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耐高温抗盐的低浓度交联聚合物体系研究

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摘要:低浓度交联聚合物技术,可以解决聚合物驱技术中所存在的聚合物用量高,耐高温抗盐性能差的问题,成为 EOR 技术领域一个新的技术发展方向。采用改进的醛类有机交联剂和高相对分子质量的部分水解聚丙烯酰胺(HPAM),开展了以改善聚合物驱为目的的低浓度交联聚合物体系研究。研究表明,该体系具有很强的成胶能力,HPAM 浓度为 150~300mg/L,交联剂浓度为 50~130mg/L 的体系,75~90℃条件下老化 180d,粘度值保持在 40.6~94.6mPa·s。与聚合物驱技术相比,可以大幅度地降低化学剂用量。该体系耐高温可达 90℃,耐矿化度可达 100000mg/L,并且可以用污水(油田产出水)配制,表现出优异的耐高温抗盐性能,可以在更高温度和矿化度的油藏使用,扩展了 HPAM 的应用领域和范围,显示出良好的应用前景。同时对交联反应机理进行了初步探索,认为交联剂和 HPAM 之间的反应主要是 HPAM 分子间的交联反应,HPAM 分子链卷曲收缩有利于分子间交联反应发生。因此,选用低水解度 HPAM 和提高水的矿化度有利于提高交联 HPAM 溶液的性能。

关键词:交联聚合物;交联剂;聚丙烯酰胺;耐高温抗盐;粘度;长期稳定性

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1 引言

老油田开发后期,原油生产成本逐年增加,开发能够大幅度降低成本的提高采收率技术成为迫切需要解决的问题。低浓度交联聚合物技术^[1,2],正是这样一项 EOR 新技术。与聚合物驱技术和调剖技术相比,其最大的技术和经济特点就是可以大幅度降低化学剂用量。因此近十几年来该技术在国内外倍受关注,成为 EOR 技术领域一个新的技术发展方向^[3,4]。

以部份水解聚丙烯酰胺(HPAM)为主的聚合物驱技术在我国获得了广泛的应用和成功,但是该技术在以下几个方面需要改进和提高:(1)聚合物用量高,使用的 HPAM 浓度一般为 1000mg/L 左右。(2)耐盐性能差,难于用污水(油田产出水)配制。(3)耐温性能差。由于发生了明显的高温水解和分子降解作用,一般认为大部分实际油藏 HPAM 可使用的上限温度为 75℃^[5~7]。我国的许多高温高矿化度油藏的地质条件适宜于实施聚合物驱技术,但由于受温度和矿化度的限制而难于应用,因此以上因素不但影响到聚合物驱技术经济效益的提高,而且限制了 HPAM 的应用范围。合成的新型聚合物可以较大幅度的提高耐高温抗盐性能,但是这类聚合物的增粘能力差,生产成本低,仍然达不到在实际高温油藏使用的目的^[8]。为此,采用了改进的醛类有机交联剂和高相对分子质量的 HPAM1285,开展了以改善聚合物驱为目的的低浓度交联聚合物体系的研究。研究表明,该体系在高温高矿化度条件下,具有很强的增粘能力,低 HPAM 浓度(150~300mg/L)交联体系不仅具有很高的粘度(40.6~94.6mPa·s),而且表现出优异的耐高温抗盐性能,有很大的应用潜力。

2 实验方法

2.1 主要试剂

HPAM1285:英国联合胶体公司产品,相对分子质量 2100 万,水解度 23%。交联剂 R:改进的醛类有机交联剂。配制水:油田清水和污水(油田产出水)。清水的 pH 值为 8.0,矿化度为 360mg/L 其离子成份为:Na⁺

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(80mg/L), Ca^{2+} (23.5mg/L), Mg^{2+} (9.5mg/L), SO_4^{2-} (20mg/L), HCO_3^- (126mg/L), Cl^- (104mg/L)。污水的pH值为9.1, 矿化度为5002mg/L, 其离子成份: Na^+ (1600mg/L), Ca^{2+} (14mg/L), Mg^{2+} (7.5mg/L), SO_4^{2-} (391.5), HCO_3^- (1816mg/L), Cl^- (1172mg/L)。

2.2 样品制备和粘度测量

称取一定量的NaCl, 交联剂R和HPAM1285, 加入到油田清水中, 搅拌2h, 配制成一定矿化度和HPAM浓度的交联HPAM溶液, 然后抽空除氧, 把HPAM溶液转移至安瓿瓶中, 用火封口。氧含量控制在1mg/L以下, 把制备好的安瓿瓶样品放在75℃和90℃的恒温箱中老化, 间隔一定时间取出安瓿瓶, 用美国生产的Brookfield粘度计, 在30℃6γ/min条件下测量已发生交联反应的HPAM溶液的粘度。

3 结果与讨论

HPAM和交联剂的浓度大小是决定HPAM溶液能否成胶以及成胶后凝胶结构形态的关键因素, 也是选用交联HPAM体系的最重要的经济评价指标。HPAM浓度太低, 不能发生有效的交联反应, 达不到所需要的粘度; HPAM浓度太高, 会形成三维网状结构的凝胶, 在地层中失去可动性而不能作为驱剂使用。确定出适宜的HPAM和交联剂的组份范围, 使交联HPAM溶液的成胶时间和粘度能够作为油藏驱剂使用。

表1 交联HPAM溶液的粘度和老化时间的关系(1DS:15000mg/L)

Table 1 The viscosity of crosslinking HPAM solutions with aged time

化学剂用量 (mg/L)	温度 (℃)	老化时间 (d)									
		0	1	2	4	6	30	60	100	140	180
H:1500 R:180	75	25.2	—	38.6	—	—	2100	—	1906	—	2080
	90	25.2	150	—	—	—	2400	—	2050	—	1980
H:700 R:130	75	7.9	—	30.8	—	—	1052	—	1216	—	1156
	90	7.9	130	—	—	—	1362	—	1552	—	1220
H:500 R:130	75	5.2	—	—	635	—	520	—	402	—	496
	90	5.2	—	91.5	—	—	480	—	380	—	502
H:300 R:130	75	3.0	—	—	—	71.5	95.1	105	95.1	96.2	94.6
	90	3.0	50.2	—	—	—	108	81.6	114	104	86.8
H:300 R:50	75	3.1	—	—	—	—	90.6	85.2	62.4	65.4	61.4
	90	3.1	—	21.6	—	—	78.5	65.2	62.6	60.6	61.3
H:200 R:130	75	2.1	—	—	—	34.2	47.6	40.6	47.6	50.6	43.4
	90	2.1	22.3	—	—	—	68.6	48.4	60.2	55.2	50.2
H:150 R:100	75	2.0	—	—	—	—	47.6	49.4	54.6	57.4	48.6
	90	2.0	—	27.6	—	—	38.6	30.8	47.4	46.5	40.6
H:100 R:70	75	1.5	—	—	—	—	13.1	22.6	18.9	16.5	17.8
	90	1.5	—	—	15.6	—	9.1	4.6	4.2	4.4	3.0
H:1000 R:0	75	17.6	—	—	—	17.1	15.1	14.4	8.3	7.2	4.6
	90	17.6	—	—	—	13.8	6.2	4.2	—	—	—

从表1可以看到:(1)75~90℃条件下交联剂R具有很强的成胶能力, 在HPAM浓度低至100mg/L时也能发生有效的交联反应, 使交联HPAM溶液的粘度大幅度增加。(2)HPAM和R用量多少直接影响到交联HPAM溶液的性能。HPAM浓度为700~1500mg/L时, 老化180d后, 交联HPAM溶液的粘度在1000mPa·s以上, 500mg/L时交联HPAM溶液的粘度也较高, 不宜作为驱剂使用。HPAM浓度为150~300mg/L, R浓度为50~130mg/L的交联HPAM溶液, 老化180d, 粘度值保持在40.6~94.6mPa·s之间, 适宜作为驱剂使用。与未加交联剂的1000mg/L HPAM溶液相比, 不但耐温性能明显提高, HPAM用量也大幅度减少, 可以节省

化学剂用量 1/2~2/3。(3)成胶时间和成胶后的粘度可以通过改变 HPAM 和 R 的用量加以调节。(4)90℃时的成胶时间比 75℃时的成胶时间短,这说明高温条件下更有利于交联剂和 HPAM 发生交联反应。

HPAM 溶液的耐盐性能较差,随着配制水矿化度的提高,HPAM 溶液粘度大幅度下降,难以实现污水配制和在高矿化度油藏实施聚合物驱技术。HPAM 交联后不但其耐温性能得到提高,其抗盐能力也大大得到改善(表 2)。从表 2 可以看出,在矿化度为 360~100000mg/L 的 NaCl 盐水中,75~90℃条件下老化 180d,既无明显的缩水现象,也保持了很高的粘度值(42.8~108mPa·s),在特高矿化度 100000mg/L 条件下也表现出优异的抗盐性能。随着矿化度的增加,交联 HPAM 溶液的成胶时间缩短,粘度值增大(表 3)。如 75℃条件下,矿化度为 360mg/L 时,交联 HPAM 溶液的成胶时间为 20d,成胶时溶液粘度 25.5mPa·s;矿化度为 7000mg/L 时,成胶时间为 7d,粘度为 38.5mPa·s;而矿化度为 15000mg/L 时,成胶时间为 5d,粘度为 51.8mPa·s。这说明,矿化度提高可以增大 HPAM 分子间交联反应的机率。

HPAM 分子链的存在形态决定着交联反应的方式。众所周知,HPAM 溶液的盐敏效应明显,矿化度的改变强烈地影响到 HPAM 分子链的存在形态。配制水矿化度越高,羧基间的静电斥力受到阳离子屏蔽作用越强,导致 HPAM 分子链处于更加卷曲收缩状态,分子链内的空间受到压缩减少,难于发生分子内交联,而是以分子间交联反应方式为主。HPAM 分子间交联反应可以更有效的增大 HPAM 分子的水动力学体积,使 HPAM 溶液粘度快速增大,交联 HPAM 溶液的成胶时间就缩短。

表 2 不同矿化度的交联 HPAM 溶液粘度和老化时间关系(HPAM:300mg/L,R:130 mg/L)

Table 2 The viscosity of crosslinking HPAM solutions in different salinity brines with aged time

矿化度 (mg/L)	温度 (℃)	老 化 时 间 (d)					
		0	30	60	100	140	180
100000	75	2.2	71.6	85.2	127	121	108
	90	2.2	85.0	116	108	102	106
30000	75	2.6	85.6	108	83.4	88.2	90.6
	90	2.6	95.1	105	95.2	88.4	87.4
15000	75	3.0	95.1	105	95.1	96.2	94.6
	90	3.0	108	81.6	114	104	86.8
7000	75	4.0	74.5	80.2	95.0	91.4	92.6
	90	4.0	60.8	65.0	80.4	74.2	76.4
4000	75	4.2	85.0	103	86.4	91.2	88.6
	90	4.2	84.5	101	92.4	95.4	85.3
2000	75	5.6	72.6	111	116	103	96.4
	90	5.6	95.0	104	106	94.8	90.6
360	75	10.7	40.6	91.6	91.4	96.4	89.4
	90	10.7	59.6	74.2	44.8	58.6	42.8

表 3 不同矿化度的交联 HPAM 溶液的成胶时间和粘度(H:300mg/L,R:130 mg/L)

Table 3 The gelling time and viscosity of crosslinking HPAM solutions in different salinity brines

成胶参数	温度 (℃)	矿 化 度 (mg/L)						
		360	2000	4000	7000	15000	30000	100000
成胶时间 (d)	75	20	7	7	7	5	4	4
	90	7	2	2	2	1	1	1
成胶粘度 (mPa·s)	75	25.5	18.2	24.1	38.5	51.6	34.6	28.6
	90	27.4	31.4	34.5	36.5	50.2	48.5	39.7

同理,若选用低水解度的 HPAM,其在低矿化度水中也应该表现出更强的成胶能力。表 4 就是水解度为 13%,相对分子质量为 1600 万的 HPAM620 在低矿化度(360mg/L)的清水中成胶性能和 HPAM1285 的比较。很明显,由于 HPAM620 的水解度低(13%),羧基含量少,羧基间的斥力弱,其分子链处于卷曲收缩状态,交联

反应主要在HPAM分子间发生,所以其成胶时间短(75℃时7d,90℃时2d),长期高温老化,粘度值在100 mPa·s以上。而HPAM1285的水解度高(23%),在清水中HPAM分子链处于更扩展状态,分子链内有较大的空间易于先发生分子内交联反应。所以其成胶时间75℃时20d,90℃时7d就比HPAM620长,长期高温老化,粘度值在42.8~89.4mPa·s之间,低于交联HPAM620溶液。因此,选用低水解度HPAM和提高配制水的矿化度有利于提高交联HPAM溶液的成胶能力。对于交联HPAM溶液而言,高矿化度是一个有利因素,而不是一个不利因素。

表5是用油田污水配制的低浓度交联HPAM溶液的粘度和老化时间的关系。300mg/L和200mg/L HPAM的交联HPAM溶液具有较强的成胶能力,良好的长期热稳定性,粘度值也高。因此用污水配制交联HPAM溶液效果良好。目前油田正面临着污水回注困难,污水外排造成环境污染等方面的压力,污水配制交联HPAM溶液的成功,无疑具有较大的经济效益和社会意义。

表4 交联HPAM1285和HPAM620溶液在清水中的粘度和老化时间的关系(HPAM:300mg/L,R:130mg/L)

Table 4 The viscosity of crosslinking HPAM1285 and HPAM620 solutions with aged time in fresh water

HPAM	温度 (℃)	老 化 时 间 (d)									
		0	2	7	10	20	30	60	100	140	180
1285	75	10.7	—	—	14.4	25.5	40.6	91.6	91.4	96.4	89.4
	90	10.7	8.6	27.4	—	—	59.6	74.2	44.8	58.6	42.8
620	75	8.6	—	16.1	35.1	—	99.2	108	118	114	104
	90	8.6	28.7	—	—	—	106	118	107	102	106

表5 油田污水配制的交联HPAM1285溶液粘度和老化时间关系

Table 5 The viscosity of crosslinking HPAM solution with aged time in oilfield produced water

化学剂用量 (mg/L)	温度 (℃)	老 化 时 间 (d)									
		0	3	8	14	30	60	100	140	180	
H:300 R:130	75	4.6	—	15.6	—	64.6	110	115	114	116	
	90	4.6	46.4	—	—	83.6	115	117	116	104	
H:200 R:130	75	2.7	—	—	18.6	43.6	45.2	57.6	39.8	42.6	
	90	2.7	—	21.7	—	41.5	35.6	30.4	26.6	28.2	

最后值得指出的是,HPAM交联后流体动力学体积增大,其在地层中的流动阻力增加,因此该项技术也被用作油藏深部流体转向技术,利用其在高渗透层具有较强的封堵能力而使后继流体转向未被波及的含油饱和度高的低渗透层^[9,10]。一些岩心实验显示,HPAM交联后会在岩心端面形成滤饼,难以通过岩心^[11],因此在实际应用时可能造成近井堵塞,影响注入能力。Han Dong等人用超大岩心模型考察低浓度HPAM交联体系的渗流特征^[4],证明交联HPAM溶液在岩心中可以边流动边成胶,凝胶在岩心中可以渗流,后继注水时表现出很高的残余阻力系数。矿场应用结果表明,交联HPAM溶液注入顺利,关井压降测试,表皮系数呈较大的负值,近井地带没有堵塞现象^[1,9,10]。采用的低浓度交联HPAM体系为延迟交联,地下成胶方法,成胶前交联HPAM溶液粘度很低。初步的岩心实验显示,其在多孔介质中的渗流特征与聚合物溶液有较大的差别,后继注水时残余阻力系数很高。交联HPAM体系的渗流特征不仅取决于组份浓度和反应程度以及岩心孔隙结构,还依赖于实验方法和手段,系统的岩心实验仍在进行中。

4 结 论

1. 有机交联剂和HPAM体系在高温高盐条件下具有很强的成胶能力。150~300mg/L HPAM和50~130mg/L交联剂的低浓度交联溶液,75~90℃条件下老化180d,粘度值保持在40.6~94.6mPa·s。和聚合物驱相比,化学剂用量可以大幅度降低。

2. 交联 HPAM 体系较大幅度的提高了 HPAM 的耐温抗盐性能,耐温可达 90℃,耐盐可达 100000mg/L,可以在更高温度和矿化度的油藏实施驱油技术,扩大了 HPAM 的应用范围。

3. 交联 HPAM 体系可以用污水配制,为解决污水回注问题提供一个经济实用的途径。

4. 交联剂和 HPAM 之间的反应方式主要是 HPAM 分子间的交联反应,HPAM 分子链的收缩卷曲有利于 HPAM 分子间交联反应发生。选用低水解度 HPAM 和提高水的矿化度都有利于提高交联 HPAM 溶液的性能。

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MODIFICATION OF CRUDE CHARACTERIZING METHOD ACTA 2000,21(4):65~69.

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Characterization is essential to modeling ill-defined systems like crude oil. Based on reasonable physical postulates and some certain mathematical model, a successful characterization model can give a reasonable description of the ill-defined parts of the crude oil, thus satisfying the requirement of reservoir phase calculation and reservoir simulation. with the present characterization methods, crude is taken as a homogeneous phase which is contrary to the fact that the crude is essentially a kind of colloid with resin and asphaltene (solid phase) suspending in it. This results in a big deviation when the present methods are applied to some of heavy oil. A modified characterization method is proposed by considering the solid (resin and asphaltene)-liquid (homogeneous oil phase) equilibrium existing in crude. Calculation of several live oil properties with the modified method was made and much better results are obtained in comparison with the present ones.

Key words: solid-liquid equilibrium; characterizing crude; asphaltene precipitation; method

STUDY ON THE LOW CONCENTRATION POLYMER CROSSLINKING SYSTEM AT HIGH TEMPERATURE AND SALINITY CONDITIONS ACTA 2000,21(4):70~74.

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The polymer flooding technology has been widely used in oilfield successfully. But there are problems such as high polymer concentration and instability in high salinity brines at elevated temperature. The technology of low concentration crosslinking HPAM can solve these problems. The improved organic crosslinker and high molecular weight HPAM are adopted to investigate the system of crosslinking HPAM for flooding application. The experimental results show that gelling ability of this system is excellent at high temperature and salinity conditions. The crosslinking HPAM system of 150~300mg/L HPAM and 50~130mg/L crosslinker has been aged for 180 days at 75~90°C, its viscosity values maintain between 40.6~94.6 mPa·s. Compared with polymer flooding, the amounts of HPAM used can be obviously reduced. This system can tolerate harsh reservoir conditions (high temperature of 90°C and high salinity of 100000 mg/L), so it offers the possibility to extend the upper temperature and salinity limit significantly for the use of HPAM in polymer flooding. The mechanism of reaction is mainly intermolecular crosslinking reaction between HPAM chain. The more coiling and shrinkage the HPAM chain, the more easily intermolecular crosslinking reaction takes place. The properties of crosslinking HPAM system may be improved by selecting lower hydrolysis degree HPAM and higher salinity brines.

Key words: crosslinking polymer; crosslinker; polyacrylamide; high temperature; salinity

PETROLEUM ENGINEERING

AN UNDERBALANCED DRILLING THEORETICAL MODEL AND ITS APPLICATION ACTA 2000,21(4):75~79.

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Based on the theory of multiphase transient flow and the general principle of underbalanced drilling, a comprehensive theoretical model dealing with underbalanced drilling is developed. The model with respect to the cocurrent flow of oil, gas, water, drilling mud and cuttings has comprehensively taken almost all the factors affecting underbalanced drilling process into account, such as the mass transfer between oil and gas, the inflow performance relationship of formation fluids, the different operating modes, etc. A numerical approach is used to solve the theoretical model. The results indicate that underbalanced drilling is a dynamic process and each relevant parameter in underbalanced drilling practice completely depends on the given conditions and the practical operating mode. This model can be effectively applied to determine the complicated multiphase flow behavior in practical underbalanced drilling.

Key words: underbalanced drilling; theoretical model; multiphase transient flow; finite difference approach; numerical simulation