A Study of Precipitation and Flocculation of Calcium Carbonate and Magnesium Hydroxide in Alkaline Flooding

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Abstract: Precipitation of multivalent ions has been recognized as a major problem in oilfield operations. In alkaline flooding, precipitation of calcium carbonate and magnesium hydroxide, known as alkaline scaling, is a major concern, despite its vital role in increasing heavy oil recovery. In this study, several types of polymers were examined to investigate their potential of minimizing the total suspended solid from injection water. It was found that certain polymers successfully reduce 99% of suspended solid from water which strongly assist flow injection system and prevent scale formation in surface and subsurface equipments.

Keywords: Alkaline Flooding, Calcium Carbonate, Precipitation, Flocculation

INTRODUCTION

The precipitation of insoluble deposits is an undesirable phenomenon in oilfield and industry technology. The noted concern has been given serious attention since precipitation and scale problems have caused considerable damage in surface and subsurface facilities. The precipitated material, which forms during injection or production processes, gets accumulated and settled on pipeline walls and which eventually forms a thick impermeable layer of scale. Moreover, the issue becomes more crucial in oilfield operations when precipitation and scale problems lead not only to formation damage but also to a decline in oil production, emergency shutdown, and production intervals (Moghadasi *et al* 2003), (Voloshin *et al* 2003; Al-Rawajfeh *et al* 2005).

Alkaline scale is known as the precipitation and deposition of calcium carbonate ($CaCO_3$) and magnesium hydroxide $Mg(OH)_2$ in alkaline solution (Cowan and Weintritt 1976). This precipitation is formed due to several factors. The main factor is the crystallization of the inversely soluble salts calcium carbonate, magnesium hydroxide and calcium sulphate, in declining rank. In alkaline flooding, as a result of increasing pH value from as high as 13.5 to near 7 at various points within the reservoir, some active hydrated material initially develops and converts to be less active and in more crystalline form. This process with adequate reactive surface, first results in precipitation of magnesium hydroxide and then calcium carbonate as the magnesium form is less soluble than the calcium form in a pH range of 9 to 11. The overall reactions mechanism governing the alkaline scale can be expressed as follows. A substantial amount of OH- ions in presence of CO_2 results in a strong alkaline aqueous solution.

$$CO_3^{2-} - H_2O \leftrightarrow CO_2 + 2OH^- \quad 2.1$$

$$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3 \quad 2.2$$

$$Mg^{2+} + 2OH^- \leftrightarrow Mg(OH)_2 \quad 2.3$$

Chemical techniques are known to be the most effective scale removal and prevention treatments in oilfield and industry operations. These include chemical precipitation, acid injection, addition of anti-scaling compounds and polyelectrolyte.

For the purpose of controlling the alkaline scale (calcium carbonate and magnesium hydroxide), several methods such as acid injection, acid forming salts, acid forming gases and polyelectrolyte techniques have been reported in the literature. Acid injection methods are based mainly on lowering the pH, in order to eliminate the scale. Different types of acids including sulphuric acid and hydrochloric acid have been proposed and used. However, using a

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strong acid such as hydrochloric acid may cause other problems like corrosion which results in increased cost of operation or production. Thus, strong acids are not recommended (York and Schorle, 1966). Some other methods were used to control alkaline scale such as the addition of acid forming salts (Ferric chloride, sodium acid, ferric sulphate and aluminium chloride). In this work, an experimental study focusing on precipitation calcium carbonate and Magnesium hydroxide has been done. The study focuses on the removal of scale forming constituents from injection water.

EXPERIMENTAL

In this study, a series of four major experiments have been conducted, Graduate Cylinder Test and Sedimentation Column Test have been carried out to study the capability of polymers in settling the solid particles from injection (brine/alkaline/polymer) water. Permeability measurements have also been done to investigate the potential of polymer in increase flow process, Flocculation Flow Test has been done to study calcium carbonate and magnesium hydroxide precipitation mechanism in dynamic process. All experiments were conducted at ambient temperature (22± 0.5°C) using sodium hydroxide solution at a constant concentration of 0.4 wt%.

Fluids and Chemicals: Pelican brine samples were collected from a heavy oil reservoir in Western Canada. The samples were analyzed by the Saskatchewan Research Council analytical lab and formulated in the lab for experimental use. The analyses of formation brine are shown in Table 1. In addition, four anionic polymers and six cationic polymers have been selected for study. Types and specification of those polymers are shown in Table 2.

Measurement of Total Suspended Solid: The main task in this study was to determine the total suspended solid for such a composition (brine/alkaline) solution, which will help in investigating capability of polymer in removing the suspended material. The base value for the total suspended solid (mg/kg) was obtained theoretically and experimentally.

The theoretical value was calculated according to the following chemical reaction;

Table 1. Analysis of Pelican Brine Composition.

Properties	Percentage (%)
Ph @ 20 °C	7.27
Chloride, mg/l	15600
Sulfate, mg/l	2
Sodium, mg/l	8900
Calcium, mg/l	380
Magnesium, mg/l	280
Iron, mg/l	0.62
Potassium, mg/l	80
Total dissolved solids, mg/l @ 110 ° C @ 180 ° C	 28020 27560
Bicarbonate as $CaCO_3$, mg/l	1360
Sulfide as H_2S, mg/g	120

Table 2. Specification of utilized Polymers.

Polymer Name	Polymer Type	Mw (MM)	Cationic Degree (%)	Hydrolysis Degree (%)
AN 934 PGO	Anionic	20	-	35
AN 934 PG1	Anionic	20	-	35
AN 910 PGO	Anionic	13	-	10
FA 920 PGO	Nonionic	10	-	<1
C 5045	Cationic	10	45-50	-
C 3035	Cationic	5-6	30-40	-
C 5015	Cationic	10	15-20	-
C 3098	Cationic	5-6	90-100	-
DC 4015	Cationic	7-8	15-20	-
DC 4070	Cationic	7-8	70	-

$$Mg^{2+} + 2\left(OH^{-}\right) = Mg(OH)_2 \quad (1)$$

$$HCO_3^{-} + (OH)^{-} = H_2O + CO_3^{2-} \quad (2)$$

$$Ca^{2+} + CO_3^{2-} = CaCO_3 \quad (3)$$

$$Ca^{2+} + HCO3^{-} + (OH)^{-} = H_2O + CaCO_3 \quad (4)$$

By calculating the reaction constant K_1, K_2, K_3, and K_4 and solubility constant Ksp, both the total suspended solid TSS (mg/kg) & total dissolved solid TDSW (mg/kg) were found to be 1600 mg/kg and 0.0284 mg/kg respectively.

The experimental measurement was studied at room temperature with a constant alkaline (0.4wt %) and polymer concentration (0.5-3 ppm). A Watman filtration paper number 41, with a fast flow property, was dried for two hours in a 105^{o}C oven and weighed until the net weight was obtained. Then the paper was carefully dropped onto a metal desk on the filtration apparatus. After all the liquid was filtrated, the wet paper was immediately measured after the last drop of liquid passed. It was then placed in an oven for drying, for two hours. The paper was weighted again and measurement was repeated twice for this step in order to reduce errors. Total suspended solid was calculated using a calculation method, as shown in Table 3.

To calculate the removal efficiency of precipitation solid, the total volume of suspended solid per litre was obtained, theoretically and experimentally. Those values were 1600 mg/kg and 1440 mg/kg, respectively. The theoretical value 1600 mg/kg was taken into consideration to calculate the removal efficiency because of possible errors appearing in the experimental result. There are two possible reasons for this error. First, during the filtration process, some particles stick on the wall of the filtration cylinder and do not form sediment on the precipitation cake. Secondly, some fine precipitation particles could pass through the filtration paper.

Settlement Test: Two main experiments were performed to select the best polymer, concentration and mixing technique. Firstly, screening test experiments were carried out in a 250 ml graduate cylinder. A volume of 200 ml, 0.4 wt% NaOH solution was used for each set of the test at different polymer concentration (1, 2, 3 and 5 ppm). Both polymer, Alkaline and brine solution were prepared at desirable concentration and a given amount of brine was added to a 1 litre plastic bottle during each experiment. Then a measured volume of alkaline solution was transferred to the bottle with a syringe. Afterward, cylinder was turned ten times from horizontal position to vertical position and left for two minutes, and then a certain volume of polymer was added to the aqueous solution with a syringe. The bottle was turned ten times from vertical to horizontal and finally the solution was poured into a graduate cylinder for measurement. Measurement starts when the interface of the precipitation begins to settle in the graduate cylinder. Both time and volume were continuously recorded until precipitation remained constant at the bottom of the cylinder. Fig. 1 shows graduate cylinder test and the experimental procedure.

Secondly, Sedimentation Test experiments were carried out at three different settlement times, 60, 35 and 45 minutes, respectively. Also, two types of mixing were used in this test. First, when settlement times were 60 and 35 minutes, a bottle-rolling technique (10 + 10) was used. Secondly, when settlement time was 40 minutes, a rotating technique was used (2 minutes mixer+15 minutes rotating at 10.5-11 rpm using a speed reducer device). Furthermore, at each settlement time,

Table 3. Measurement of total suspended solid.

Sample	Polymer (C) ppm	Vol.(kg)	W (B)	W.dry (B+P)	W.wet (B+P)	W.dry (B+P+S)	TS (g)	TDS (g)	TSS (mg/kg)
Brine+NaOH	0	0.5298	34.1981	34.3389	34.7408	34.3608	0.0219	0.0108	21
AN 934 PG1	3	0.5100	36.8713	37.0073	37.3854	37.0238	0.0165	0.0103	12
C 5015	3	0.5119	34.1963	34.3350	34.7646	34.3533	0.0183	0.0117	13
AN 934 PG1	0.5	0.5247	36.8696	37.0073	37.3692	37.0255	0.0182	0.0097	17
C 5015	0.5	0.5102	28.4493	28.5926	29.0016	28.6114	0.0188	0.0111	15

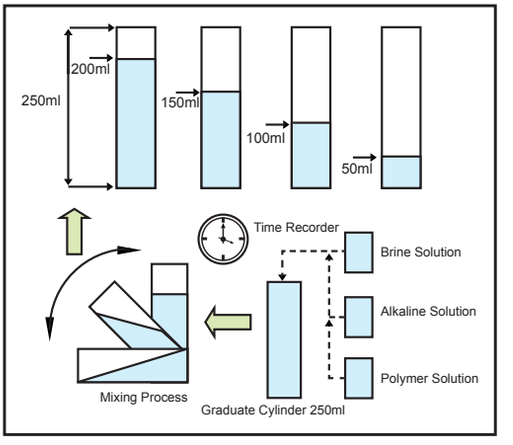
B: Beaker P: Paper S: Sedimentation TS: Total solid
TDS: Total Dissolved Solid TSS: Total Suspended Solid

the removal efficiency of each type of polymer was investigated (AN 934 PG1 and C 5015) at three polymer concentrations (0, 0.5 and 3 ppm). Total suspended solid and settlement time for each polymer concentration was obtained. Fig. 2 illustrates sedimentation column test apparatus and procedure.

Permeability Test: The objective of this test is to understand the capability of polymer in increasing the flow process. Polymer particles combine with small precipitation particles and form larger particles. Consequently, the solution liquid travels between particles and the process becomes much faster. Permeability of precipitation cake was measured at constant pressure and at volumes of solution ((3 kg, 750 gram). Both, concentrations of alkaline solution and polymer were constantly maintained at 0.4% and 3 ppm, respectively. After mixing, the solution was left overnight for settlement and the following day the solution was carefully and repeatedly added to the filtration cylinder. This test was undertaken for 40-60 hours until all the liquid filtrated through a filter paper. During the test, data for pressure, time and filtrated volume were recorded at regular intervals by using a constant rate slow pump filtration. A pressure gauge was used to measure pressure values during the experiment.

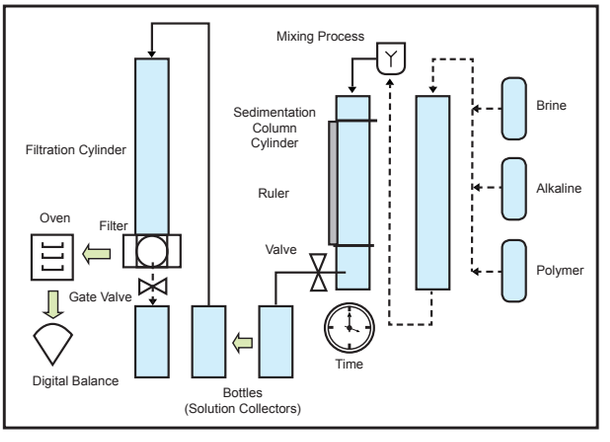


A



B

Fig. 1. Settlement Test. (A) Graduate Cylinder equipment; (B) Test Procedure.



A



B

Fig. 2. Sedimentation Test. (A) Test Procedure; (B) Test Apparatus.

Flocculation Flow Test: Efficiency of polymer usage during injection flow process was evaluated throughout this test. By giving sufficient mixing time to alkaline and polymer solution, polymer particles were allowed to communicate and get attached with other particles forming large flogs. Two sets of flocculation experiments were accomplished, a screening test with only alkaline and brine and then with a polymer AN 935 PG1 at 3 ppm. Measurement of total suspended solid and removal efficiency was performed and good results were obtained. Fig. 3 shows experimental set up for Flocculation Flow Test.

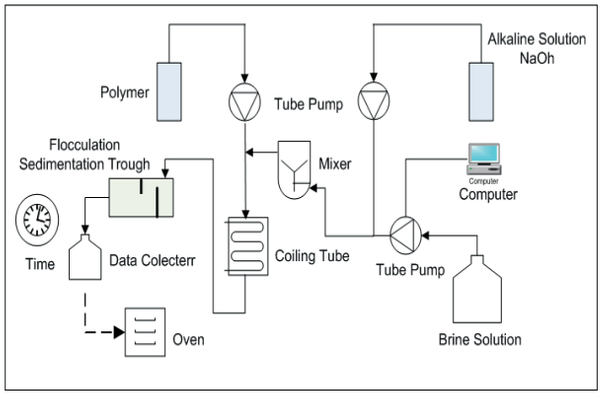
A flocculation sedimentation trough model was designed to measure the removal efficiency of suspended solid from clear liquid. Precipitation settled in a flocculation sedimentation trough and clear liquid was collected from the model output. A premixing tube (DI 7/16" and V 46.3 ml) was used to mix the suspension liquid brine and alkaline before settlement in the trough. The test was carried out at serious flow rates and two different techniques were developed for flocculation mixing positions (Flat & Wave). At last, data for removal efficiency of anionic polymer was determined.

RESULTS AND DISCUSSION

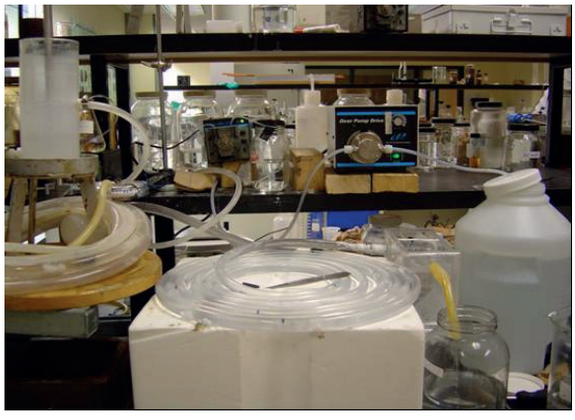
Selection of Polymers: In this study, Graduate Cylinder Test, and Sedimentation Column Measurement were carried out to screen best polymers for Pelican injected water brine. Two polymers (AN 935 PG1 & C 5035) were selected out of ten. Those polymers have provided the faster settlement time as shown in Fig. 4. During screening test, time was regularly recorded at certain reading volumes (150 ml, 100 ml, and 150 ml (again 150 ml)). Those volumes were plotted against time at where precipitation surface was, and then the sedimentation speed was obtained using the following equation:

Results show the settlement rate has the best settlement efficiency when 3 ppm polymer concentration is used, as described in Fig. 5. At constant polymer concentration (3 ppm), the settlement rate achieves its optimum value, as compared with other concentrations. This polymer concentration is a proper concentration that could be used in future experiments to demonstrate the polymer potential of precipitation removal of calcium carbonate and magnesium hydroxide from injection water. Among two different mixing techniques, results of sedimentation experiments show that rotating technique using speed reducer device at 10.5-11 rpm provide good mixing status. Moreover, values acquired of total suspended solid confirm proper polymer concentration is 3 ppm as showing in Fig. 6.

Permeability Measurement: Filtration test results indicate the polymer accelerates the flow process. As the size of particles increase, more and wide channels are created through the precipitation cake. Thus, the cake permeability becomes higher. However, when all precipitation sediment is on the filtration cake, the permeability reaches its minimum value. The effect of polymer can be seen through a comparison where no polymer is added to a solution and at 3 ppm polymer concentration.



A



B

Fig. 3. Flocculation Flow Test. (A) Test Procedure; (B) Experimental Set up.

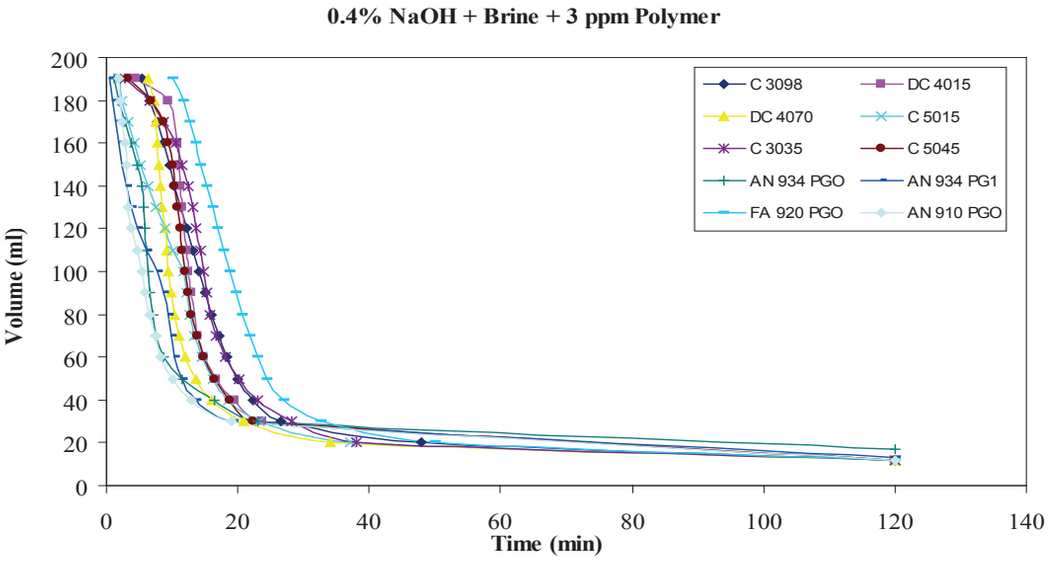


Fig. 4. Settlement rate of polymers at 3 ppm polymer concentration.

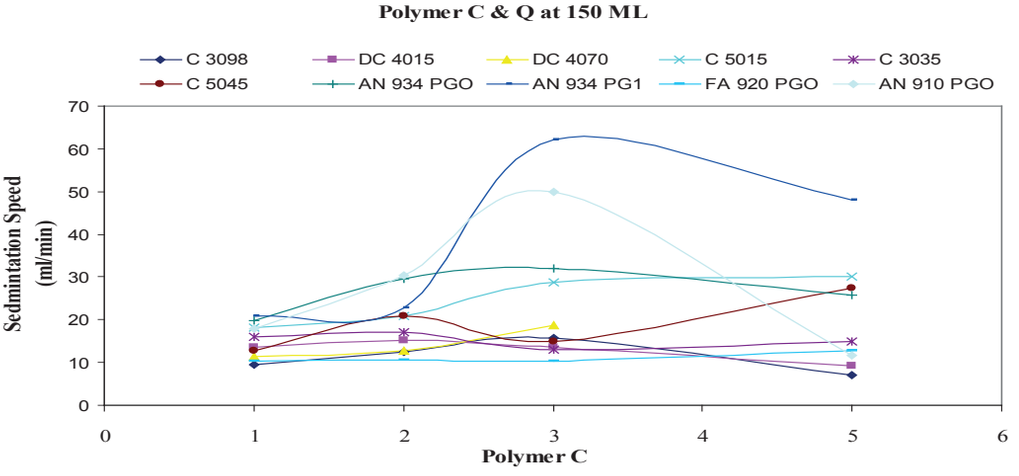


Fig. 5. Sedimentation Rate for all Polymers at a Constant Volume of 150 ml.

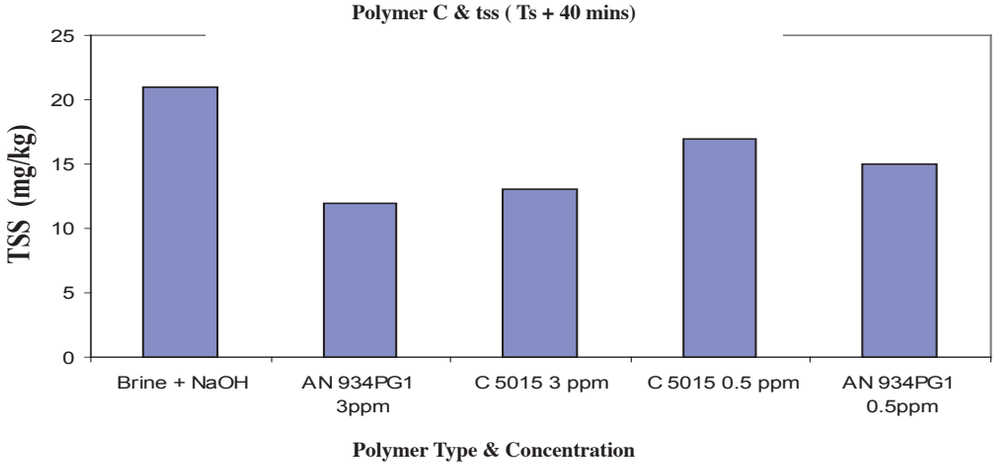


Fig. 6. Total Suspended Solid Data at a Sedimentation Time of 40 Minutes.

The filtration permeability is higher in presence of polymer than when no polymer added. However, the permeability declines during the filtration process as more sediment particles settle on the filtration paper and the cake's thickness increases. Fig. 7 illustrates permeability measurements for 3 kg solution.

Flocculation & Removal Efficiency Test: To represent the injection flow process, flocculation flow experiments were performed to investigate the polymer potential of increasing the removal efficiency and to reduce the total suspended solid from the clear liquid. Results show that at a low flow rate, the amount of solid particles increase slowly with increase of flow rate, until it reaches a certain value called critical flow rate. Beyond critical flow rate, solid particles in the clear liquid tend to increase rapidly. This phenomenon is represented in flocculation screening test where no polymer was added to solution. Afterward, in second test when polymer was added to the suspension liquid, 99% removal efficiency of suspended solid in clear liquid was obtained. This percentage indicates the success of using polymer for injection water treatment. Results also clearly demonstrate the necessity of using certain techniques of polymer handling in order to achieve high removal efficiency values. Fig. 8; represent removal efficiency of Anionic polymer.

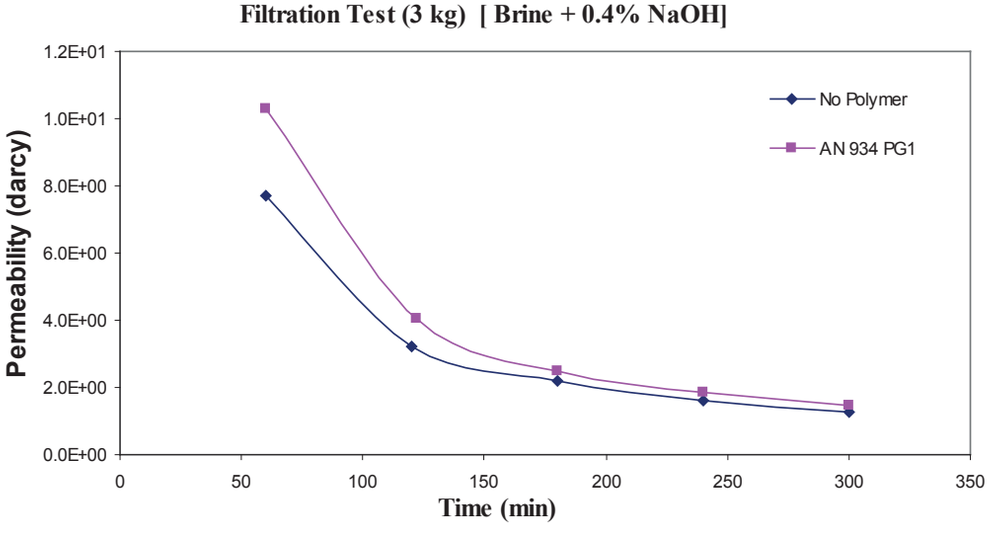


Fig. 7. Permeability Measurement for 3 kg solution.

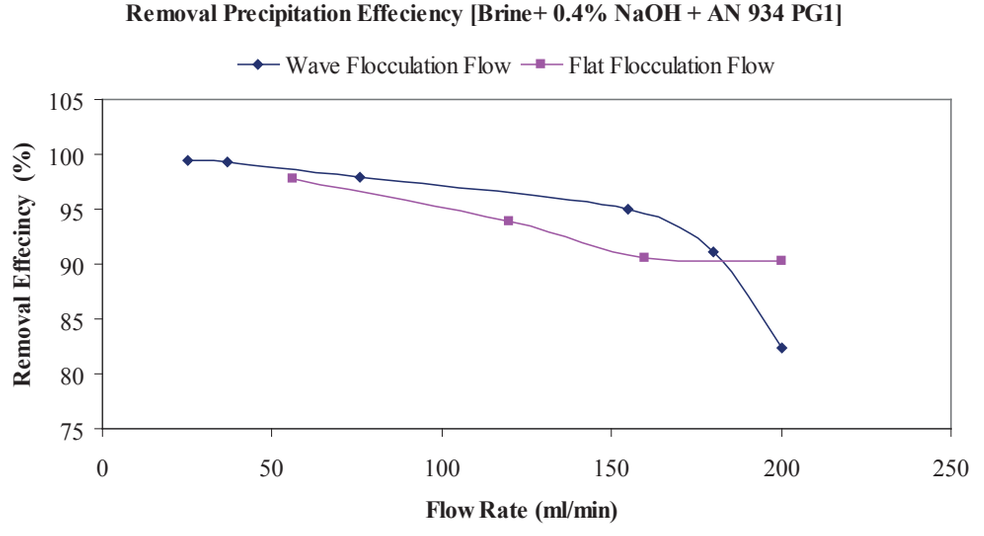


Fig. 8. Removal Efficiency of Anionic Polymer AN 934 PG1.

CONCLUSIONS

Based on the presented results, the following conclusions can be drawn:

1) Experiments of settlement and sedimentation rates indicate anionic polymers have better precipitation removal efficiency than cationic polymers and are highly recommended for use in practical implementation.
2) The prerequisite experimental setup for all precipitation tests was designed to measure the feasibility of polymer by reducing the total suspended solid from injection water.
3) The maximum removal efficiency was achieved by using Anionic polymer AN 934 PG1 at 3 ppm concentration and it reached 99%.

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