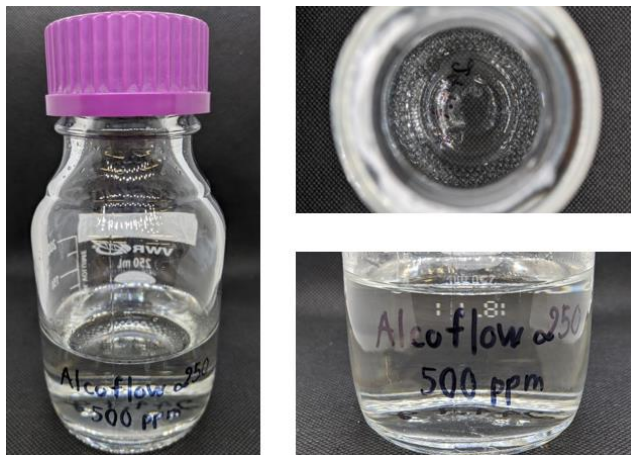| Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
500	0	100%
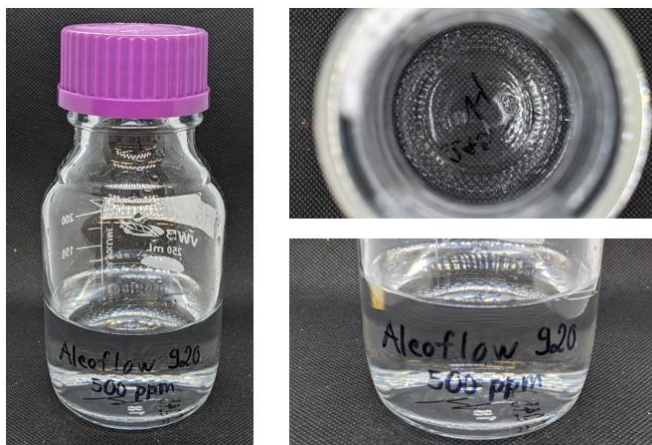
Figure 3.9: 500ppm Alcoflow 920 bottle after cooling down for 36 hours at 23°C. No precipitate crystals observed.

3.3.1.5. POLYstim PCS-252

POLYstim PCS-252 is known as a permanent clay stabilizer. Clay stabilizer is a specialty chemical to prevent the relocation or swelling of clay particles in reaction to water-based fluid (Schlumberger). Clay stabilizer acted to hold the clay platelets in position. Clays consists of cations, mostly sodium. The crystalline layer of sodium occupies base exchange positions in the clay lattice structure. With the water contact, the cations are solubilized which induce the instability and swelling in clay. As clays swell, the formation permeability become lower which delays the production. Therefore, clay stabilizer reduces clay swelling by providing a cation to replace sodium which is a native solubilized clay cation (Riteks). In this study, permanent clay stabilizer was selected to test its inhibition efficiency in halite scale precipitation as it has certain properties that are necessary for halite scale inhibition. A 500ppm amount of POLYstim PCS-252 was added to a bottle of salt and water mixture. The bottle was heated in oven at 105°C in 4 hours, then at 115°C for another 4 hours, and 2 additional hours to ensure invisible salts to completely dissolve. The bottle was kept in switched-off oven for 36 hours to cool down to 23°C (see Materials and Method for more details). Then, it was removed from the oven to observe the precipitation. No crystals were observed in the bottle (see Figure 3.10). Hence, the precipitate weight was 0g and the inhibition efficiency was 100% (see Table 3.7). This inhibitor was totally effective when comparing its precipitate weight (0g) to the blank precipitated weight (1.5560g). Besides holding the clay in position, in this study, clay stabilizer was also able to retain the halite crystals in position. This retention kept small halite crystals from binding and growing into a larger crystal. Thus, POLYstim PCS-252 could be used as a halite scale inhibitor, and further studies are suggested to identify its minimum inhibitor concentration for halite scale.

Table 3.7: POLYstim PCS-252's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

| Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
500	0	100%
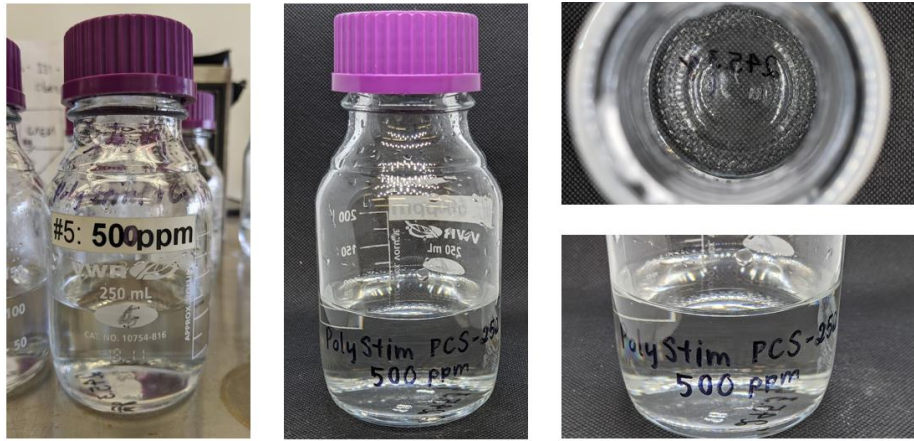
Figure 3.10: 500ppm POLYstim PCS-252 bottle after cooling down for 36 hours at 23°C. No precipitate crystals observed.

3.3.1.6. Silica inhibitor

Silica inhibitor used in this study is from Lubrizol and is used to prevent the formation of silica scale. Silica deposition is induced from several causes including polymerization, coprecipitation with other minerals, precipitation with other multivalent ions, and biological activity in the water (Gill, 1993). To inhibit silica scale, it is important to stop silica polymerization at early stages by preventing the growth of large particles and their attachment to surfaces (Al-Saadi and Al-Haddabi, 2019). As temperature decreases, silica solubility also decreases (Weng, 1995). Since silica and halite inhibitor are both attempting to prevent small crystals to grow larger,

this silica inhibitor was selected to test in this halite scale study. A 500ppm amount of silica inhibitor was added to a mixture of salt and water in a bottle, heated at 105℃ for 4 hours, then 115℃ for 4 more hours, and 2 additional hours at 115℃ to ensure that all salts including the invisible ones dissolved in water. The bottle was kept in the switched-off oven for 36 hours to cool down to 23℃ (see Materials and Method for more details). Then, it was removed from the oven to detect the precipitation. No crystals were observed in the bottle (see Figure 3.11). Therefore, the precipitate weight was 0g and the inhibition efficiency was 100%. The addition of silica inhibitor significantly improved the blank solution's precipitate weight (1.5560g) and inhibition efficiency (0%) (see Table 3.8). Silica inhibitor's polymeric structure prevented halite crystal from growing by interfering the attachment of smaller crystals and dispersing them in the solution. Thus, small crystals failed to grow larger. Silica inhibitor could be used as a halite scale inhibitor and is suggested to have further studies to find the minimum inhibitor concentration for halite scale.

Table 3.8: Silica inhibitor's inhibition results with and without the inhibitor after cooling down for 36 hours at 23℃.

| Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
500	0	100%

Figure 3.11: 500ppm silica inhibitor bottle after cooling down for 36 hours at 23°C. No precipitate crystals observed.

3.3.1.7. Conclusions

Six inhibitors in group one was tested, and successfully inhibited halite scale precipitation at 500ppm concentration (see Figure 3.12). There were no crystals noticed in any of the 500ppm concentration bottles, hence their precipitate weight was 0g and inhibition efficiency was 100% (see Table 3.9). They effectively interrupted the surface adhesion of small halite crystals to hamper the formation of a larger crystal. The concentration amount tested above may exceed the minimum inhibitor concentration of group-one inhibitors. Thus, further tests are recommended to identify the minimum inhibitor concentration of group-one inhibitors. Overall, it could be concluded that group one inhibitors are effective in inhibiting halite scale.at 500ppm concentration.

Table 3.9: Group one inhibitors' inhibition results after cooling down for 36 hours at 23°C.

Inhibitor	Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
Alcoflow 250	500	0	100%
Alcoflow 750	500	0	100%
Alcoflow 920	500	0	100%
POLYstim PCS-252	500	0	100%
Silica inhibitor	500	0	100%
CMC-Na salt	200	0.1927	88%
CMC-Na salt	500	0	100%

Inhibition efficiency, %
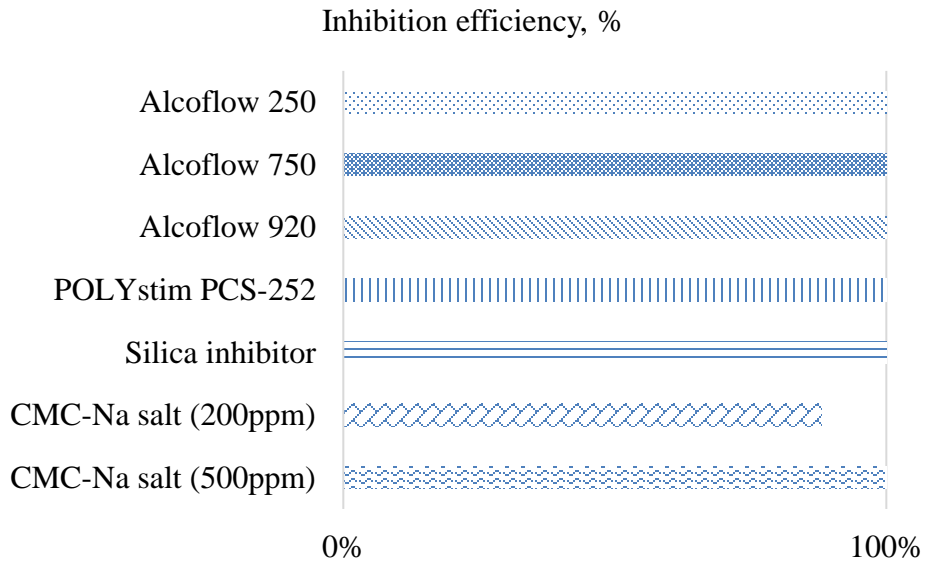
Figure 3.12: Group one inhibitors' inhibition efficiency.

3.3.2. Group two (iron cyanides)

3.3.2.1. Sodium ferrocyanide ($Na_4Fe(CN)_6$)
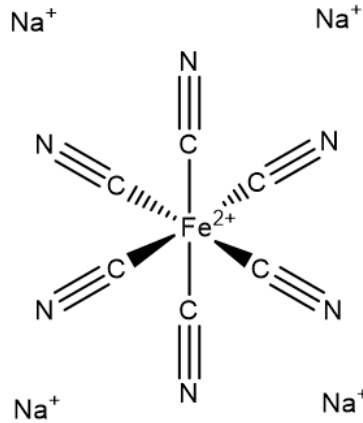
Figure 3.13: Chemical structure of sodium ferrocyanide.

Sodium ferrocyanide is one of the iron cyanides coordination compounds (see Figure 3.13). It is also known as yellow Prussiate of Soda. Sodium ferrocyanide is produced from a combination of hydrogen cyanide (HCN), ferrous chloride ($FeCl_2$), and calcium hydroxide ($Ca(OH)_2$) (Gail et al., 2011). Although the inhibitor contains cyanide group, sodium ferrocyanide has a low toxicity and safe for human daily intake ($0 – 0.025$mg/kg body weight) (World Health Organization). The strong attachment of iron with cyanide does not easily release cyanide freely. In the Europe, sodium ferrocyanide is used as an anticaking agent for table salt additives (Aggett et al., 2018). In chemical industry, sodium ferrocyanide is used as a solid separation agent (EPA). In petroleum industry, it is used for removal of mercaptans. Having certain applications that are useful for halite scale inhibition study, sodium ferrocyanide was suggested to test in this study to identify its inhibition efficiency in halite scale precipitation. A 50ppm amount of sodium ferrocyanide was added in a mixture of salt and water in a bottle. The bottle was heated at 105°C for 4 hours, then at 115°C for 4 more hours, and an additional of 2 hours at 115°C to ensure salts dissolved, including

the invisible ones. The bottle was kept in switched-off oven for 36 hours to cool down to 23℃ (see Materials and Method for more details). Then the bottle was removed from the oven and observed for precipitation. There were no crystals detected in the bottle (see Figure 3.14). Hence the precipitate weight and the inhibition efficiency were resulted as 0g and 100% in Table 3.10, respectively. The addition of 50ppm sodium ferrocyanide significantly enhanced the inhibition efficiency when comparing to the blank solution. In this study, it could be seen that sodium ferrocyanide effectively inhibited halite scale precipitation. While 50ppm of sodium ferrocyanide successfully prevented halite scale in this study, it is unknown whether this concentration is the minimum inhibitor concentration of sodium ferrocyanide for halite scale. Thus, further studies are suggested to identify sodium ferrocyanide concentration threshold in halite scale inhibition.

Table 3.10: Sodium ferrocyanide's inhibition results with and without the inhibitor after cooling down for 36 hours at 23℃.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.5560	0%
50	0	100%
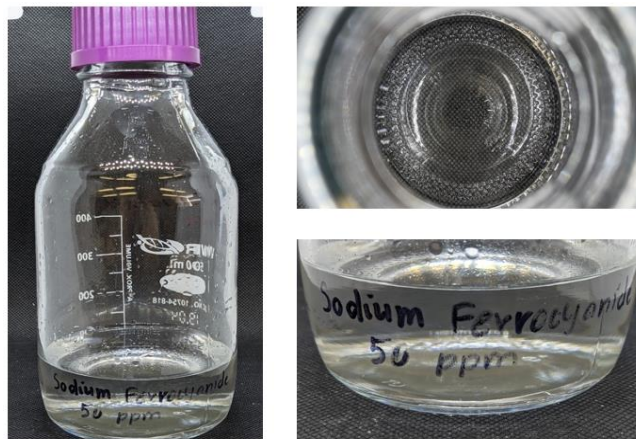
Figure 3.14: 50ppm sodium ferrocyanide bottle after cooling down for 36 hours at 23°C. No precipitate crystals observed.

3.3.2.2. Potassium ferrocyanide ($K_4Fe(CN)_6$)
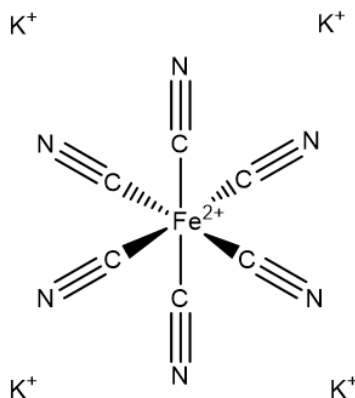
Figure 3.15: Chemical structure of potassium ferrocyanide.

Potassium ferrocyanide is an inorganic compound and one of the iron cyanides. It is also known as yellow Prussiate of Potash. Potassium ferrocyanide has a complicated polymeric structure which consists of octahedral $[Fe(CN)_6]^{4-}$ in the middle crosslinked with K^+ ions that are attached to the cyanide ligands (Willans et al., 2009) (see Figure 3.15). Potassium ferrocyanide is a reaction product of Prussian blue (iron (III) ferrocyanide) and potassium hydroxide (KOH)

achieved by a French chemist Pierre Joseph Macquer in 1752 (Macquer 1752; Munroe et al., 1902). However, in nowadays production, potassium ferrocyanide is produced industrially from hydrogen cyanide (HCN), ferrous chloride (FeCl$_2$), and calcium hydroxide (Ca(OH)$_2$). Potassium ferrocyanide is applied in certain areas of industry. It is mostly used as an anticaking agent in road salt and table salt (Gail et al., 2011). In the Europe, potassium ferrocyanide is authorized in two food categories as salt substitutes (Aggett et al., 2018). In agricultures, potassium ferrocyanide is used as a fertilizer for plants (Mekong Chemicals). With certain applications that are necessary for halite scale inhibition, potassium ferrocyanide was selected to test in this study to identify its inhibition efficiency. A 500ppm amount of potassium ferrocyanide was added in a mixture of salt and water in a bottle. The bottle was heated at 105°C for 4 hours, then at 115°C for 4 more hours, and 2 additional hours at 115°C to ensure invisible salts dissolved in the water. The bottle was kept in the oven for 36 hours to cool down to 23°C (see Materials and Method for more details). Then the bottle was removed from the oven and observed for precipitation. No crystals were observed in the bottle. Therefore, the precipitate weight was 0g and the inhibition efficiency was 100% (see Table 3.11). Comparing to the blank solution, the addition of potassium ferrocyanide significantly improved the inhibition efficiency. Thus, potassium ferrocyanide could be used as a halite scale inhibitor.

Table 3.11: Potassium ferrocyanide's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

| Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.5560	0%
500	0	100%

3.3.2.3. Potassium ferricyanide ($K_3Fe(CN)_6$)
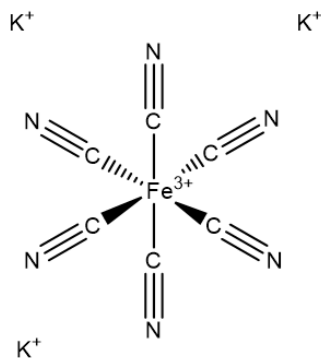
Figure 3.16: Chemical structure of potassium ferricyanide.

Potassium ferricyanide is a compound and one of the iron cyanides. Its other name is red Prussiate of Potash. This inhibitor has a bright red color and contains an octahedrally coordinated ($Fe^{3+}(CN)_6$) centers crosslinked with three K^+ ions that are attached to the cyanide ligands (Figgis et al., 1969) (see Figure 3.16). When dissolved in water, potassium ferricyanide has a green-yellow fluorescence. This chemical was discovered by German chemist, Leopold Gmelin, in 1822 (Gmelin, 1822; Idhe, 1984). It has a variety of chemistry applications. In photography, potassium ferricyanide is used as an oxidizing agent to remove silver from color negatives and positives during processing which is known as bleaching process. Since iron has a strong attachment to cyanide, potassium ferrocyanide has low toxicity as cyanides are not freely released from the compound. In the medical field, potassium ferricyanide is an ingredient in blood glucose meters to use for diabetics (Wikipedia). As potassium ferricyanide also has the same iron cyanide anion as potassium ferrocyanide, it was thus selected to test in this study to identify the inhibition efficiency at different concentrations. A 50ppm, 200ppm, and 500ppm amount of potassium ferricyanide was added to three individual bottles of salt and water mixture. Three bottles were

heated in oven at 105°C for 4 hours, and at 115°C for 4 more hours, and 2 additional hours at 115°C to ensure small invisible salts fully dissolved. The bottles were kept in switched-off oven for 36 hours to cool down to 23°C. Then, the bottles were removed from the oven and observed for precipitation (see Figure 3.17). There were no crystals detected from any bottles (see Figures 3.18 – 3.20). Comparing with blank solution, the addition of potassium ferricyanide in the solution significantly improved the inhibition efficiency regardless different concentrations (see Table 3.12). Potassium ferricyanide effectively prevented halite scale from growing by interfering between small halite crystals and destabilize the attachment between them so that they could hardly form a larger crystal. At 50ppm concentration, the lowest concentration in this study, potassium ferricyanide still had an absolute inhibition efficiency. Thus, it could be concluded that potassium ferricyanide is a very effective halite scale inhibitor. However, it is unknown whether 50ppm is the minimum inhibitor concentration of potassium ferricyanide. Thus, further studies are suggested to identify the lowest inhibition concentration of potassium ferricyanide for halite scale.

Table 3.12: Potassium ferricyanide's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.5560	0%
50	0	100%
200	0	100%
500	0	100%
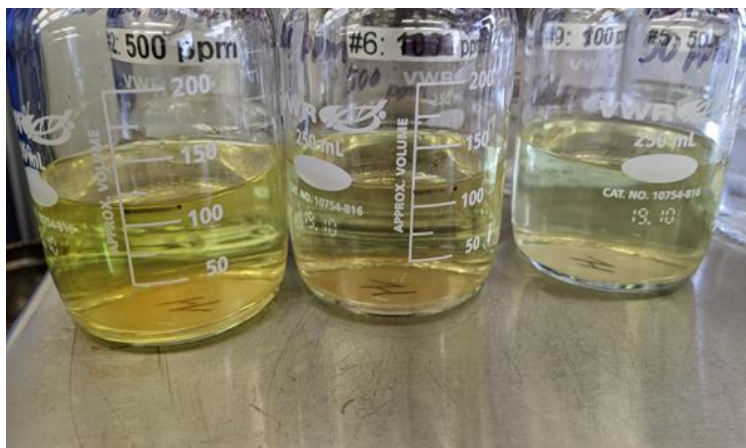
Figure 3.17: Potassium ferricyanide (500ppm, 200ppm, and 50ppm, from left to right) bottles after cooling down for 36 hours at 23°C. No precipitated crystals observed in any bottles.
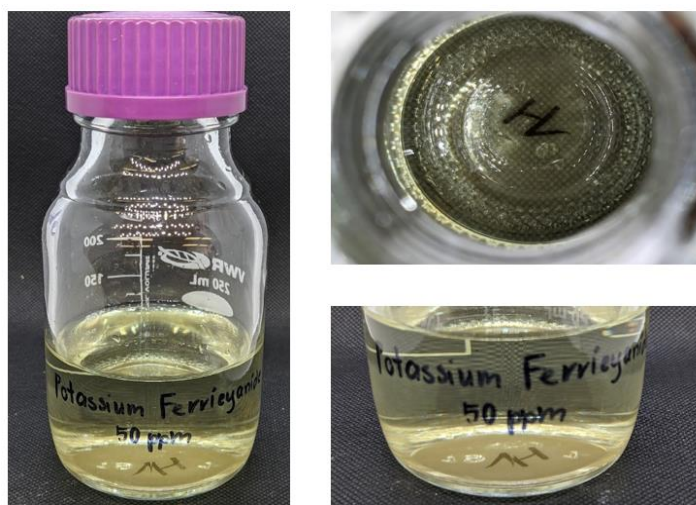
Figure 3.18: 50ppm potassium ferricyanide bottles after cooling down for 36 hours at 23°C. No precipitated crystals observed.
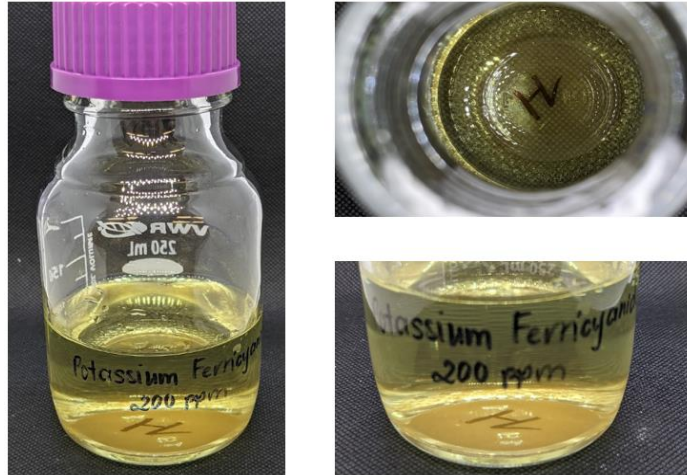
Figure 3.19: 200ppm potassium ferricyanide bottles after cooling down for 36 hours at 23°C. No precipitated crystals observed.
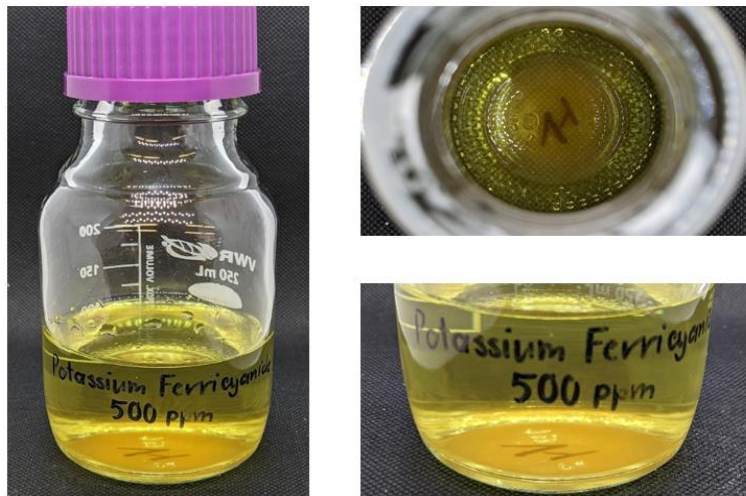
Figure 3.20: 500ppm potassium ferricyanide bottles after cooling down for 36 hours at 23°C. No precipitated crystals observed.

3.3.2.4. Conclusions

The three iron cyanides tested in this study were all effective in inhibiting halite scale precipitation (see Figure 3.21). Sodium ferrocyanide and potassium ferricyanide successfully prevented halite crystals growth at the lowest concentration (50ppm) tested in this study. A

500ppm potassium ferrocyanide was used to test and successfully prevented halite scale precipitation. However, it is unknown whether these concentrations were the minimum inhibitor concentration of group-two inhibitors. Thus, further studies are suggested to identify their inhibition threshold with halite scale.

Inhibition efficiency, %
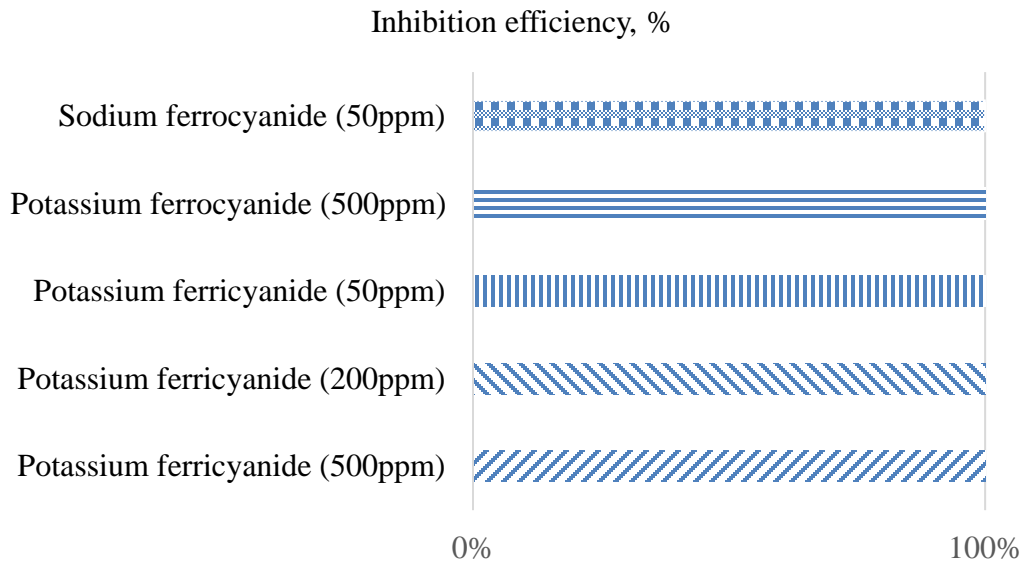
Figure 3.21: Group two inhibitors' inhibition efficiency.

3.3.3. Group three (small molecules)

Nine inhibitors were included in this group including DTPA-K$_5$, DTPMPA, Salicylaldehyde, TEPA, Dien, DMSO, Trinohex Ultra, TREN, and NTAA.

3.3.3.1. Diethylenetriamine penta(methylenephosphonic acid) (DTPMP)
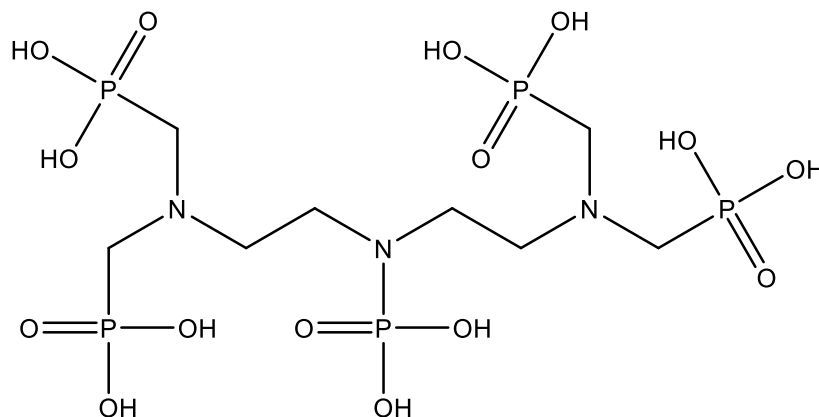
Figure 3.22: Chemical structure of DTPMPA.

Diethylenetriamine penta(methylene phosphonic acid) (DTPMPA) is multidentate chelating agent (see Figure 3.22). It is also known as a phosphonate, which is widely applied as a crystallization inhibitor. DTPMPA is used to study in the investigation of dynamic and kinetics of sodium sulfate crystallization with various organophosphonic acids. It is sometimes performed as a ligand for Ce^{3+} complexes characterization by luminescence spectroscopy (Sigma Aldrich). DTPMPA is known as sulfate, carbonate scale inhibitor other than halite scale inhibitor (TER Chemicals). There are different applications of DTPMPA including detergents and cleaning agents, water treatment, scaling inhibitor, deflocculating agent/settling retarder, and anticorrosion agent (Wikipedia). As a multiscale inhibitor, DTPMPA was selected to test in this study to determine its inhibition efficiency in halite scale. A 500ppm amount of DTPMPA was added to a mixture of salt and water in a bottle, heated at 105°C for 4 hours, then at 115°C for 4 more hours, and 2 additional hours at 115°C to ensure that all invisible salts dissolved in water. The bottle was kept in the switched-off oven for 36 hours to cool down to 23°C (see Materials and Method for more details). As the bottle was removed from the oven, there were no crystals in the bottle

observed (see Figure 3.23). Thus, precipitate weight was a 0g and the inhibition efficiency was 100% for 500ppm DTPMPA solution (see Table 3.13). In this case, DTPMPA was able to control the collision between tiny halite crystals by its disturbance so that small crystals failed to grow larger. Therefore, DTPMPA could be used as a halite scale inhibitor. However, further tests are recommended to identify the minimum inhibitor concentration of DTPMPA for halite scale.

Table 3.13: DTPMPA's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.5560	0%
500	0	100%
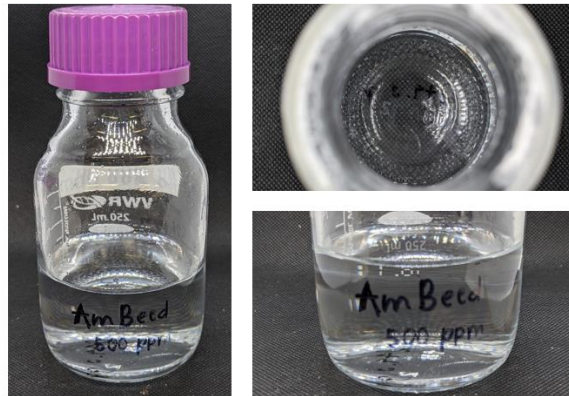
Figure 3.23: 500ppm DTPMPA bottle after cooling down for 36 hours at 23°C.

3.3.3.2. Diethylenetriaminepentaacetic acid, pentapotassium salt (DTPA-K$_5$)
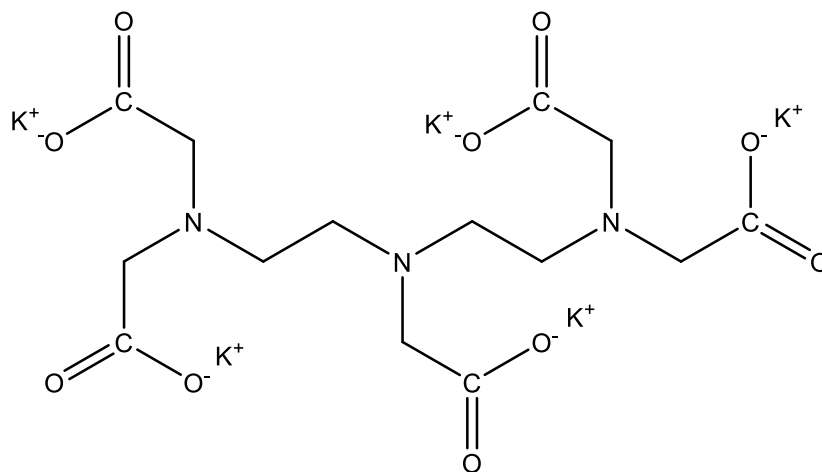
Figure 3.24: Chemical structure of DTPA-K5.

Diethylenetriaminepentaacetic acid potassium, or DTPA-K$_5$, is an aminopolycarboxylic acid, with a diethylenetriamine backbone, and five carboxymethyl groups (Buckingham and Macdonald, 1996) (see Figure 3.24). DTPA-K$_5$ structure is similar to polycarboxylate but has shorter chains. DTPA also has different applications in certain fields and industries. In wood industry, DTPA is used in peroxide bleaching of pulp. DTPA is predominantly used as chelating agent for metal ions. The Centers for Disease Control and Prevention (CDC) stated that Zn-DTPA and Ca-DTPA are safe and effective to treat those who have contaminated internally by plutonium, americium, and curium (Centers for Disease Control and Prevention). In medical field, DTPA is used as an MRI contrasting agent which alters magnetic resonance behavior of protons and increases images contrast (Caravan et al., 1999). In agriculture, Fe-DTPA is used as an aquarium plants fertilizer. More importantly, it is also suitable to dissolve oil field scales such as barite scale other than halite scale (Nouryon). As DTPA-K$_5$ has necessary properties and applications for halite inhibition study, it was suggested to test in this study. A 500ppm amount of DTPA-K$_5$ was added

to a mixture of salt and water in a bottle, heated at 105°C for 4 hours, then at 115°C for 4 more hours, and 2 additional hours at 115°C to ensure that all dissolved in water. The bottle was kept in the switched-off oven for 36 hours to cool down to 23°C (see Materials and Method for more details). As the bottle was removed from the oven, white, clear, solid cubic crystals were observed in the bottle (see Figure 3.25). The results in Table 3.14 showed that DTPA-K_5 had a very limited effects on halite scale inhibition when it only had 11% of inhibition efficiency. DTPA-K_5 could not effectively interrupt the adhesion between small halite crystals and but tolerate them to construct to larger crystal. Even though DTPA-K_5 was similar to polycarboxylate, it could not successfully prevent halite precipitation. Thus, polycarboxylate with longer chain would be more effective in preventing halite precipitation. But overall, DTPA-K_5 is not an effective halite scale inhibitor as its inhibition efficiency on halite scale precipitation at 500ppm concentration was significantly low.

Table 3.14: DTPA-K_5's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.5560	0%
500	1.3878	11%
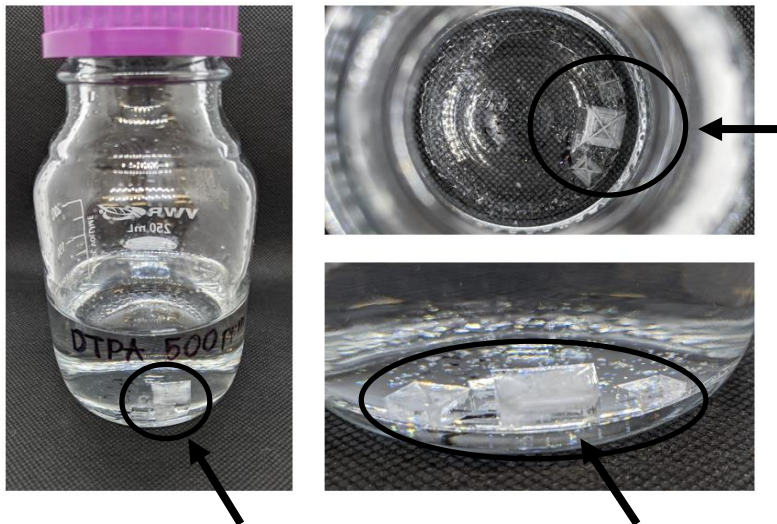
Figure 3.25: 500ppm DTPA-K₅ bottle after cooling down for 36 hours at 23°C. Arrows show remaining crystals.

3.3.3.3. Salicylaldehyde
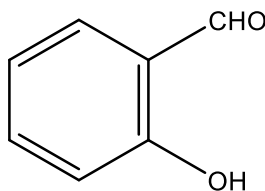
Figure 3.26: Chemical structure of salicylaldehyde.

Salicylaldehyde is an organic compound and one of the three isomers of hydroxybenzaldehyde (Budavari, 1989) (see Figure 3.26). Salicylaldehyde is known as a predecessor of chelating agents. In food industry, salicylaldehyde is used a flavoring agent for baked goods, chewing gum, frozen dairy, gelatin, etc. (O'Neil, 2013). Additionally, this inhibitor is also used in cosmetology products such as perfume or shampoo. As a flavoring agent, salicylaldehyde enhances the taste or the aroma of the product as they were damaged after the processing (O'Neil 2013). It is also used in preparing salicylaldehyde phenyl hydrazine, an indicator for the titration of organometallic reagents (Sigma Aldrich). As salicylaldehyde has

certain properties that could be employed for halite scale inhibition study, salicylaldehyde was thus selected to test in this study. A 500ppm amount of salicylaldehyde was added to a mixture of salt and water in a bottle, heated at 105°C for 4 hours, then at 115°C for 4 more hours, and 2 additional hours at 115°C to ensure all invisible salts dissolved in water. The bottle was kept in the switched-off oven for 36 hours to cool down to 23°C (see Materials and Method for more details). The bottle was then removed from the oven to observe for precipitation. A large white, pyramidal crystal was noticed (see Figure 3.27). The crystal was removed from the bottle, dried, and weighed. With a larger precipitate weight than blank solution's (see Table 3.15), salicylaldehyde is certainly not a halite scale inhibitor. The addition of salicylaldehyde could not prevent crystal from attaching and growing larger. Moreover, its precipitate weight was almost twice the blank's. Salicylaldehyde might be, by decreasing the solution polarity, increasing more precipitation. Therefore, salicylaldehyde is not recommended to use for halite scale inhibition.

Table 3.15: Salicylaldehyde's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

| Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.5560	0%
500	2.9876	-93%
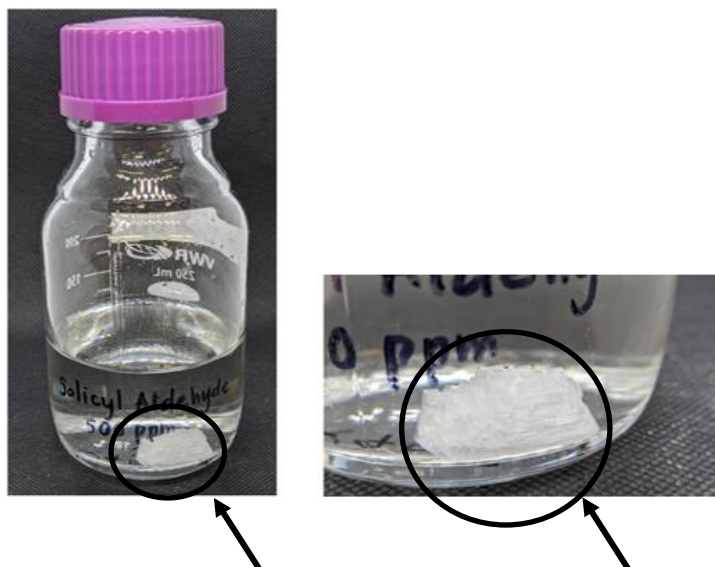
Figure 3.27: 500ppm salicylaldehyde bottle after cooling down for 36 hours at 23℃. Arrows show remaining crystals.

3.3.3.4. Tetraethylenepentamine (TEPA)
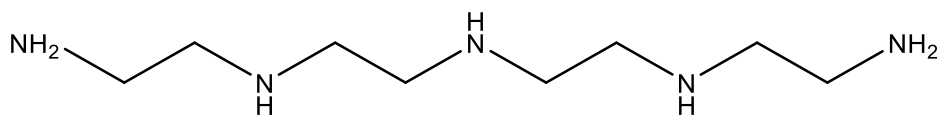
Figure 3.28: Chemical structure of TEPA.

Tetraethylenepentamine (Tetrene, or TEPA) is an organic compound and belongs to ethyleneamine chemical class. It contains linear, branched, cyclic molecules (Nouryon) (see Figure 3.28). TEPA has a yellow viscous liquid and is soluble is most organic solvents and water. TEPA is used as additives in fuels or lubricating oil products. Besides, it is also used as a hardener or curing agent in epoxy chemistry. In wood industry, it is used as a wet-end processing additive in the manufacture of paper pulp (U.S. Food & Drug Administration). In other industries, TEPA is also used as corrosion inhibitors and anticaking agent (EPA). As TEPA has certain properties and applications that are necessary to the halite scale inhibition study, it was selected to test its

inhibition efficiency in halite scale precipitation. A 500ppm amount of TEPA was added to a mixture of salt and water in a bottle, heated at 105℃ for 4 hours, then at 115℃ for 4 more hours, and 2 additional hours at 115℃ to ensure that salts dissolved in water. The bottle was kept in the switched-off oven for 36 hours to cool down to 23℃ (see Materials and Method for more details). The bottle was then removed from oven to observe for precipitation (see Figure 3.37). Several crystals precipitated at the bottom of the bottle were observed. Crystals were removed from the bottle, dried, and then weighed. In Table 3.16, it could be seen that TEPA had a very little to no effect in halite inhibition. The precipitate weight of inhibited solution was almost equivalent to the blank's precipitate weight. Thus, TEPA is not a halite scale inhibitor and would not be studied further in halite scale inhibition.

Table 3.16: TEPA's inhibition results with and without the inhibitor after cooling down for 36 hours at 23℃.

| Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.5560	0%
500	1.4006	10%
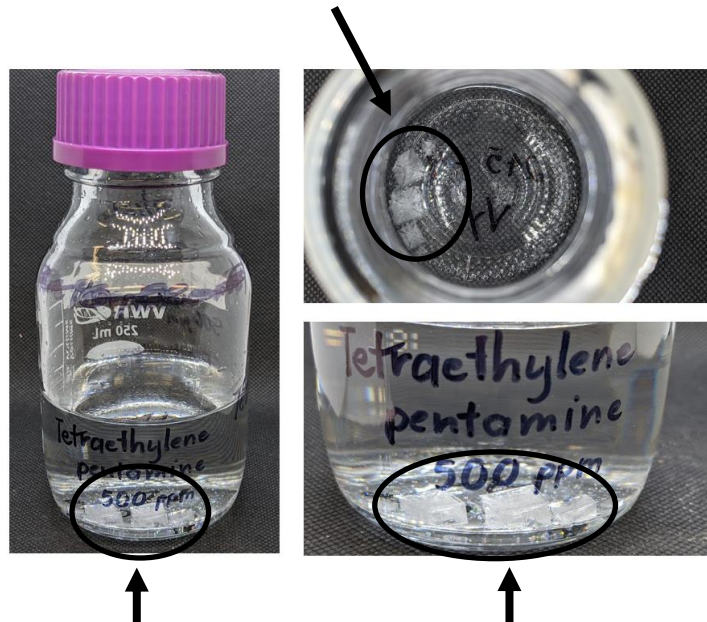
Figure 3.29: 500ppm TEPA bottle after cooling down for 36 hours at 23°C. Arrows show remaining crystals.

3.3.3.5. Diethylenetriamine (Dien)
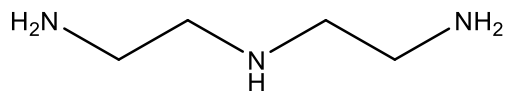
Figure 3.30: Chemical structure of Dien.

Diethylenetriamine (dien) is an organic compound and has the formula $HN(CH_2CH_2NH_2)_2$ (see Figure 3.30). This inhibitor is very soluble in water and polar organic solvents but not in oil. Dien is commonly used as curing agent for epoxy resins in epoxy adhesives (Brydson, 1999). In chemistry, it can be a tridentate ligand forming complexes (Crayton et al., 1963). Dien is also used in making propellent (Hydyne) for liquid-fuel rockets (Lerner, 2009; Morgan, 2008). With diverse applications in different industries and properties that are relevant for halite scale inhibition, dien was selected to test in this study. The precipitated crystals were observed and collected after the test (see Figure 3.31). It could be seen dien solution's precipitate weight was higher than blank

precipitate weight (see Table 3.17). Dien might be, by decreasing the solution polarity, increasing more precipitation. This shows that dien was ineffective in preventing halite scale growth. Therefore, it is not a halite scale inhibitor and would not be suggested for any further halite scale inhibition studies.

Table 3.17: Dien's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

| Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.5560	0%
500	1.7300	-12%

Figure 3.31: Precipitated crystals collected from a 500ppm Dien solution.

3.3.3.6. Dimethyl Sulfoxide (DMSO)
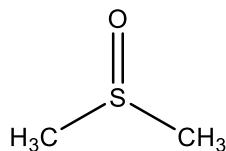
Figure 3.32: Chemical structure of DMSO.

Dimethyl Sulfoxide (DMSO) is an organosulfur compound with the formula $(CH_3)_2SO$ (see Figure 3.32). DMSO is a polar aprotic solvent which means it dissolves both polar and nonpolar compounds. Since DMSO is less toxic than other chemicals in its class, it is frequently used as a solvent for most chemical reactions with salts. It is also widely used as an extractant in biochemistry and cell biology (Exact Antigen, 2009). In biology, DMSO is used in polymerase chain reaction (PCR) to inhibit secondary structures in DNA template or primers (Charkrabakti, 2001). For typical medicine, DMSO is used as a topical analgesic, which prevents inflammatory and oxidation (Geiss, 2001). DMSO is a non-toxic solvent (LD_{50}, rat, 14500mg/kg) (Science Lab, 2018). As DMSO has certain properties and applications that are necessary for halite inhibition study, it was selected to test in this study. A 500ppm amount of DMSO was used to test. The precipitate weight in Table 3.18 showed that DMSO had minimal effect in halite scale inhibition. The highest inhibition efficiency was only about 26% which was not a significant improvement comparing to other inhibitors tested in this study. Moreover, DMSO precipitated crystals shape were almost like blank precipitate crystals' shape (see Figure 3.33). Thus, DMSO is not a halite scale inhibitor and no further studies about halite scale inhibition is necessary for DMSO.

Table 3.18: DMSO's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

| Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
500	1.15	26%

Figure 3.33: A 1.1500g precipitated crystals collected from a 500ppm DMSO solution.

3.3.3.7. Trinohex Ultra
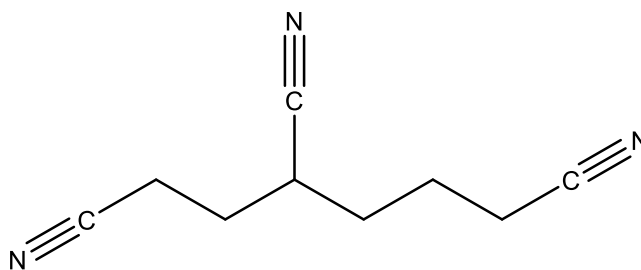
Figure 3.34: Chemical structure of 1, 3, 6 – hexanetricarbonitrile (Trinohex Ultra).

Trinohex Ultra (1,3,6-hexanecarbonitrile) is introduced from Ascend as an electrolyte additive proven to improve the performance and life extension of lithium-ion batteries (see Figure

3.34). It forms a protective film around the cathode, which prevents the dissolution of metal ion, electrolyte decomposition, and attack of hydrogen fluoride. This inhibitor is also used in reducing gas formation across cathode and electrolyte chemistries (Ascend). As Trinohex Ultra's certain functionalities could be useful for halite inhibition study, it was chosen to test at 500ppm in this study. Precipitate crystals collected almost had equivalent weight and similar shape with the blank precipitate (see Table 3.19 and Figure 3.35). Overall, there was no improvement in mitigating the halite inhibition with Trinohex Ultra. Thus, Trinohex Ultra is not a halite scale inhibitor and no further studies about halite scale inhibition is necessary.

Table 3.19: Trinohex Ultra's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
500	1.44	7%

Figure 3.35: A 1.4400g precipitated crystals collected from a 500ppm Trinohex Ultra solution.

3.3.3.8. Tris(2-aminoethyl)amine (TREN)
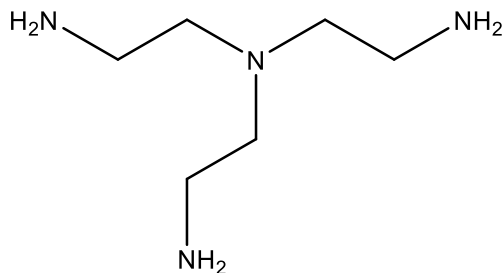
Figure 3.36: Chemical structure of TREN.

Tris(2-aminoethyl)amine (TREN) is an organic compound with the formula $N(CH_2CH_2NH_2)_3$. This soluble liquid consists of a tertiary amine center with pendant primary aminoethyl groups that adhere with the surface atoms to provide a scaffold assembly (see Figure 3.36). The name TREN is a crosslinking agent in the synthesis of polyamine networks and a tripodal ligand. In chemistry, TREN is used as building block for cryptands. In wastewater treatment, TREN is grafted with carbon nanotube for use in solid phase extraction of metal ions. It is known as a chelating agent for surface treatment of silica nanoparticles (Sigma Aldrich). As TREN's specific applications and functions are important for halite scale inhibition, it was chosen to test in this study. Precipitate crystals were collected and weighed (see Table 3.20). It could be seen that TREN had no inhibition efficiency in halite crystals. The precipitate weight of TREN solution was nearly equivalent to the blank's precipitate weight. The crystal morphology of inhibited crystals also had similar characteristics with the blank crystals (see Figure 3.37). Thus, TREN is not a halite inhibitor and further studies on halite inhibition is not recommended.

Table 3.20: TREN's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
500	1.560	0%

Figure 3.37: A 1.5600g of precipitate crystals collected from a 500ppm TREN solution.

3.3.3.9. Nitrilotriacetamide (NTAA)
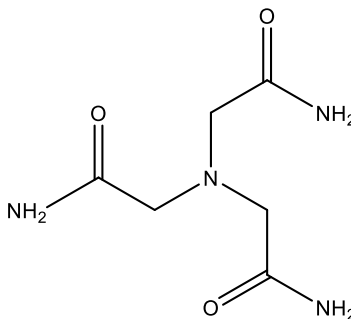
Figure 3.38: Chemical structure of NTAA.

Nitrilotriacetamide (NTAA) was first introduced as an anticaking agent used in food (Bromby et al., 1961). Until late 1960s, NTAA was applied in oil and gas industry (Roland and Ralston 1965; Ralston and Persinski 1968). NTAA has a formula $C_6H_{12}N_4O_3$ (see Figure 3.38). NTAA is known as a halite scale inhibitor in the industry (Guan et al., 2008; Hebert et al, 2016; Lu et al., 2014; Lu et al., 2015; Wylde and Slayer, 2013; Zhang et al., 2018). In this study, NTAA inhibition result was used as a benchmark to evaluate the inhibition performance of other inhibitors. A 100ppm, 200ppm, and 500ppm amount of NTAA were used to test. For 200ppm and 500ppm, as there were no crystals observed, the precipitate weight of two concentrations were 0g and the inhibition efficiency was 100% (see Table 3.21). However, small, white, irregular-shaped crystals detected in 100ppm bottle (see Figure 3.39). The precipitate was collected and weighed (0.2100g). The inhibition efficiency estimated was 87%. NTAA performed excellently in inhibit halite scale at 200ppm and 500ppm concentration. At 100ppm concentration, inhibition efficiency decreases relatively. Small precipitate crystals had dendritic form and were very fragile. However, these crystals could be removed easily by gas or water flow as they are lightweight and very breakable. Thus, in some cases with minor halite scale problem, 100ppm amount of NTAA can also be considered to use.

Table 3.21: NTAA's inhibition results with and without the inhibitor after cooling down for 36 hours at 23°C.

Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
0	1.556	0%
100	0.210	87%
200	0	100%
500	0	100%

Figure 3.39: Precipitate crystals collected from a 100ppm NTAA solution.

3.3.3.10. Conclusions

Group three has a total of nine inhibitors and two inhibitors showed to have excellent performance in inhibiting halite scale which are DTPMPA and NTAA. Further studies for DTPMPA to identify its minimum inhibitory concentration is recommended. While DTPA and TEPA also had some inhibition effects on halite scale, their inhibition efficiency was quite poor comparing to DTPMPA. Therefore, DTPA and TEPA is not recommended to use in halite scale inhibition as they have very limited performance. Besides, these two inhibitors would probably need to be used with higher concentration, but this approach is probably uneconomical in scale inhibition treatment.

Five inhibitors including salicylaldehyde, dien, DMSO, Trinohex Ultra, and TREN were ineffective for halite inhibition. These inhibitors were not only able to prevent halite crystal growth, but they also overly precipitated which depreciated the inhibition efficiency beyond the blank precipitate limit. These inhibitors absolutely had no inhibition effect on halite crystals. Thus,

they would be not recommended to do any further studies in halite scale inhibition as it is unnecessary.

Table 3.22: Group three's inhibition efficiency results

Inhibitor	Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
DTPMPA	500	0	100%
DTPA-K$_5$	500	1.3878	11%
TEPA	500	1.4006	10%
Salicylaldehyde	500	2.9876	-93%
Dien	500	1.7300	-12%
DMSO	500	1.1500	26%
Trinohex Ultra	500	1.4400	7%
TREN	500	1.5600	0%
NTAA	500	0	100%
	200	0	100%
	100	0.21	87%

4. SUMMARY AND CONCLUSIONS

In this study, novel halite scale inhibitors were identified by using a modified and improved static bottle test method. Eighteen inhibitors were classified into three groups and tested to identify their inhibition efficiency in halite scale precipitation. Ten out of eighteen inhibitors showed to have outstanding performance in halite scale inhibition (see Table 4.1 and Figure 4.1).

Six out of nine inhibitors are in group one, the polymers. Group one inhibitors completely inhibited halite scale at 500ppm concentration. Effective inhibitors in group one is suggested to conduct further studies to determine their minimum inhibitor concentration with halite scale. For CMC-Na inhibitor, the concentration for future tests is suggested between 200ppm and 500ppm.

Other effective inhibitors are in group two, the iron cyanides. Potassium ferricyanide showed to have excellent at it successfully inhibited halite scale at different concentrations. Future test is recommended for potassium ferricyanide in halite scale inhibition. Sodium ferrocyanide also effectively prevented halite crystal growth at a concentration of 50ppm. Thus, sodium ferrocyanide is also suggested to test at lower concentration to identify its minimum inhibitor concentration. Another inhibitor in group two, potassium ferrocyanide, also successfully prevented halite precipitation at 500ppm concentration. Also, three inhibitors are suggested to study the effect of iron oxidation state and the effect of cations on inhibition efficiency in the future.

The last inhibitor, DTPMPA, is in group three, the small molecules. DTPMPA performed remarkably in preventing halite crystal formation. DTPMPA is also recommended to have further test to identify the concentration threshold limit of this inhibitor.

The inhibition efficiency of these ten inhibitors were also compared with the benchmark inhibitor, NTAA, and they all had equivalent inhibition efficiency to NTAA. As they all performed

excellently like NTAA and were first-time tested in halite inhibition study, ten inhibitors are concluded as novel halite scale inhibitors.

Table 4.1: Summary of 18 inhibitors' inhibition results.

Group	Inhibitor	Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
Polymer	CMC-Na salt	200	0.1927	88%
		500	0	100%
	Alcoflow 250	500	0	100%
	Alcoflow 750	500	0	100%
	Alcoflow 920	500	0	100%
	POLYstim PCS-252	500	0	100%
	Silica inhibitor	500	0	100%
Iron cyanides	Potassium ferrocyanide	500	0	100%
	Sodium ferricyanide	50	0	100%
	Potassium ferricyanide	50	0	100%
		200	0	100%
		500	0	100%
Small molecules	DTPMPA	500	0	100%

Table 4.1: Continued.

Group	Inhibitor	Concentration, ppm	Precipitate weight, g	Inhibition efficiency, %
Small molecules	DTPA-K$_5$	500	1.3878	11%
	TEPA	500	1.4006	10%
	Salicylaldehyde	500	2.9876	-93%
	Dien	500	1.7300	-12%
	DMSO	500	1.1500	26%
	Trinohex Ultra	500	1.4400	7%
Benchmark	NTAA	100	0.2100	87%
		200	0	100%
		500	0	100%
Blank	None	0	1.5560	0%

Inhibitor efficiency, %

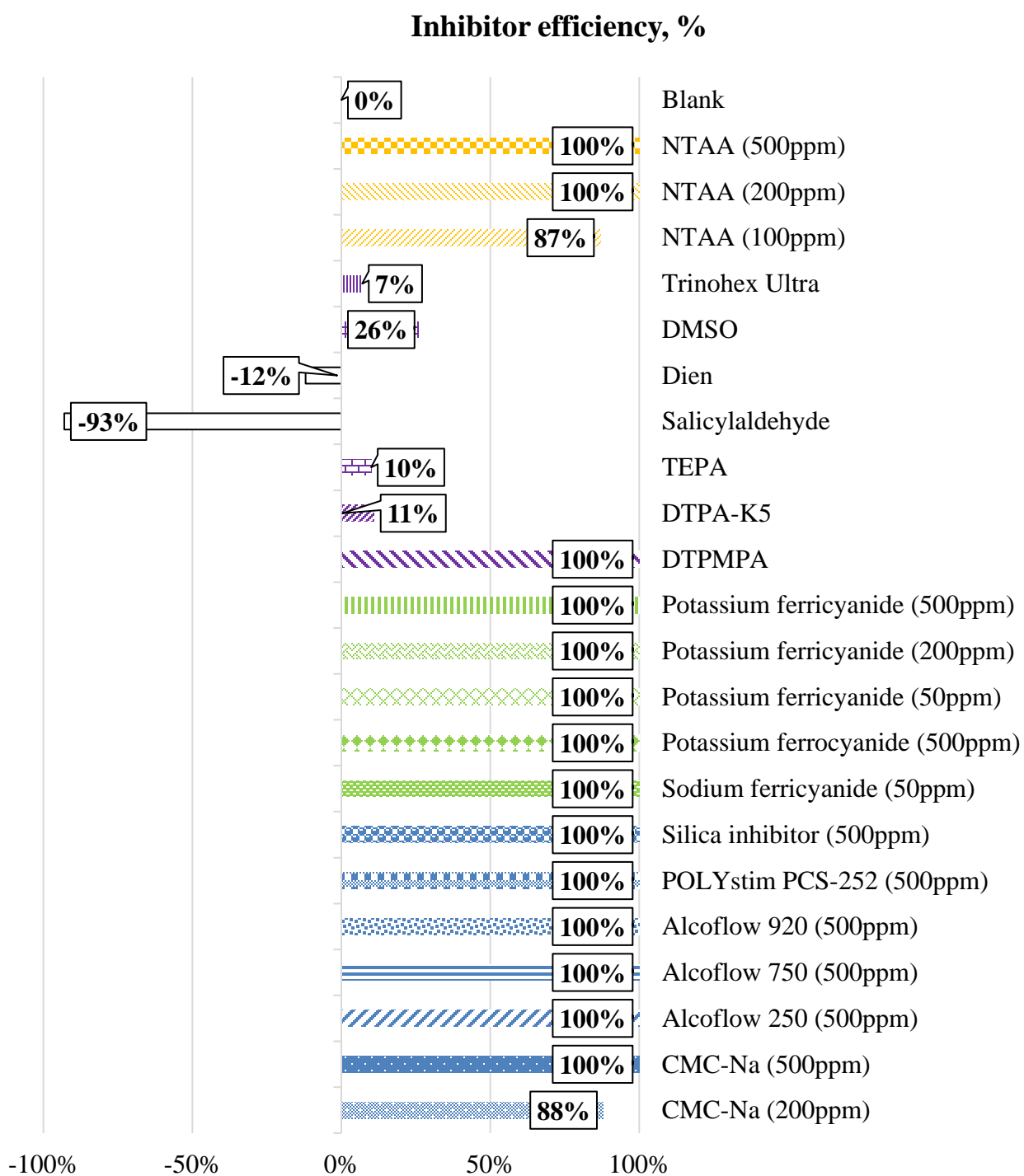|	Efficiency
Blank	0%
NTAA (500ppm)	100%
NTAA (200ppm)	100%
NTAA (100ppm)	87%
Trinohex Ultra	7%
DMSO	26%
Dien	-12%
Salicylaldehyde	-93%
TEPA	10%
DTPA-K5	11%
DTPMPA	100%
Potassium ferricyanide (500ppm)	100%
Potassium ferricyanide (200ppm)	100%
Potassium ferricyanide (50ppm)	100%
Potassium ferrocyanide (500ppm)	100%
Sodium ferricyanide (50ppm)	100%
Silica inhibitor (500ppm)	100%
POLYstim PCS-252 (500ppm)	100%
Alcoflow 920 (500ppm)	100%
Alcoflow 750 (500ppm)	100%
Alcoflow 250 (500ppm)	100%
CMC-Na (500ppm)	100%
CMC-Na (200ppm)	88%

Figure 4.1: Inhibition efficiency of 18 inhibitors tested in this study shown in the plot.

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