空气辅助蒸汽吞吐低温催化氧化实验研究

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摘要:为了加快空气辅助蒸汽吞吐过程中氧气的消耗速度,减少尾气中氧气体积分数和大幅度降低稠油的粘度,利用高压反应釜对新疆油田J230井区951217井稠油进行注空气低温催化氧化室内条件的筛选。尾气组成、氧化稠油酸值、粘度和族组分等分析结果表明,在200 ℃条件下,当催化剂FeL质量分数为0.1%,空气压力为1.2 MPa,反应72 h时,稠油酸值为8.37 mg/g,粘度为3 787 mPa·s,氧化后尾气中氧气体积分数为4.75%;利用氧化油70 g、水30 g和助剂R1 0.07 g搅拌乳化后,乳状液的粘度为42 mPa·s,降粘率达到96.77%。因此,在空气辅助蒸汽吞吐稠油过程中,通过添加催化剂可以加快氧气的消耗,添加助剂可以大幅度降低稠油的粘度,从而有利于提高稠油采收率。

关键词:蒸汽吞吐 空气 低温氧化 催化 降粘
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在油层条件下,注入空气与原油接触会发生2种反应[1-2],即高温氧化反应和低温氧化反应。稠油注空气低温氧化速度慢,尾气中氧气体积分数高将导致焖井和开采期间存在安全问题[3-5],同时,稠油的氧化将导致其粘度升高[6],对提高采收率不利。空气低温催化氧化技术是一种利用空气替代氮气辅助蒸汽吞吐的提高稠油采收率技术。其原理是利用催化剂提高氧气和原油的氧化速度,降低注入空气中氧气体积分数,同时利用氧化产生的石油酸生成表面活性剂,降低稠油的粘度,并利用残余气体的弹性能提高稠油采收率。唐晓东等[7]利用水溶性催化剂SP-1催化氧化辽河稠油样品,王焕梅等[8]利用油溶性催化剂环烷酸铜催化氧化渤海SZ36-1稠油。结果表明,催化氧化能明显降低尾气中氧气体积分数,同时氧化稠油经降粘助剂处理后,降粘率分别为99.99%和96.66%。在新疆油田J230井区的蒸汽吞吐现场,井口温度为300 ℃左右,由于热传导和热损失导致近井地带温度为200 ℃左右。因此,笔者对200 ℃条件下新疆油田J230井区951217井稠油进行了空气低温催化氧化实验研究。

1 实验准备

实验原料为新疆油田J230井区951217井稠油(50 ℃时粘度为1 301 mPa·s),自制了6种有机酸锰、铜、镍、钴、铁和锌催化剂(代号分别为MnL,CuL,NiL,CoL,FeL和ZnL)和助剂R1。实验仪器包括WDF-0.5L型高压反应釜,NDJ-8S数字显示粘度计(在50 ℃和125 s^{-1}的条件下采用4号转子),SQ-206型气相色谱仪。

在高压反应釜中,加入100 g稠油,取一定质量分数的催化剂,在一定的空气压力、温度为200 ℃、搅拌速度为200 r/min等条件下,考察不同实验条件对稠油催化氧化效果的影响。以反应前后稠油的粘度、族组分、酸值和尾气中氧气体积分数作为评价指标。应用NDJ-8S数字显示粘度计测定油品粘度;根据SY/T 5119—1995[9]测定族组分;根据GB/T 4945—2002[10]测定酸值;应用SQ-206型气相色谱仪测定尾气中氧气体积分数。

2 实验参数优选

2.1 催化剂种类

在空气压力为1.0 MPa和反应时间为24 h的条件下,考察质量分数为0.1%的6种催化剂对稠油催化氧化效果的影响(图1)。由图1可见,与无催化剂的对照样相比,经过不同种类的催化剂处理后,氧化稠油的粘度和酸值都增加,但反应后尾气中的氧

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气体积分数降低。其中，催化剂NiL，CoL和FeL催化氧化后酸值增加相对较多，分别比对照样增加了40.6%，38.2%和47.7%，其中催化剂FeL对氧化稠油酸值影响最大。6种不同的催化剂对稠油的氧化都有促进作用，其中NiL，CoL，FeL和ZnL能有效降低氧化后尾气中氧气体积分数，分别比对照样降低了66.2%，67.0%，64.2%和62.7%。考虑到经济性和酸值的影响，最终优选催化剂为FeL。

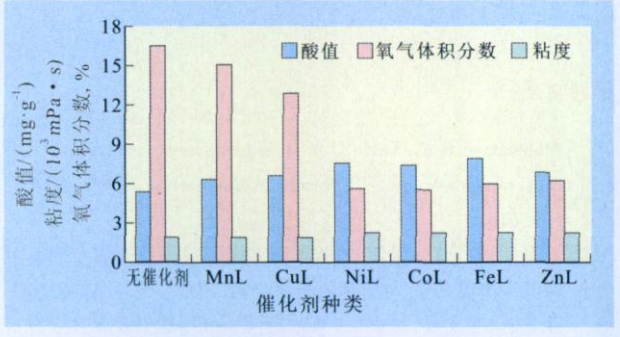

图1　催化剂种类对稠油酸值和粘度及尾气中氧气体积分数的影响

2.2　催化剂质量分数

在空气压力为1.0 MPa和反应时间为24 h的条件下，考察不同质量分数的催化剂FeL对稠油催化氧化效果的影响（图2）。由图2可见，随着催化剂质量分数增加，粘度、酸值增加，尾气中氧气体积分数从15.01%降低至4.02%。其中，催化剂FeL质量分数为0~0.1%时，氧化油粘度随催化剂质量分数的增加从1 827 mPa·s上升到2 251 mPa·s，其酸值从5.32 mg/g增加到7.86 mg/g。当质量分数超过0.1%时，两者趋于稳定。考虑到经济性，最终催化剂FeL的优选质量分数为0.1%。

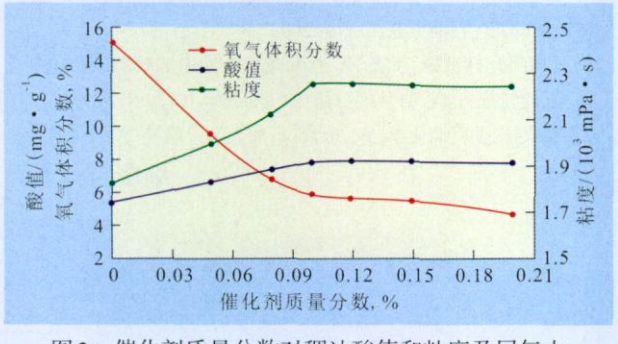

图2　催化剂质量分数对稠油酸值和粘度及尾气中氧气体积分数的影响

2.3　空气压力

在催化剂FeL质量分数为0.1%，反应时间为24 h的条件下，考察了不同空气压力对稠油催化氧化效果的影响（图3）。由图3可见，随着空气压力的增加，氧化稠油的粘度和酸值增加，而氧化后尾气中的氧气体积分数先减小后增加。当空气压力由0.8 MPa升高到1.8 MPa时，氧化稠油的粘度由2 159 mPa·s升高到5 370 mPa·s，酸值由6.52 mg/g增加到8.13 mg/g。在空气压力较低时，稠油与空气间发生的吸氧氧化反应消耗了大部分氧；当空气压力为1.2 MPa时，尾气中氧气体积分数为6.29%；但随着空气压力的继续增大，稠油消耗的氧气量有限，则尾气中氧气体积分数表现为增加。因此，实验的空气压力确定为1.2 MPa。

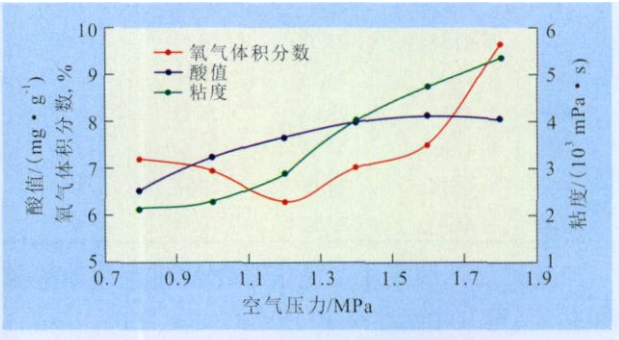

图3　空气压力对稠油酸值和粘度及尾气中氧气体积分数的影响

2.4　反应时间

在空气压力为1.2 MPa和催化剂FeL质量分数为0.1%的条件下，考察不同反应时间对稠油催化氧化效果的影响。由图4可以看出，随着反应时间的延长，尾气中氧气体积分数下降，氧化稠油的粘度升高。在72 h之前，氧化稠油的粘度从2 168 mPa·s升高到3 787 mPa·s，其酸值从6.15 mg/g增加到8.37 mg/g。72 h后粘度升高速度加快，120 h时达到6 130 mPa·s，而酸值稳定在8.30 mg/g；尾气中的氧气体积分数随反应时间逐渐减小，72 h时，氧气体积分数降至4.75%，120 h时降至4.03%。实验结果表明反应时间越长，氧气消耗越多，同时氧化稠油粘度上升越快。

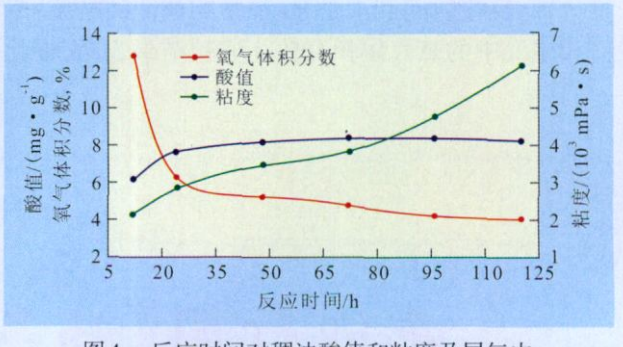

图4　反应时间对稠油酸值和粘度及尾气中氧气体积分数的影响

进一步对氧化稠油族组分研究发现（表1），反应时间越长，饱和烃、芳香烃质量分数增加，胶质质

量分数从32.22%减少至22.74%，而沥青质质量分数从1.86%增加至4.96%。胶质在催化剂的作用下，一部分裂解为轻质组分（饱和烃和芳香烃），一部分缩聚为沥青质[11-12]。沥青质质量分数的增加是导致氧化稠油粘度升高的主要原因，同时，空气中氧气氧化稠油组分为石油酸，导致酸值增高。

表1　J230井区951217井稠油族组分分析

反应时间/h	饱和烃质量分数，%	芳香烃质量分数，%	胶质质量分数，%	沥青质质量分数，%
0	43.52	22.4	32.22	1.86
12	45.58	23.07	29.15	2.20
24	47.17	23.54	26.19	3.10
48	47.59	23.83	25.22	3.36
72	47.85	24.13	23.87	4.15
96	48.14	24.15	23.16	4.55
120	48.03	24.27	22.74	4.96

通过对不同反应时间下催化氧化后稠油酸值和粘度、尾气中氧气体积分数的变化分析，并结合现场吞吐焖井时间，优选72 h作为稠油催化氧化的反应时间。

2.5　助剂R1

分别取951217井氧化油70 g、水30 g和不同质量分数的助剂R1在搅拌下乳化，考察助剂R1的质量分数对氧化稠油粘度的影响。实验结果表明，助剂R1有利于氧化稠油的乳化。在助剂R1质量分数（占氧化稠油的比例）为0.06%～1.2%时，氧化油的降粘率为91.78%～96.77%。当助剂R1质量分数为0.1%时，乳状液的粘度为42 mPa·s，降粘率为96.77%。

3　结论

在稠油的催化氧化过程中，催化剂的种类与质量分数、反应时间和助剂R1都影响稠油的粘度、酸值和尾气中的氧气体积分数。实验结果表明，催化氧化过程降低了尾气中氧气体积分数，但同时导致氧化稠油粘度、酸值和沥青质质量分数增高。助剂R1的加入将大大降低氧化稠油粘度。

在100 g稠油中加入催化剂FeL质量分数为0.1%，空气压力为1.2 MPa，温度为200 ℃，搅拌速度为200 r/min，反应72 h时，尾气中氧气体积分数降至4.75%。当氧化油70 g、水30 g和质量分数为0.1%的助剂R1搅拌乳化后，乳状液粘度为42 mPa·s，降粘率为96.77%。

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degree, 3 levels of single well's residual oil potential have been divided after polymer flooding, which can be classified as high, medium and low. According to planar distribution of residual oil geological reserves, 2 enrichment areas after polymer flooding, which are mainly located in prime sand body and weak well pattern controlling parts, are pointed out as well. The research process and results can provide certain methodological and theoretical references on the forecasting of residual oil and the rational adjustment and potential tapping after polymer flooding.

Key words: post-polymer flooding; residual oil; distribution law; area splitting and superposition; recovery degree

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Yao Chuanjin, Lei Guanglun, Gao Xuemei et al. Study on indepth profile control and flooding of pore-scale elastic microspheres under heterogeneous condition. *PGRE*, 2012, 19(5): 61-64.

Abstract: Due to the particularity of design principle for pore-scale elastic microspheres profile control and flooding technology, the particle-pore size matching factor was introduced and through heterogeneous parallel sandpack experiments, the plugging property of elastic microspheres under different particle-pore size matching relationship and the effect of permeability ratio on the ability of profile improvement were studied. Based on this, field test of pore-scale elastic microspheres under heterogeneous condition was carried out. Indoor experimental results show that in a better particle-pore size matching factor range, the residual resistance factor and plugging rate of sandpacks are the maximum as well as plugging effect; elastic microspheres can prefer to plug high permeability layer selectively so as to make the diversion rate of high and low permeability tube all tend to 50%, which indicates that elastic microspheres have significant selectivity on permeability; permeability ratio has an important effect on profile control an flooding performance of elastic microspheres and under condition of better particle-pore size matching factor range and lower permeability ratio, the profile improvement of elastic microspheres is better. Field test results show that when the particle-pore size matching factor is 1.52 and the permeability ratio is 3.1, the elastic microspheres can control the water injection profile effectively and the profile improve ability of target layer 65 and 67 is up to 98%; it is scientific to guide the field test of elastic microspheres profile control and flooding using particle-pore size matching factor and permeability ratio.

Key words: heterogeneous; elastic microspheres; particle-pore size matching factor; sealing property; permeability ratio; field test

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Yang Shuai, Dai Caili, Zhang Jian et al. Influence of polymer residue property on EOR after polymer injection for offshore oilfield. *PGRE*, 2012, 19(5): 65-68.

Abstract: As the hydrophobically associating polymer in Bohai Suizhong 36-1 reservoir has the character of high degree of hydrolysis and low intrinsic viscosity, laboratory has carried out the residual-recycled experiments to investigate the sealing characteristics with the changes in degree of hydrolysis and intrinsic viscosity. Residual resistance factor and recovery appreciation are determined by the physical simulation method, to study the effect of formation sealing performance and recovery evaluation by the change of polymer degree of hydrolysis and intrinsic viscosity. The results of laboratory experiments indicates that the sealing characteristics of the interacted production which originates from the reaction of residual polymer with high degree of hydrolysis and low intrinsic viscosity and recycled agent is much better than the single polymer with the residual resistance factor reaching more than 20, which lowers the intrinsic viscosity, that is, the higher the degree of hydrolysis, the better the sealing performance. The enhanced oil recovery experiments also indicate that the method can improve the recovery by 9.4%. The result of visualized simulation experiment also validates the viewpoint.

Key words: residual polymer; intrinsic viscosity; degree of hydrolysis; reutilization; enhance oil recovery

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Li Caifeng, Guo Liaoyuan, Cao Gongze et al. Research and field application of activator formulas to endogenous microorganism, Gudao Zhongyi Ng3 block. *PGRE*, 2012, 19(5): 69-71.

Abstract: The activation of Zhongyi Ng3 of Gudao after polymer flooding by means of different activator formulas is studied herein. Screening results reveal that the optimal composition of the activator formula is as follows (g/L): glucose 4, peptone 0.4, yeast extract 0.2, NH_4NO_3 0.4, $(NH_4)_2PO_4$ 0.2. The detailed results show that, at 65 ℃ and 10 MPa the endogenous microorganism can be activated evidently to 1.48×10^9 cfu/mL via the activator formula consisted of glucose and yeast extract powder. Simultaneously, the concentration of acetic acid is increased distinctly about 600 mg/L and the surface tension of water is reduced to 33.2 mN/m. Physical simulation experiment shows that the endogenous microorganism can enhance the oil recovery by 6.4 percent with the activator formula. Field test shows that the amount of this activator formula to Zhongyi Ng3 block is 405 t by the end of June 2011, and the cumulative oil yield increases by 1.0×10^4 t.

Key words: endogenous microorganism; stimulation agent; physical simulation; nutrient system; Gudao oilfield

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Luo Qiang, Wu Yongfeng, Li Dongwen et al. Steam stimulation with air by low-temperature oxidation at presence of additives. *PGRE*, 2012, 19(5): 72-74.

Abstract: The objective of this study is to investigate parameters for low-temperature oxidation of heavy oil on the volume fraction of

oxygen in the end gas and acid value, viscosity and group composition of the oil with additives in the high temperature autoclave. The heavy oil was from the producing well 951217 in the Block J230 of Xinjiang Oilfield. It is found that the acid value of the oxidized oil is 8.37 mg/g and its viscosity is 3 787 mPa · s but oxygen volume fraction decreases to 4.75 vol% after 72 h with 0.10 wt% catalyst of FeL and air injected at 1.2 MPa and 200 ℃. Furthermore, the viscosity of emulsion is 42 mPa · s at 50 ℃ after mixing 70 g oxidized oil, 30 g water and 0.07 g caustic additives R1. Good results can be achieved through decreasing the volume fraction of oxygen with catalyst and reducing the viscosity of heavy oil with caustic additives during the process of cyclic steam with air.

Key words: steam stimulation; air; low-temperature oxidation; catalysis; viscosity reduction

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Zhang Enlei, Gu Daihong, He Shunli et al. Experiment study on effect of impurities on CO_2 drive. *PGRE*, 2012,19(5): 75-77.

Abstract: Carbon dioxide flooding is a promising tertiary oil recovery technology in respect both to technical and, if operating costs are properly controlled, to economic benefit. Moreover, the injection of this greenhouse gas also has environmental merits. Flue gas from power plants and natural CO_2 gas is the main available source of the CO_2, however, CO_2 sources are rarely pure. Purifying the flue gas will increase operating costs significantly. Therefore, understanding the roles of impurities in fluid phase behavior and miscibility characteristics is necessary for designing a cost-effective CO_2 enhanced oil recovery process. This paper studies the effect of the different impurities in the CO_2 stream on the phase behavior and the MMP. With the effect of impurities on the CO_2 MMP, it is shown that the presence of intermediate hydrocarbon gas solvents in the CO_2 gas stream can reduce the CO_2 MMP, whereas, the N_2 and CH_4 tend to have the opposite effect. EOS simulation is demonstrated to be an effective toll to analyzing the miscibility of oil-gas systems. Core flood tests are conducted to investigate the oil recovery behavior resulting from CO_2 injection. The ultimate oil recoveries of the tests show that the miscibility and near-miscibility have the same mechanism. The presence of intermediate hydrocarbon gas solvents in the CO_2 gas stream can enhance the ultimate recovery, whereas, the N_2 and CH_4 tend to have the opposite effect.

Key words: CO_2 drive; minimum miscibility pressure; impurities; slim tube test; displacement experiment

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Lou Yi, Yang Shenglai, Zhang Xing et al. Experimental research on CO_2 miscible flooding by advanced gas injection in low permeability reservoir-case of H79 block, Jilin oilfield. *PGRE*, 2012,19(5):78-80.

Abstract: In order to enhance the oil recovery in low permeability reservoir by CO_2 miscible flooding through advanced gas injection, its feasibility is tested in laboratory. The minimum miscible pressure is determined by micro-tubes tests; the laboratory result of CO_2 miscible flooding by advanced gas injection with long core physical simulation device is researched and the result is compared with that of synchronous gas injection and water flooding. The ultimate recovery of CO_2 miscible flooding by advanced gas injection is 77.03%, synchronous gas injection is 73.09% and water flooding is 56.47%. Results show that, since the advanced gas injection can increase the formation pressure and energy, the oil's viscosity is reduced and its mobility is increased because gas injected in advance is contacted with oil, recovery of advanced gas flooding is higher than that of synchronous gas injection and water flooding.

Key words: low permeability reservoir; CO_2 miscible flooding; advanced gas injection; physical simulation; Jilin oilfield

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Zhang Jiyao, Gao Ruimin, Yu Huagui et al. Preliminary study about oxygen consumption of injecting air into low-temperature and low-pressure reservoir. *PGRE*, 2012,19(5):81-83.

Abstract: The Ganguyi blocks is the main production area of Yanchang oilfield, the main developing oil layer is Chang 6 reservoir with low pressure, low permeability and low temperature characteristics. Since 2007, the air-foam enhance oil recovery technology is used, and it achieved good results. An instrument is used to simulate the oxygen consumption of injecting air into a reservoir with 30 ℃ and 6 MPa, and the oxygen content diminishes with index, it will drop under the explosion limit after 80 days, and it can run out if the time is long enough, the law is verified in field test based on a low-temperature and low-pressure reservoir. So, the air-foam enhance oil recovery technology can be used in the low-temperature and low-pressure reservoir.

Key words: low-temperature and low-pressure reservoir; air injection; oxygen consumption; Yanchang oilfield; Ganguyi blocks

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Wang Duanping, Yang Yong, Niu Shuanwen et al. Layer block classification evaluation and adjustment of complicated fault block oil reservoir. *PGRE*, 2012,19(5):84-87.

Abstract: In order to improve the water flooding recovery factor of the fault block oil reservoir and adapt to the needs of the development, this paper considers the static geological features and dynamic development features, then, it proposes layer block classification method of comprehensive evaluation for complicated fault block oil reservoir. A single sand body is the classification object in the vertical, moreover, the cutting of fault block and the change of lithological boundary are considered in the plane. In other words, using "layer block" for the basic elements of the reservoir classification, this paper classifies and evaluates precisely the fault block oil reservoir, and proposes combination of different layers block developed and adjustment program. The practice shows that this method is the base for carrying out potential assessment and adopting the accurate adjustment policies, it has the guiding signifi-