

## Experimental Study of Chemical Flooding Using New Chemical Component to Enhance Oil Recovery

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**Abstract:** The objective of this research study is to introduce of new chemical component to Enhanced Oil Recovery (EOR). Crude Terephthalic Acid (CTA) as a macromolecule and one of the isomers of the three phthalic acids is an intermediate product of petrochemical industries which can be used as an alternative to the traditional Hydrolyzed Poly Acryl Amide (HPAM). Crude Oil samples from an Iranian oil field were selected to be used during the flooding tests. Comparison between water flooding and CTA flooding as a secondary oil recovery process revealed that the recovery was improved by 10% when CTA was used. The effect of various injection rates and different concentration of chemical solutions on the recovery factor have been checked and the results showed that high CTA concentrations and low injection rates are the optimum criteria for higher oil recovery efficiency and this chemical as a viscous surfactant and IFT reducer, would be stable in extreme conditions of high salinity and high temperature and therefore, it can be used for reservoirs with high salinity and temperature, too.

**Keywords:** Chemical flooding, CTA, EOR, sand packed model

### INTRODUCTION

Polymers are chemical compounds which consist of repetitive units called monomers that can be added to the injected water through an oil reservoir to achieve IOR (Improved Oil Recovery). The main purpose of polymer injection during water flooding is to decrease the mobility of the injected water by increasing the solution viscosity and decreasing the rock permeability. Polymer is used to increase the viscosity of the injection fluid for better profile control (Berger and Lee, 2006). Poly Acryl Amide is a condensation polymer with an unusual and useful property. The structure of Poly Acryl Amide is similar to that of polyethylene, but having a hydrogen on every other carbon replace by an amide group,  $-\text{CONH}_2$ . The molecule is composed of repeating  $-\text{CH}_2-\text{CH}(\text{CONH}_2)-$  units (Sung-Hua, 2007). The amide groups allow for linking between polymer strands. The  $-\text{CONH}_2$  group from one molecule can react with the same group of another molecule, forming a link between them with the structure  $-\text{CONHCO}$  (Zeynali *et al.*, 2006). Aparecida and Silva studied polymer injection projects in Brazil and they expressed that Polymer flooding is the best established of the chemical enhanced oil recovery. Laboratory and field

application have shown that the polymer flooding process is most effectively applied in the early stage of a water flooding project when the mobile oil saturation is still high (Aparecida de Melo *et al.*, 2002). Today partially hydrolyzed Poly Acryl Amide is widely used in water handling and EOR processes to displace more oil and increases the recovery efficiency of water flooding process by modifying the water/oil mobility ratio, as an anionic coagulant. Partially hydrolyzed Poly Acryl Amide is used as a pushing fluid in the oil injection wells to improve sweep efficiency of water flood into oil reservoirs. Polymer flooding is most common chemical enhanced process for improving oil recovery factor in oil fields Compare to water flooding. Polymer basically increases the injection water viscosity and reduces the porous media permeability, then improves the vertical and aerial sweep efficiency. The objective of polymer flooding is to reduce water-oil mobility ratio, which with reducing mobility ratio, sweep efficiency is increased and oil recovery is enhanced (Du, 2004). In actual a water-soluble polymer is added to injecting water so that it can increase the solution viscosity because of its high molecular, that causes the water mobility into reservoir is reduced and polymer solution can be better sweep oil and

oil recovery is increased compare to water injection. Therefore it can sweep the more area of oil bearing reservoir and delay the breakthrough time as well. During a standard water flooding, breakthrough time relatively come up fast and water fingering takes place into the oil bunk because of high mobility of water, therefore its sweep efficiency will be reduced (Perry *et al.*, 1982; Du, 2004). Polymers because of increasing injection water viscosity, causes that the fingering effect will be reduced into oil reservoirs and the sweep efficiency can be improved (Alban and Gubitta, 1999). Hydrolyzed Poly Acryl Amide (HPAM) and Xantan gum as synthetic and natural polymer respectively, are usually used in polymer flooding both in field and pilot projects. In 1964, Pye and Sandi established that polymer flooding can increase oil recovery compared to water flooding, they expressed that partially Hydrolyzed Poly Acryl Amide (HPAM) can reduce the mobility of displacing water with increasing its viscosity and improve the sweep efficiency of flooding process (Du, 2004). Fulin *et al.* (2006) utilized high concentration of HPAM polymer solution through flooding studies for Canadian oil field and illustrated the promising effect of HPAM to increasing recovery factor is around 21% (OOIP) (Fulin *et al.*, 2006). Zhang and Halliburton (2006) studied Alkaline-Surfactant-Polymer (ASP) flooding during the EOR process of a Chinese oil field and stated that combination of this material can be improved oil recovery compared to polymer flooding lonely sufficiently (Zhang *et al.*, 2006). Kotler *et al.* (2007) studied the influence of combination of polymer (mobility control agent), surfactant (reducing IFT agent) and a small bi-functional molecule (increasing solubility agent and reducing salinity effect) during flooding to enhanced oil recovery factor and deduced that oil recovery can be increased by 20% OOIP (Originally Oil in Place) (Kotler *et al.*, 2007). Yadali stated that Micellar-polymer and alkaline flooding are regarded as the two major chemical flooding processes. Micellar flooding (also known as micro emulsion flooding or surfactant flooding) is a process which a surfactant slug is injected into the formation followed by a larger slug of water containing polymer (normally a high-molecular-weight polymer) which improves mobility and sweep efficiency (Yadali, 2009). This study concerns the chemical flooding process to improve oil recovery using CTA which is an intermediate product of petrochemical companies. A sand packed model was utilized to investigate the various properties of CTA related to its flooding ability. Crude Terephthalic Acid (CTA) was used in this study as a macro monomer that can increase water viscosity because it belongs to polyesters family with relatively high molecular weight. The objective of this study is to reduce water-oil mobility ratio, using various concentration of CTA that in this investigation was replaced by HPAM. It was found that although viscosity property of CTA is very less than HPAM but because of IFT property of CTA

further percent of oil could be recovered that it was observed during our experiments. Experiments are designed to study effects of injection rate, concentration, temperature and salinity on flooding processes. Too this work will investigate a new polymer having some advantages which enable it to overcome the obstacles encountered by polymer flooding at high temperatures and high salinity.

## MATERIALS AND METHODS

**Crude terphthalic acid:** CTA which is an abbreviation for "Crude Terephthalic Acid " is one isomer of the three phthalic acids. It is mostly used as a commodity chemical, substantially as a beginning compound for making of polyester (specifically PET). It has the chemical formula  $C_6H_4(COOH)_2$  and known as 1, 4-benzenedicarboxylic acid as well. In order to find out how well the CTA will do, a comparison between it and water is made during flooding process and the result are shown on Fig. 1. As one can see, the CTA flooding has more recovery factor around 10% than water injection. Besides, because of the production of CTA near the Iranian oil field; it was opted for this study during flooding processes. Water flooding can be replaced by CTA flooding in secondary stage because in the time of tests, there is neither signs of adsorption on sand surface nor reduction of absolute permeability are recognized.

**Methodology:** In this study work, considering polymer flooding, a cylindrical sand packed model was built. A glassy cylinder with 2.5 cm inside diameter and 25 cm height was packed with two sizes of sand (50 and 100 mesh number). After packing, both sides of pipe were covered with fine metallic tissues and the fitting were connected over there. At the first, the porosity and permeability were measured. When the set up was prepared,  $CO_2$  flooding was done so that the trapped air would go out and then the model was weighted. An adequate amount of Water was injected and the model was weighted again to calculate the pore volume

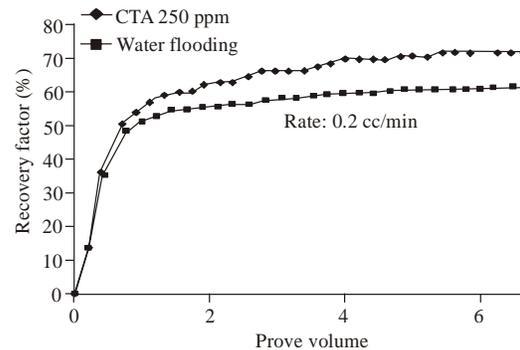


Fig.1: Comparison between CTA and water flooding in secondary state

Table 1: Solution properties

Solution No.	CTA concentration (ppm)	Watertype	TDS(ppm)	Solution viscosity(Pa*s)	Oil viscosity (Pa*s)
1	0	Fresh	1200	0.000976	0.00635
2	100	Fresh	1200	0.002400	0.00635
3	250	Fresh	1200	0.002700	0.00635
4	500	Fresh	1200	0.003600	0.00635

Table 2: Characterization of experiments

Test No.	K(Darcy)	Porosity (%)	Injection rate(cc/min)	CTA Co. (ppm)	Solution viscosity (Pa*s)	Vol. of injection (P.V.)	RF (%)
1	6.76	37.496	1.7	250	0.0027	6.466	0.609
2	6.78	37.496	1.0	250	0.0027	5.783	72.000
3	6.76	37.496	0.2	250	0.0027	4.7283	72.307
4	6.23	31.247	0.4	250	0.0027	5.624	63.026
5	7.23	7.4960	0.6	250	0.0027	4.769	76.000
6	6.93	37.496	0.8	250	0.0027	4.668	62.227
7	6.81	37.496	1.0	500	0.0036	7.755	85.000
8	7.92	43.746	0.2	500	0.0036	2.989	63.727
9	7.48	39.996	0.6	500	0.0036	5.216	72.888
10	7.39	38.746	3.0	500	0.0036	7.365	83.867

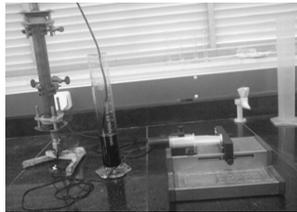


Fig. 2: Schematic of the model

and porosity. Permeability was calculated by employing Darcy’s law and injecting the model, using a water source positioned at a sufficient height and the produced flow rate was measured. After characterizing the model, the oil flooding was done using a very precise syringe pump and the connate water was measured. Later than, the model was prepared and the experiments were started (Fig. 2). Various CTA solutions were injected in secondary state until no more oil will leave the model and during the test, the volume of oil and polymer solution is going out the model and the time of depletion were recorded. Crude Oil samples from an Iranian oil field were selected to be used during the flooding tests. CTA solutions were made in concentrations of 100, 250 and 500 ppm, respectively. Because of low solubility of CTA, the solutions were heated up to 70°C while it was stirred. Fortunately, the made solutions were uniformed during the tests. In efforts to investigate the effect of solution viscosity on recovery factor, three different concentrations were prepared. Table 1 shows the solution properties. Experiments were performed as previously described. Solutions with different concentrations were injected in a constant rate (0.6 cc/min) and three tests were done in constant concentration (250 ppm) at different rates. Table 2 illustrates the characterizations of experiments. This research study was carried out in Enhanced Oil Recovery (EOR) Research Center located in Shiraz, Iran in 2007, and experiments related to PVA, was carried out in Iran Polymer and Petrochemical Institute (IPPI) in August and September 2011.

## RESULTS AND DISCUSSION

**IFT reducing property of CTA:** To check the IFT reducing property of CTA an experiment was performed. After preparing the model a 250 ppm solution of HPAM was injected in secondary stage until no more oil can leave the model and then a solution of CTA with 250 ppm concentration was injected in tertiary state. The 250 ppm solution of CTA increases the viscosity of water up to 2.5 cp which is less than the HPAM, but it could recover more oil from the sand packed model (Fig. 3). Therefore this may be attributed to surfactant behavior of CTA. In addition theoretically CTA belongs to polyester groups which make soap foam when solve in water.

**Effect of concentration of injecting solution on recovery factor:** Injections of CTA solution with three concentrations were done. Injections were doing until no more oil could leave the model. As it was expected the solutions with more concentration can recover further original oil in place from the sand packed model. The results of injection with various concentrations are shown on Fig. 4. Since more viscous solution will displace oil across the model ideally and invade more area of the model, the breakthrough time will delay and the viscous fingering effect will be mitigated. Therefore, the recovery factor and sweep efficiency will rise. The results from the experiments, also, verify this physical concept.

**Effect of injection rate on recovery factor:** Injection experiments were implemented at three rates of injection in order to find out the relation of flooding rate and recovery factor with injecting of high rate solution which expected to bypass the bulk of oil can also impose more pressure drop on porous medium. Therefore the fingering effects may further be observed as well as coning phenomenon will be included because of unbalancing between gravitational forces and viscous forces at high

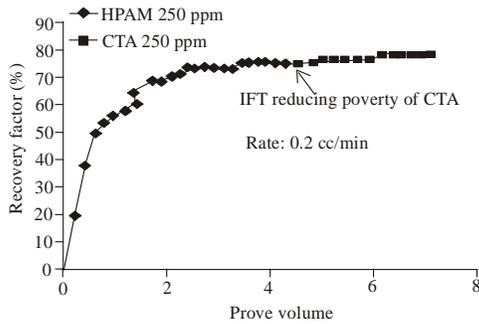


Fig. 3: IFT reducing property of CTA

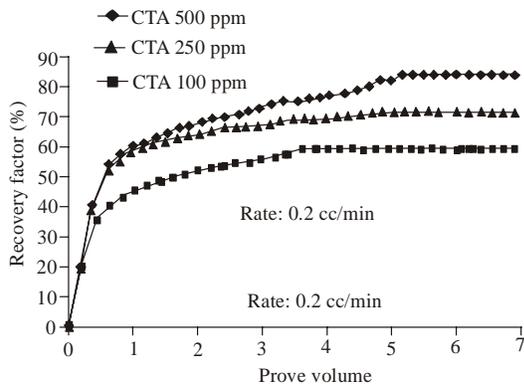


Fig. 4: Effect of solution concentration on recovery factor

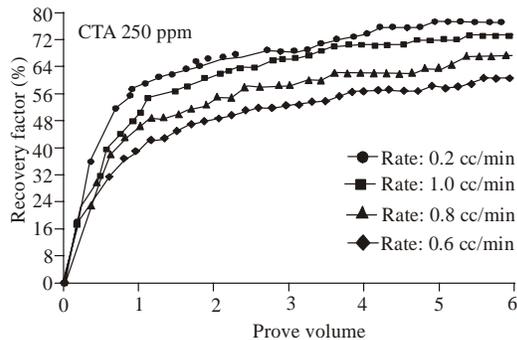


Fig. 5: Effect of injection rate on recovery factor

rates. The results are exhibited in Fig. 5. Since high rate of injection cause to sweep less area of model and also, the movement of solution through the model is more longitudinal, the breakthrough time will decrease and recovery factor will reduce as well.

**Extreme salinity and temperature:** The high salt concentration decreases efficiency of a polymer solution, especially by decreasing its viscosity. At some salinity level, the relative viscosity of PHPA becomes constant (Zeynali *et al.*, 2006). It is concluded that HPAM is not a good candidate for the reservoirs with high salinity. On

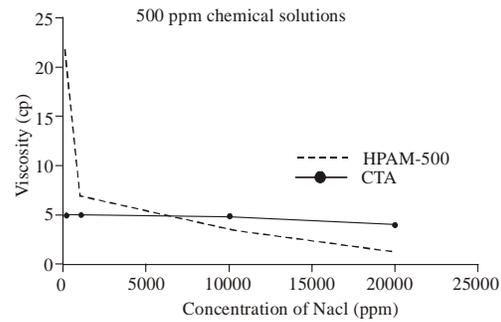


Fig. 6: Comparison between HPAM and CTA in various salinity

the other hand, Polymers are very sensitive to the thermal effect. At high temperature, the rate of hydrolysis of poly acryl amide polymers is significant over reservoir time scales. Thus, the hydrolysis and the corresponding change in viscosity as the polymer flows through the reservoir, should be taken into account. It is believed that most of the polymers decompose at high temperatures and their applications will be hindered. Previous works in this area showed that the reservoirs with temperature higher than 300°F should usually be avoided for using HPAM (Standford, 1964). In addition, temperature rise leads to a delay in achievement of full adsorption on the rock surface. Therefore, more pore volume of polymer solution is necessary (Fulin *et al.*, 2006). Also, water viscosity slightly decreases with increasing temperature.

**Effect of salinity on efficacy of CTA solution:** Generally proved that the concentration of anionic compounds such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  have some effects on flooding processes which are imposed on oil reservoirs to improve recovery factor. Salinity which specially means concentration of  $\text{Na}^+$  has a drawback on Hydrolyzed Polyd Acryl Amide (HPAM) efficiency during polymer flooding and reduces the its helpfulness, therefore HPAM should be used for such reservoirs which have low brine concentration. However, CTA shows resistance against salinity up to 2500 ppm. Figure 6 illustrates a comparison between Dow Pusher 500 poly acryl amide and CTA solutions related to effect of NaCl concentration on their viscosity. Hence, CTA could be a suitable candidate for polymer flooding processes of reservoirs with high salinity concentration. As expected, experimental results confirmed that with adding NaCl to PVA solution, its viscosity not only decreases with increasing salinity, but increases and therefore, this polymer will be stable at high salinity. Adding PVA to water lowers the surface tension effectively and surface tension of aqueous PVA solution decreases significantly with increasing NaCl concentration. It is significantly important that PVA is not decomposed at high concentrations of NaCl. Maximum

viscosity has been observed at 1.2 wt% NaCl. Therefore, in oil reservoirs with high salinity, this polymer could act as a viscous surfactant and it can be used. Figure 7 illustrates the viscosity of PVA NaCl solution in different concentrations.

**Effect of temperature on effectiveness of CTA solutions:** Adequate temperature ranges in which polymers remain stable without degradation are very sensitive to types of polymer. It is believed that most polymers will be decomposed at high temperatures and so miss their applicability. Reservoirs with temperature higher than 300°F should usually be avoided for using poly acryl amide because it loses their viscofying property at that temperature. But CTA can sustain temperature up to 250°C without missing its property for the reason that it is contained of benzoic loop in its structure which is very stable. The thermal stability of terephthalic acid was inspired from the effort of Randolph and Edward (2007). They performed Thermal Gravimetric Analysis (TGA) on two samples of Crude Terephthalic Acid (CTA) and two samples of PTA. One of the PTA samples and one of the CTA samples was tested in an air environment, while the other two samples were tested in a nitrogen environment. The results of analysis of TGA showed that thermal degradation and sublimation of terephthalic acid over a temperature range starting at 0°C and ending at 350°C (Randolph and Edward, 2007). To evaluate the effect of temperature on PVA polymer solution, some other experiments were done. In this case, PVA solution in various concentrations was prepared and the solution was heated up to 482°F, and it was observed that PVA solution could sustain temperature up to 482°F without missing its property and our experiments indicated that this polymer is stable at high temperatures, confirming previous study showing thermal decomposition of PVA takes place at temperature above 48°F. The same was done for HPAM solution and it was observed that thermal decomposition of HPAM takes place above 25°

### CONCLUSION

Experiments showed that CTA can improve water flooding efficiency about 10% OOIP at secondary state. Although the viscofying property of CTA solution is less compared to HPAM solution but it was used here because of its availability and economical aspects. CTA flooding at low rates shows more recovery factor because the fingering and bypassing effects will be mitigated. When CTA is flooded at high concentration, more recovery will be obtained since the more viscous solution will be obtained and mobility ratio will close to unity. Since CTA is belong to polyesters groups so that its solution exhibits the effect on reduction of interfacial tension between oil

and water. CTA is able to sustain the high salinity as well as keep its stability property at high temperatures. . We strongly recommend PVA because of its Thermal and electrolyte stability and IFT reduction compare to HPAM. Because viscosity of PVA solution increases in high salinity and also can act as gel polymer in very high salinity, it could be used for polymer flooding in oil reservoirs with such an extreme conditions. Accordingly, HPAM is decomposed at high temperatures and reservoirs with temperature higher than 300°F should usually be avoided for using HPAM, while PVA, due to its thermal stability can be utilized in reservoirs with high temperature above 480°F.

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