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Adsorption of Calcium and Magnesium Ions and Thickening Effect

REN Jiawei[a],*; ZHOU Xisheng[b]

[a]Key Laboratory of Enhanced Oil Recovery of Education Ministry Northeast Petroleum University Daqing, Heilongjiang, China.
[b]Exploration and Development Research Institute of Daqing Oilfield Company Ltd. Daqing China.
*Corresponding author.

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Abstract

According to the viscosity loss serious problem of sewage preparation polymer solution in Daqing oilfield, studied the impact of anion and cation on the polymer solution viscosity and proposed improvement measures. Research show that the cationic has great effect on polymer solution viscosity and order is: Fe^{2+}>Fe^{3+}>Mg^{2+}(Ca^{2+})>Na^{+}(K^{+}). Configuration requirements are: the Na^{+}, K^{+} content less than 3,000 $mg·L^{-1}$, preferably less than 1,000 $mg·L^{-1}$. Ca^{2+} content control less 200 $mg·L^{-1}$, Mg^{2+} content control less 100 $mg·L^{-1}$. It should be strictly controlled the Fe^{2+}, Fe^{3+} content. Anionic had no effect on the viscosity loss of HAPM solution. Mg^{2+} and Ca^{2+} are the main factors for the viscosity variation of polymer solution. To use of sodium humate solution which compound by turf and NaOH complexed Ca^{2+} and Mg^{2+}, reduced the impact of Ca^{2+} and Mg^{2+} on the polymer solution viscosity, so reached oilfield reinjection water viscosity standards. Research show that polymer solution viscosity lossed seriously when Ca^{2+} and Mg^{2+} content in 0 ~ 200 $mg·L^{-1}$, viscosity loss rate reached maximum 63.2% and 70.7%, respectively. The adsorption ratio of Ca^{2+} reached 77.50% when amount of sodium humate solution were 8mL. Similarly, the adsorption ratio of Mg^{2+} reached 83.60% when amount of sodium humate solution were 6mL. This indicated that sodium humate have great adsorption to Ca^{2+} and Mg^{2+}. Indoor experimental results confirmed the feasibility of using sodium humate complexed Ca^{2+} and Mg^{2+} to prevent viscosity of polymer solution reduced, and provides a reference for the field test.

Key words: Calcium and magnesium ions; Sodium humate; Complexe; Viscosity loss; Adsorption

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INTRODUCTION

Polymer flooding technology as the main technical measures in Daqing Oilfield had been widely used and developed. But with polymer flooding scale increases, the amount of fresh water which needed also increases with surge. If oilfield produced water can not reach equilibrium with the back fluence, the excess sewage must be treated and anti-handling. Not only increase the economic costs but also likely to cause environmental pollution. Therefore urgently need to solve the problem of water reinjection. However, their presence of sewage formulated polymer solution viscosity loss, including the impact of salinity, bacteria, oxygen and other major factors. Han (2008) believe that the salinity is the main reason for reducing the viscosity of the polymer solution. Lü (2010), Cui, Lü, and Hai (2014) believe that high metal cation is a major factor affecting the viscosity of the polymer solution. Ma (2010) believe that the salinity and metal ion content are the main factor affecting the viscosity of the polymer solution. Yang and Luo (2005) studied show that ferrous iron ions and ferric ion are the main reason, which caused polymer solution viscosity reduction. Ding, Zhang and Ma (2015) studied salinity effect on the viscosity of polymer solution by orthogonal test. But there had no considered anions' effect on the viscosity of polymer solution. So this research studied the effect of anions and cations on the viscosity of polymer solution. What is more, proposed the use of sodium humate complex calcium and magnesium ions in wastewater to reduce the impact of calcium and magnesium ions on the polymer solution viscosity (Ross & Peter, 1996). Provide a reference for reducing high concentration calcium and magnesium ions in the field sewage treatment.

1 EXPERIMENTAL

1.1 Experimental Drugs and Equipment

(a) $CaCl_2$, $MgCl_2$ were both analytical grade（Producted from Harbin chemical reagents plant）. Humic acid sodium mixture configure by the NaOH (2mol·L^{-1}) and peat solution (0.369 g·L^{-1}), after a period of uniform heating by electric furnace and then take the upper liquid (Han, Yang & Zhang, 1999). Polymer: HPAM (polyacrylamide, average molecular weight 25,390,000), producted from Daqing Refining and Chemical Company. The sewage selected from Lamadian and water quality analysis are shown in Table 1.

(b) The main instruments and equipments include Brinell DV-II viscometer(Produced from the American company Brookfield), HAAKE rheometer (Produced by Germany), MYP11-2 type magnetic stirrer (Produced from Shanghai), DK-98-Ⅱ type electronic universal electric furnace (Produced from Tianjin) and Setra-EL-410S electronic balance(Produced from American).

1.2 Experimental Methods

Preparation polyacrylamide solutions of the mass concentration of 1,500 mg·L^{-1} and then heated for 2 hours at 45℃. Then measured the apparent viscosity with HAAKE rheometer and Brinell viscometer at 45℃, 7.34 s^{-1} (Wang, Cheng & Wu,1998).

Table 1
The Sewage Water Quality Analysis of La

Sewage Source	Main ion content mg/L									Viscosity /mPa·s
	K^++Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	CO_3^{2-}	Fe	SO_4^{2-}	Salinity	
La	1278.6	22.6	9.4	842.7	1376.1	95.8	0.2	13.0	3638.4	3.0

2 RESULTS AND ANALYSIS

2.1 Effect of Na^+, K^+ on the Polymer Solution Viscosity

Added sodium ions and potassium ions to the polymer mother liquor, the viscosity measurement results are shown in Figure 1.

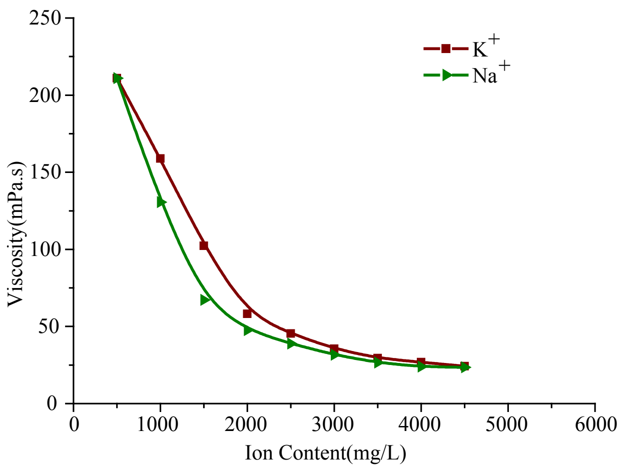

Figure 1
The Effect of Na+、K+ on the Viscosity of the Polymer Solution

From Figure 1 we can see that the viscosity of polymer solution has been declining with the amount increase of sodium ions and potassium ions. What is more, the effect on viscosity of sodium ions ia larger than potassium ions. But viscosity decline slowing when sodium ions and potassium ions' content more than 2000 mg·L^{-1}. This is because the concentration of sodium ions increase the negative charges of polymer molecules carboxylate ions become weaken, at the same time, the electrostatic repulsion between the molecules and inside polymer molecules are also become weaken (Wang, 1999). And molecular structure curl, internal friction reduction between molecules. For this reason, sodium ions and potassium ions' content must less than 3,000 mg·L^{-1}, and it should be better less than 1,000 mg·L^{-1}.

2.2 Effect of Mg^{2+}, Ca^{2+} on the Polymer Solution Viscosity

Added calcium and magnesium ions to the polymer mother liquor, which diluted with deionized water (Taylor, 1995), the viscosity measurement results are shown in Figure 2.

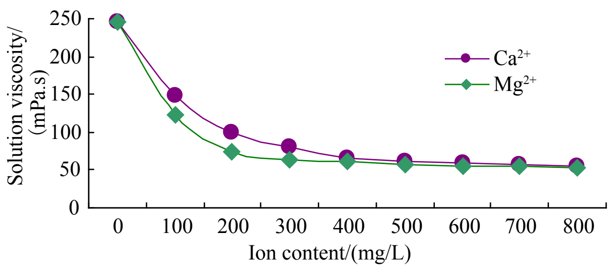

Figure 2
The Effect of Ca^{2+}, Mg^{2+} on the Viscosity of the Polymer Solution

From Figure 2 we can see that the solution viscosity exist heavy losses when calcium and magnesium ions' content in 0-200 mg·L^{-1} With calcium and magnesium ions content raise, the viscosity of polymer solution loss increase. The polymer solution viscosity reduction because calcium and magnesium ions caused polymer molecule condensation and molecular chain contraction (Chen, Song & Fan, 1998), simultaneously occured hydration, resulting in polymer flocculation and sedimentation (Aoba, Moreno, & Shimoda, 1992). However, the effect of calcium ions on polymer solution viscosity less than magnesium ions, because the ionic radius of calcium ions large than magnesium ions, calcium ions polarity and the ability of compression the electric double layer less than magnesium ions after ionizing (Jing, Wang & Han, 2008). Thus calcium ions and magnesium ions' content generally requires less than 200 mg·L^{-1}.

2.3 Effect of Fe^{2+}, Fe^{3+} on the Polymer Solution Viscosity

Added fresh $FeSO_4$ and FeCl3 solution into the polymer mother liquor, which diluted with deionized water. The viscosity measurement results are shown in Figure 3.

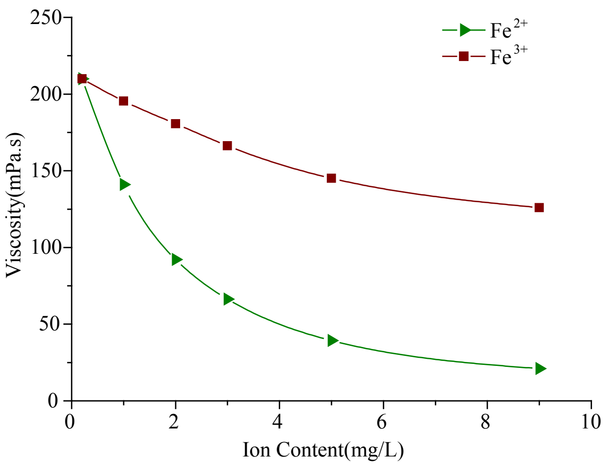

Figure 3
The Effect of Fe2+, Fe3+ on the Viscosity of the Polymer Solution

From Figure 3 we can see that the viscosity of polymer solution had a sharp decline and then the viscosity curve of polymer solution leveled off with ferrous iron ions content increase. The viscosity loss rate of polymer solution reached 81.92% when ferrous iron ions used 5 mg·L^{-1}. From viscosity curve of polymer solution we know a little ferrous iron ions will have heavy influence on the viscosity of polymer solution (Zhao & Yue, 2005). This is due to the catalytic action of ferrous iron ions, polymer solution macromolecular chains produced degradation, thus reducing the viscosity of polymer solution (Li, Whitworth & Lee, 2003). With the increase of ferric ion content, polymer solution occurs flocculation lead to viscosity decrease of polymer solution, but the decline extent is far less than the impact of ferrous iron ions. So in the field need to strictly controlled ferrous iron ions and ferric ion content.

2.4 Calculate of Viscosity Loss Strength

Added fresh $FeSO_4$, $FeCl_3$, $MgCl_2$ and NaCl solution into the polymer mother liquor, which diluted with deionized water. Then prepare single factors of sewage with 1,500 mg·L^{-1} mass concentrations determine the initial and after 40 days' viscosity.

Determine the ξ as viscosity loss rate, calculated as follow (Doran, Carini, Fruth, Drago & Leong, 1997):

$$\xi = \frac{\eta - \eta'}{\frac{\eta}{\eta_{dio}} \times c \times t} \quad (1)$$

There, ξ is viscosity loss rate, mPa·s/(mg· L^{-1}·d^{-1}); η is the initial viscosity of the polymer solution，mPa·s: η' is polymer solution viscosity after a period of time, mPa. s: η_{dio} is initial viscosity of the deionized water polymer solution，mPa·s; C is cation content of the polymer solution, mg·L^{-1}; t is stability test time, *d*.

As it can be seen from Table 2, the affect order of the cation influence polymer solution viscosity loss is: Fe^{2+}> Fe^{3+}> Mg^{2+}(Ca^{2+})> Na^{+}(K^{+})

Table 2
The Result of Cationic Viscosity Loss

Ion type	Mg^{2+}	Fe^{3+}	Na^{+}	Fe^{2+}
ξ/mPa·s/(mg·L^{-1}·d^{-1})	28.09	227.68	0.027	591.62

Experimental results show that ferric ion had the greatest impact on polymer solution viscosity, and followed were calcium and magnesium ions, potassium and sodium ions had the minimum effect. However, consider the actual block factors, the block had less ferric ion, and therefore the main factors affecting the viscosity of the polymer solution are calcium and magnesium ions. Thereby increasing the viscosity of the polymer solution when preparation polymer solution should first be removed by calcium and magnesium ions.

2.5 Effect of Anionic on Polymer Solution Viscosity

Added the NaCl, $NaHCO_3$, Na_2CO_3 and Na_2SO_4 into the polymer mother liquor, which diluted with deionized water (Pellegrino, Gorman & Richards, 2007). The viscosity measurement results are shown in Figure 4. Figure 4 is a viscosity curve of polyacrylamide solution with each inorganic salt concentration change. As it can be seen, in the same cation concentration, NaCl, $NaHCO_3$, Na_2CO_3 and Na_2SO_4 made polymer solution viscosity decreased slightly, but there had been little difference between values. This results description that anion had no effect on the viscosity of polymer solution, this minor difference of viscosity change due to different PH value of the solution (Gulde, Heatley, Karanfil, Rod & Myers, 2003). While from Figure 4 we can see that, polymer solution viscosity decreases with the increase of the concentration of the cationic. This further validate that anion had no effect on the viscosity of polymer solution when there had same cation, and the viscosity changes are mainly from the cation affected (Bradley, 2000).

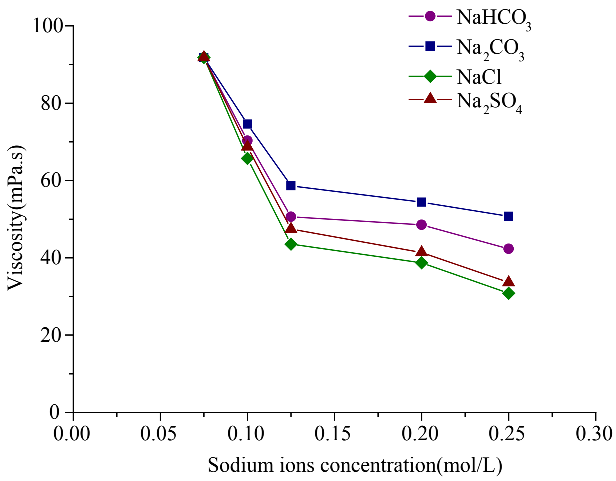

Figure 4
The Effect of Anionic on the Viscosity of the Polymer Solution

2.6 Humic Acid Sodium Adsorption Thickening Effect on Calcium and Magnesium Ion

Humic acid not only has a variety functional groups but also has complex structure (Sirivedhin, McCue & Dallbauman, 2004), which has a strong adsorption properties and reactivity (Aoba, Moreno, & Shimoda,1992). Since the negatively charged of humic acid sodium surface can react with heavy metal ions, which will take advantage of ions exchange, coordination reaction and adsorption to remove calcium and magnesium ions. However, humic acid is expensive, it can be formulated with NaOH and peat instead humic acid sodium to treat the calcium and magnesium ions in sewage (Anazaw & Ohmori, 2001). The adsorption results are shown in Figure 5.

From Figure 5 we know that adsorption on calcium ion increase with the mixture solution gain. The adsorption rate reached 77.50 percent when humic acid sodium used 8.0mL. However, appear a negative absorption rate when humic acid sodium amount is less than 1.5 mL. Because humic acid sodium mixture will release some calcium ion when adsorption calcium ions (Valentini, Maggi, Crespi, & Berzero, 2005). The effective adsorption group content small and calcium ion release content more than amount of adsorption when the mixture solution used less than 1.5mL, therefore appear a negative absorption rate. Magnesium ions also have the same trend. Mg2+ takes place ion exchange and complexation reaction with sodium humic the various effective action groups because Mg2+ has small radius and strong adsorption capacity. Adsorption on magnesium ions increase with the NaOH and mixture solution gain. The adsorption rate of magnesium reached 83.60% when mixture solution amount reach 6.0 mL, showing the effect of magnesium ion adsorption is better than calcium ion. With further increase in the amount of humic acid sodium adsorption rate of increase leveled off, humic acid sodium complexing balanced with calcium and magnesium ion (Adoor, Manjeshwar, Bhat & Aminabhavi, 2008).

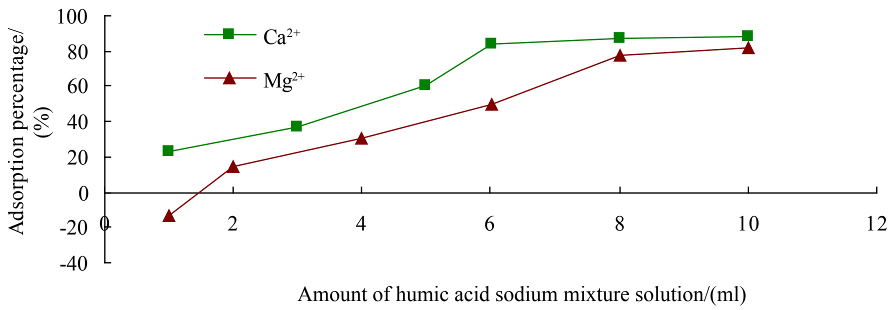

Figure 5
The Adsorption Effect of Ca^{2+} and Mg^{2+}

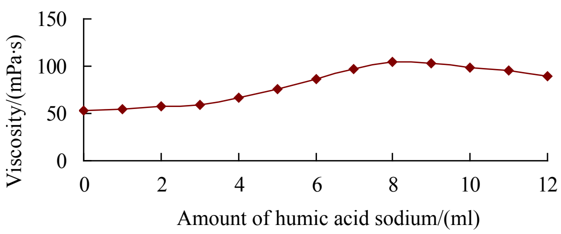

Figure 6
Viscosity Variation Curve With the Amount of Humic Acid Sodium

Figure 6 shows the viscosity variation curve with the amount of humic acid sodium. It found that when humic acid sodium amount is less than 3mL, the viscosity increases slowly, when the amount between 3-8 mL, the viscosity increased rapidly, indicating the effect of calcium and magnesium ions completed preferable. And when the amount of humic acid sodium reached 8mL the viscosity of polymer solution achieves the highest 104.6 mPa·s, at this time had the best complex effect. But the viscosity of polymer solution reduces when the amount of humic acid sodium increases again. The reason is the completing agent has reached equilibrium with the calcium and magnesium ions, reduced the impact of calcium and magnesium ions on the solution viscosity (Slaveykova, Dedieu, Parthasarathy, & Hajdu, 2009). Therefore, it cannot have great influence on the viscosity of polymer solution by increasing amount of humic acid sodium.This method enables recovery of sewage reached oilfield reinjection viscosity standards, with good adsorption thickening effect, can provide a reference for the field trials.

CONCLUSION

(a) At the 45 ℃ condition, the cationic has great effect on polymer solution viscosity and order is: $Fe^{2+}>Fe^{3+}>Mg^{2+}(Ca^{2+})>Na^{+}(K^{+})$.

(b) The anionic had no effect on the viscosity loss of polyarcylamide solution, and the main affect viscosity change factors of polyarcylamide solution were cationic.

(c) The presence of calcium and magnesium ions can cause polymer flocculation and sedimentation, severely reducing the viscosity of the polymer solution, and influence produced water utilization.

(d) This method can effectively remove calcium and magnesium ions in water with the increase in amount of humic acid sodium, while humic acid sodium and calcium and magnesium ions reach equilibrium adsorption rate does not increase.

(e) Polymer solution viscosity increase significant after calcium and magnesium ions complexed with humic acid sodium, can achieve water reinjection viscosity standards, provide a reference for the field trials.

REFERENCES

Adoor, S. G., Manjeshwar, L. S., Bhat, S. D., & Aminabhavi, T. M. (2008). Aluminum-rich zeolite beta incorporated sodium alginate mixed matrix membranes for pervaporation dehydration and esterification of ethanol and acetic acid. *Journal of Membrane Science, 318*(1-2), 233-246.

Anazaw, K., & Ohmori, L. H. (2001). Chemistry of surface water at a volcanic summit area, Norikura, central Japan: multivariate statistical approach. *Chemosphere,* 456-7.

Aoba, T., Moreno, E. C., & Shimoda, S. (1992). Competitive adsorption of magnesium and calcium ions onto synthetic and biological apatites. *Calcified Tissue International,* 512.

Bradley, R. (2000). *Pilot testing high efficiency reverse osmosis on gas well produced water.* Proceedings of the International Water Conference (61st Annual Meeting), Pitts-burg, PA.

Chen, T. L., Song, Z. Y., Fan, Y., Hu, C. Z., Qiu, L., & Tang, J. X. (1998). Adsorption of basic fibroblast growth factor onto Dacron vascular prosthesis and its biological efficacy. *SPE Reservoir Evaluation and Engineering, 1*(1), 24-29.

Cui, M. L., Lü, C. Y., & Hai, Y. Z. (2014). Influence of bivalent cation on viscosity of polymer solution in high calcium and magnesium reservoir. *Science & Technology Review,* (01), 30-33.

Ding, Y. J., Zhang, J. C., & Ma, B. D. (2015). Tackification measures and mechanism of polymer solution prepared by sewage. *Oilfield Chemistry,* (01), 123-127.

Doran, G. F., Carini, F. H., Fruth, D. A., Drago, J. A., & Leong, Y. C. (1997). *Evaluation of technologies to treat oil field produced water to drinking water or reuse quality*. Proceedings of the Annual SPE Technical Conference, San Antonio, Texas.

Han, Y. G. (2008). Discussion on the issue of viscosity of polymer solution prepared by oilfield sewage. *PGRE, 15*(6), 68-70.

Han, D. K., Yang, C. Z., Zhang, Z. Q., Lou, Z. H., & Y. I. Chang, Y. I. (1999). Recent development of enhanced oil recovery in China original research article. *Journal of Petroleum Science and Engineering, 22*(1-3), 181-188.

Jing, G. X., Wang, Y., & Han, C. J. (2008). The effect of oilfield polymer-flooding wastewater on anion-exchange membrane performance. *Desalination, 220,* 386-393. (Proceedings Greece 2007).

Kennedy, R. A., & Peter J. Stewart, P. J. (1996). The kinetics of adsorption of calcium and magnesium ions on to an insoluble sodium polyphosphate. *Drug Development and Industrial Pharmacy,* 227.

Li, L. X., Whitworth, T. M., & Lee, R. (2002). Separation of inorganic solutes from oil-field produced water using a compacted bentonite membrane. *Journal of Membrane Science, 217,* 215-225.

Lü, X. (2010). The research on influence factor of the preparation of polymer solution with produced water. *Journal of Southwest Petroleum University (Science & Technology Edition),* (03), 162-166+201.

Ma, Y. M. (2010). Preparing polymer solution with higher salinity sewage of polymer flooding field. *Science Technology and Engineering, 23,* 5637-5364.

Murray-Gulde, C., Heatley, J. E., Karanfil, T., Rod-gers J. H. Jr., & Myers, J. E. (2003). Performance of a hybrid re-verse osmosis-constructed wetland treatment system for brackish oil field produced water. *Water Research, 37,* 705-713.

Pellegrino, J., Gorman, C., & L. Richards, L. (2007). A speculative hybrid reverse osmosis electrodialysis unit operation. *Desalination, 214,* 11-30.

Sirivedhin, T., McCue, J., & Dallbauman, L. (2004). Reclaiming produced water for beneficial use: Salt removal by electrodialysis. *Journal of Membrane Science, 243,* 335-343.

Slaveykova, V. I., Dedieu, K., Parthasarathy, N., & Hajdu, R. (2009). Effect of competing ions and complexing organic substances on the cadmium uptake by the soil bacterium Sinorhizobium meliloti. *Environmental Toxicology and Chemistry,* 284.

Taylor, K. C. (1995). Mechanism of adsorption of anionic dye from aqueous solutions onto organobentonite. SPE Reservoir Evaluation and Engineer-ing. SPE 29008, 675-690.

Valentini, G. M. T., Maggi, L., Crespi, C. V., Berzero, A. (2005). Preliminary results on the immobilisation of radionuclides from waters with specific adsorbers based on phosphate salts. *Annali di chimica,* 9411.

Wang, D. M., Cheng, J. C., Wu, J. Z. (1998). Adsorption of water-soluble dyes onto modified resin. *SPE Journal,* 49018, 313-317.

Wang, Q. M., et al. (1999). Theoretical research on polymer flooding, Petroleum Geology, & Oilfield Development in Daqing, 18(4), 1-5.

Yang, H. J., & Luo, P. Y. (2005). Factors for and control of polymer degradation in recycled produced water solutions. *Oilfield Chemistry,* (02), 158-162.

Zhao, R. B., & X. G. Yue, X. G. (2005). Flowing characteristics of 2-acrylamide-2-methyl propane-sulfonic-acid copolymer solution in porous medium. *Journal of Acta Petrolei Sinica, 26*(2), 85-97.