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# 复杂缝网压裂二氧化碳悬浮支撑剂技术及悬砂性能\*

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**摘要:**滑溜水压裂液由于其自身黏度低、携砂能力弱,往往无法满足压后支撑剂对复杂缝网的高效充填。基于气泡悬砂理论,文章提出一种CO<sub>2</sub>悬浮支撑剂技术,并室内试验评价了常温常压、高温高压条件下滑溜水中CO<sub>2</sub>悬砂效果。研究表明,悬浮支撑剂表面改性涂层能起到稳定的气-固桥联作用,通过吸附CO<sub>2</sub>有效降低支撑剂密度,大幅减缓支撑剂在滑溜水中的沉降速度(0.15 cm/min),降低幅度为99%,从而实现滑溜水“低伤害、高携砂”的效果;常温常压下CO<sub>2</sub>悬砂性能主要受滑溜水黏度影响,悬浮程度及稳定悬浮时长随滑溜水压裂液黏度增大而增加,基本不受砂比影响;高温高压下,二氧化碳为超临界状态(SC-CO<sub>2</sub>),但其依旧能吸附在悬浮石英砂表面起到一定的悬浮作用,使得大量的悬浮石英砂在搅拌过程中被悬浮起来。因此,CO<sub>2</sub>悬浮支撑剂技术能显著提高滑溜水压裂液的携砂能力,对降低复杂缝网压裂砂堵风险及提高油气井改造效果具有重要意义。

**关键词:**缝网压裂;滑溜水;SC-CO<sub>2</sub>;桥联效应;悬浮程度

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## 0 前言

我国油气资源增储上产已步入了非常规油气时代,预计新增探明储量的70%、新建产能的50%以上来自于非常规油气资源。水平井段内多缝压裂工艺技术的进步,有力支撑了我国非常规油气资源的规模建产<sup>[1-3]</sup>。针对非常规油气储层体积改造广泛应用的滑溜水压裂液体系,相较线性胶、交联胶压裂液,具有成本低、储层伤害小、造复杂缝网能力强等优点<sup>[4]</sup>,但是由于其自身黏度较低,携砂能力较弱,矿场应用主要利用大排量水力冲击携砂<sup>[5]</sup>,导致砂比难以提高且支撑剂铺置不均匀<sup>[6-7]</sup>,从而无法实现“高效充填、全缝导流”的缝网压裂模式<sup>[8]</sup>,因此,极大限制了体积压裂的增产能力,导致非常规油气井普遍面临产量递减快、采出程度低等问题。

鉴于大规模水力压裂滑溜水携砂能力不足的问题,大量学者开展了“砂液一体化”的悬浮支撑剂攻关研究<sup>[9]</sup>,以期提高支撑剂对压裂裂缝的高效充填。目前已开发了3大类悬浮支撑剂:第1类为轻质和超轻质支撑剂<sup>[10]</sup>,主要利用低密度材料或内部空心的方式降低支撑剂的密度,达到在压裂液中悬浮的效果,但制备成本高、价格昂贵,且存在水敏、老化等现象<sup>[11]</sup>,此外,大量使用超轻质支撑剂经济不可行;第2类为自悬浮支撑剂<sup>[12]</sup>,主要由内部骨料和表面涂层组成,骨料为陶粒和石英砂等常规支撑剂,表面涂层为水凝胶或聚合物,当自悬浮支撑剂进入压裂液时,表面涂层可快速溶胀或增稠,从而降低自身密度或增加自身周围压裂液黏度,达到在压裂液中悬浮的效果<sup>[13]</sup>,但该类支撑剂的表面涂层存在破胶难和储层伤害严重等问题,工艺技术还有

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待进步<sup>[14]</sup>;第3类为气悬浮支撑剂<sup>[15]</sup>,主要通过常规支撑剂表面进行气悬浮剂的喷涂改性,形成具有分子厚度的、可高效稳定吸附气泡的涂层<sup>[16]</sup>,从而使伴注气体能够环绕吸附在支撑剂颗粒表面,降低支撑剂的密度,达到绝大部分支撑剂颗粒在压裂液中悬浮的效果,且不会带来额外储层伤害<sup>[17-18]</sup>。

水力压裂伴注CO<sub>2</sub>过程中,气/液态CO<sub>2</sub>流经地面高压管汇到达井底储层,由于储层温度和压力相对于井口都会大幅度升高,导致其状态由气/液态转变为超临界状态(SC-CO<sub>2</sub>)<sup>[21-22]</sup>,在搅拌过程中的超临界CO<sub>2</sub>与水互不相溶,呈球珠状分散在水溶液中,且该过程CO<sub>2</sub>密度始终介于0.2~0.8 g/cm<sup>3</sup><sup>[23]</sup>。

基于气泡悬砂理论,本文设想利用压裂伴注CO<sub>2</sub>来悬浮支撑剂,通过开展常温常压和高温高压下滑溜水中CO<sub>2</sub>悬砂效果试验评价,明确不同黏度、不同砂比下CO<sub>2</sub>悬砂增效效果,以此形成CO<sub>2</sub>悬浮支撑剂技术,解决滑溜水压裂携砂能力弱的问题,推动非常规油气储层高效充填全缝导流的缝网压裂技术进步。

## 1 实验部分

### 1.1 材料与仪器

液态CO<sub>2</sub>,纯度99.99%;聚合物乳液FDR420,主要成分为线性聚丙烯酰胺,江苏富森科技股份有限公司;普通石英砂,粒径为380~212 μm(40~70目);悬浮石英砂,粒径为380~212 μm(40~70目),在石英砂表面进行悬浮剂喷涂改性所得,涂层主要由分子膜厚度的覆膜剂(主要成份为具有长链的季铵盐)、表面吸附稳定剂(甲基三乙氧基硅烷)和促进黏合剂(二乙烯三胺)组成,悬浮剂加量为0.5%,喷涂改性前后石英砂的性能基本不变,体积密度分别为1.51、1.49 g/cm<sup>3</sup>,视密度分别为2.59、2.53 g/cm<sup>3</sup>,破碎率分别为8.03%、7.39%。配液用水为去离子水。

MHY-2000B型吴茵混调器,北京美华仪科技有限公司;可视化高温高压搅拌釜,耐压≤40 MPa、耐温≤100 ℃,自主研发;ZNN-D6型六速旋转黏度计,青岛恒泰达机电设备有限公司。

### 1.2 实验方法

#### 1.2.1 压裂液的配制

向500 mL去离子水中加入质量分数为0.2%的

FDR420聚合物乳液,并用搅拌器快速搅拌1~2 h。

#### 1.2.2 压裂液黏度的测试

采用六速旋转黏度计,在温度为25 ℃、剪切速率为170 s<sup>-1</sup>下测试压裂液的黏度。

#### 1.2.3 常温常压下CO<sub>2</sub>悬砂能力评价

将500 mL滑溜水压裂液加入吴茵混调器的玻璃杯中,并将连接CO<sub>2</sub>气源的软管插入玻璃杯中,按一定砂比称取悬浮石英砂加入吴茵混调器玻璃杯中;盖上吴茵混调器玻璃杯盖子,打开CO<sub>2</sub>气源减压阀,向玻璃杯中通入CO<sub>2</sub>气体,持续吹扫5 min使玻璃杯中空气被CO<sub>2</sub>完全置换,关闭CO<sub>2</sub>气源减压阀,密闭玻璃杯盖子;打开吴茵混调器电源,调整转速至3000~4000 r/min,持续搅拌10 s左右关闭电源,静置观察不同实验时间下支撑剂沉降堆积高度。引入悬浮程度( $\eta$ )对悬砂效果进行定量评价,具体见式(1):

$$\eta = \left(1 - \frac{h_t}{H}\right) \times 100\% \quad (1)$$

式中: $h_t$ —实验时间 $t$ 下支撑剂沉降堆积高度,mm; $H$ —支撑剂完全沉降堆积高度,mm。

#### 1.2.4 高温高压下CO<sub>2</sub>悬砂能力评价

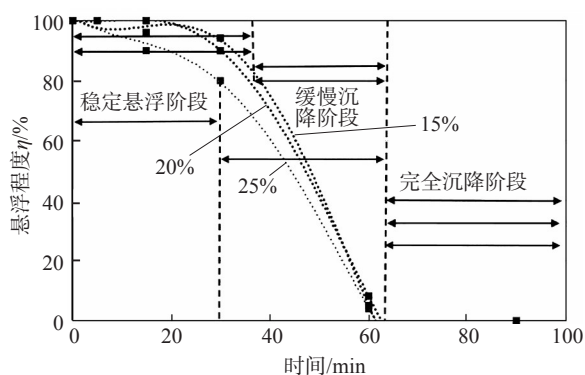
按砂比15%称取悬浮石英砂(或悬浮石英砂)加入高温高压搅拌釜中;打开高温高压搅拌釜上部出口阀,再打开CO<sub>2</sub>气源减压阀,向搅拌釜中通入CO<sub>2</sub>气体,持续吹扫5 min后使搅拌釜中空气被CO<sub>2</sub>完全置换,关闭搅拌釜上部出口阀,继续通入CO<sub>2</sub>气体约6 min,关闭气源阀;打开高温高压搅拌釜电源,设置温度为80 ℃,然后打开平流泵及液体进口阀,流速设置为5 mL/min,向搅拌釜中泵注滑溜水压裂液,待釜体内压力升至25 MPa时关闭平流泵和进液阀;打开磁力搅拌器开关,调整转速至200 r/min,观察并拍照记录超临界CO<sub>2</sub>悬砂效果,实验完毕后,关闭搅拌釜电源,打开泄压阀。

## 2 结果与讨论

### 2.1 常温常压下CO<sub>2</sub>悬砂性能

#### 2.1.1 砂比对CO<sub>2</sub>悬砂性能的影响

不同砂比条件下CO<sub>2</sub>悬砂效果如图1所示。在黏度为18 mPa·s的滑溜水压裂液(FDR420聚合物乳液加量为0.2%)中,伴注CO<sub>2</sub>能较好地悬浮40/70

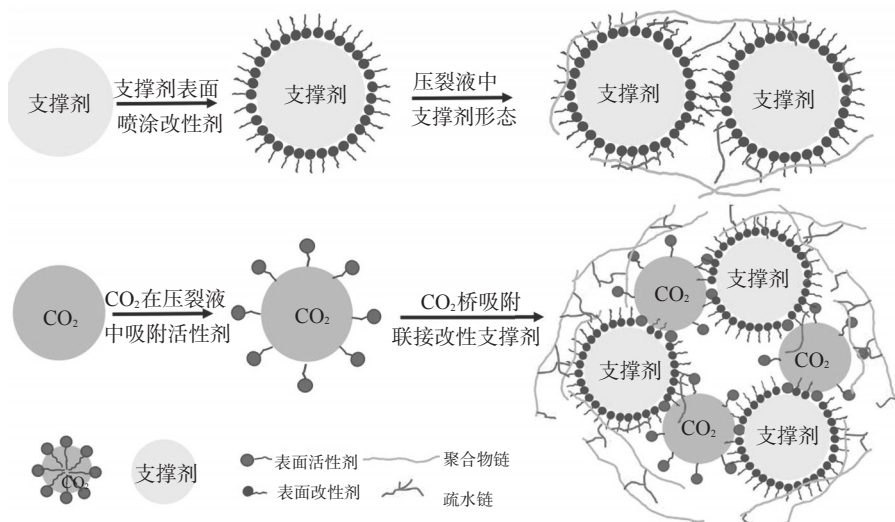
图1 不同砂比条件下CO<sub>2</sub>悬砂效果Fig.1 CO<sub>2</sub> suspended sand effect under different sand ratios

目悬浮石英砂,且悬浮程度基本不受砂比(15%、20%、25%)的影响。此外,CO<sub>2</sub>悬砂稳定性呈现一定的规律,大致可分为3个阶段:第一阶段表现为CO<sub>2</sub>稳定悬砂阶段,即悬浮石英砂在CO<sub>2</sub>作用下维持全悬浮状态(悬浮程度 $\geq 80\%$ ),且悬砂时长均达30 min,如砂比为20%时,初始悬浮程度为100%,30 min时悬浮程度为94%,该阶段悬浮程度略降低(降低幅度仅6%);第二阶段表现为缓慢沉降阶段,即悬浮石英砂开始逐渐缓慢沉降,该阶段持续时长约30 min,如砂比为20%时,30 min时悬浮程度为94%,60 min时悬浮程度下降到5%,悬浮程度大幅降低(降低幅度为89%);第三阶段为完成沉降阶段,即悬浮石英砂完全沉降在杯底。

分析认为,支撑剂悬浮的关键在于改性支撑剂能稳定吸附CO<sub>2</sub>分子,其核心在于支撑剂表面改性涂层起到的桥联作用。支撑剂改性后表面涂层对

CO<sub>2</sub>分子具有强吸收和良好控制效能,涂层主要由分子膜厚度的覆膜剂(成份主要含具有长链基团的季铵盐)、吸附稳定剂(甲基三乙氧基硅烷)和促进黏合剂(二乙烯三胺)组成。如图2所示,在压裂液环境中覆膜剂增强了气态、液态或超临界CO<sub>2</sub>与支撑剂间的相互作用能(范德华相互作用能、双电层斥力位能、疏水相互作用力及水化斥力),吸附稳定剂和促进黏合剂使得CO<sub>2</sub>分子与支撑剂表面覆膜分子之间具有强吸附作用,最终CO<sub>2</sub>分子与支撑剂间稳定结合。因而,CO<sub>2</sub>气泡与改性支撑剂颗粒在压裂液中形成聚集体,其密度得以有效降低,从而实现在滑溜水压裂液中的悬浮。

CO<sub>2</sub>悬砂和沉降机理依赖于CO<sub>2</sub>气泡桥联作用及时变规律。如图3所示,在稳定悬浮阶段,悬浮石英砂完全被CO<sub>2</sub>气泡包裹形成聚集体,此时部分CO<sub>2</sub>气泡与悬浮石英砂直接接触,在桥联作用下形成稳定桥效应,产生稳定CO<sub>2</sub>气泡悬砂作用;在稳定CO<sub>2</sub>气泡外面还附着部分不稳定CO<sub>2</sub>气泡,形成的聚集体密度低于压裂液,从而使石英砂处于全悬浮状态。在缓慢沉降阶段,不稳定CO<sub>2</sub>气泡逐渐破裂或逸散,此时CO<sub>2</sub>气泡包裹悬浮石英砂的聚集体密度逐渐增加,当超过压裂液密度时悬浮石英砂开始逐渐沉降;但由于稳定CO<sub>2</sub>气泡悬砂作用,悬浮石英砂的沉降速度非常缓慢(沉降速度约为0.15 cm/min),仅为相同条件下普通石英砂沉降速度的0.2%(沉降速度约为75 cm/min)。最终,悬浮石英砂完全沉降于杯底,但此时悬浮石英砂外表仍包裹少量稳

图2 CO<sub>2</sub>桥吸附联接改性支撑剂颗粒并形成悬浮聚集体示意图Fig.2 Schematic diagram of CO<sub>2</sub> bridge adsorption connecting modified proppant particles to form suspended aggregates

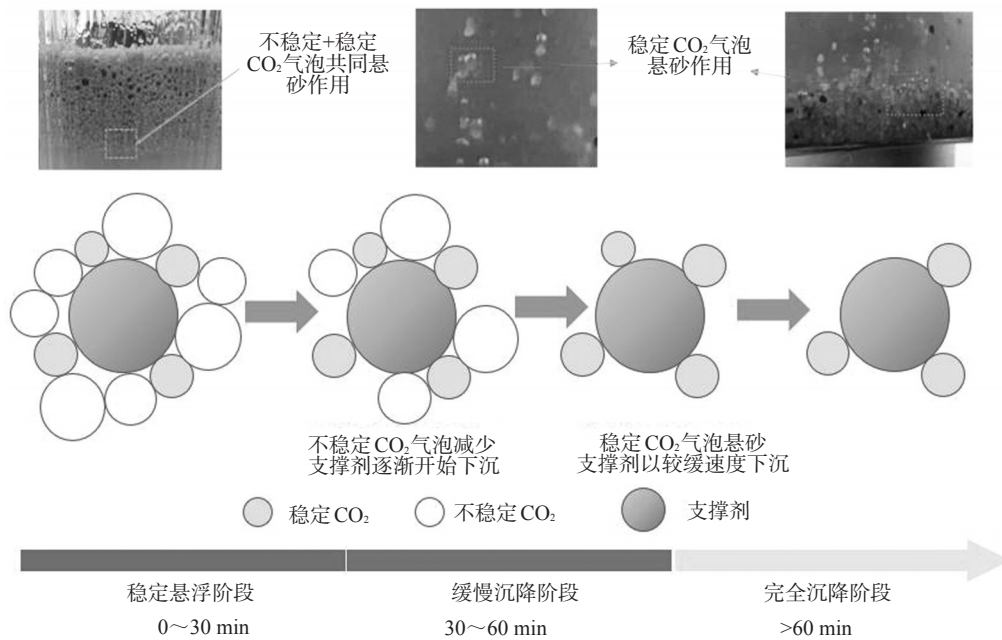


图 3 悬浮石英砂微观悬浮机理及时变规律

Fig.3 Microscopic suspension mechanism and time-varying rule of suspended quartz sand

定 CO<sub>2</sub> 气泡, 其密度仍小于普通石英砂, 处于蓬松状态, 易被水流带动。

### 2.1.2 黏度对 CO<sub>2</sub> 悬砂性能的影响

按砂比 15% 将悬浮石英砂加入不同黏度 (9、14、18 mPa·s) 的滑溜水压裂液中, 不同黏度下 CO<sub>2</sub> 悬砂效果如图 4 所示。伴注 CO<sub>2</sub> 均能较好地将悬浮石英砂悬浮, 悬砂效果同样呈现出 3 个阶段, 但悬砂时长显然受滑溜水压裂液黏度的影响。

第一阶段表现为 CO<sub>2</sub> 稳定悬砂阶段, 即悬浮石英砂在 CO<sub>2</sub> 作用下维持全悬浮状态 (悬浮程度 ≥ 80%), 稳定悬砂时长随压裂液黏度的增大而延长,

黏度为 9 mPa·s 时悬砂时长仅为 15 min, 而黏度为 18 mPa·s 时悬砂时长可达 30 min。第二阶段表现为缓慢沉降阶段, 即悬浮石英砂开始逐渐缓慢沉降, 沉降阶段时长也随压裂液黏度的增加而增长。当黏度为 9 mPa·s 时, 在 30~60 min 已经完全沉降在杯底, 沉降速度为 0.25 cm/min; 当黏度为 14 mPa·s 时, 在 60 min 时悬浮程度仅为 2%, 沉降速度为 0.17 cm/min; 当黏度为 18 mPa·s 时, 在 60 min 时悬浮程度为 6%, 沉降速度为 0.15 cm/min。第三阶段为完成沉降阶段, 即悬浮石英砂完全沉降在杯底。

分析认为, 悬浮石英砂的悬浮依赖于 CO<sub>2</sub> 气泡桥效应作用, 但压裂液的黏度会影响 CO<sub>2</sub> 气泡逸散、破裂速度, 从而影响了悬浮石英砂沉降时变规律, 进而影响了 CO<sub>2</sub> 悬砂时长。随着压裂液黏度的增大, CO<sub>2</sub> 气泡不易逃散且气泡表面变得更加牢固, 因而悬浮石英砂在稳定悬浮阶段具有更长的稳定悬浮时间。在缓慢沉降阶段, 悬浮石英砂的沉降速度也受压裂液黏度的影响, 随着压裂液黏度的增大, 聚合物大分子与悬浮石英砂表面之间的接触面积增大, 从而使悬浮石英砂与聚合物大分子之间的摩擦力增大, 宏观表现为悬浮石英砂沉降速度变慢。

通过上述分析认为, 在黏度为 9~18 mPa·s 的

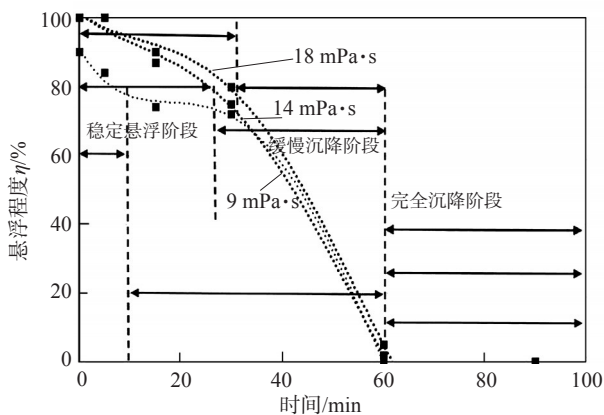


图 4 不同黏度下 CO<sub>2</sub> 悬砂效果

Fig.4 CO<sub>2</sub> suspended sand effect under different viscosity

低黏滑溜水压裂液中伴注CO<sub>2</sub>均能使悬浮石英砂具有较好的悬浮性能,从而确保悬浮石英砂在裂缝中运移更远,提高压裂缝网的充填效率。

## 2.2 高温高压下超临界CO<sub>2</sub>悬砂性能

在78.9℃、25 MPa的条件下,在黏度为18 mPa·s的滑溜水压裂液中,伴注SC-CO<sub>2</sub>并不能悬浮40/70目普通石英砂。在搅拌作用下,大部分普通石英砂沉降在釜底,仅有少量普通石英砂随着搅拌能够悬浮,同时此过程中产生了许多绵密的“超临界气泡”。

在78.9℃、25 MPa的条件下,在黏度为18 mPa·s的滑溜水压裂液中,伴注SC-CO<sub>2</sub>能悬浮40/70目悬浮石英砂。在搅拌过程中,釜底大量悬浮石英砂被悬浮起来,且悬浮石英砂表面聚集吸附着“超临界气泡”SC-CO<sub>2</sub>,在动态搅拌过程中具有良好的悬浮性能。由此,高温高压下SC-CO<sub>2</sub>对悬浮石英砂仍具有较好的悬浮效果。

分析认为,在高温高压条件下,表面未改性的普通石英砂难以与SC-CO<sub>2</sub>发生桥接效应,导致只有少量的普通石英砂在搅拌过程中被悬浮起来;而经过表面改性后的悬浮石英砂则会与SC-CO<sub>2</sub>发生桥接效应,即SC-CO<sub>2</sub>能稳定吸附在悬浮石英砂表面,使悬浮石英砂自身密度降低,大量的悬浮石英砂在搅拌过程中被悬浮起来。通过理论分析和实验现象认为,高温高压条件下CO<sub>2</sub>悬浮支撑剂技术仍能保持悬浮石英砂较好的悬浮能力,从而改善支撑剂的输运和铺置效果。

## 3 结论

改性CO<sub>2</sub>悬浮支撑剂技术能实现滑溜水“低伤害、高效悬砂”的效果。其悬砂机理为CO<sub>2</sub>和悬浮支撑剂之间存在桥联作用使得支撑剂表面改性涂层能稳定吸附CO<sub>2</sub>分子,从而降低支撑剂密度,大幅度降低悬浮支撑剂在滑溜水压裂液中的沉降速度。

常温常压下,CO<sub>2</sub>悬浮支撑剂状态分为3个阶段:全悬浮阶段、缓慢沉降阶段、完全沉降阶段,其悬砂性能主要受滑溜水黏度的影响,随着滑溜水压裂液黏度增大,悬浮程度逐渐增加。CO<sub>2</sub>悬浮支撑剂的悬砂性能基本不受砂比影响,在30 min内始终能保持全悬浮状态(悬浮程度≥80%)。

高温高压下,CO<sub>2</sub>为超临界状态(SC-CO<sub>2</sub>),搅动过程中形成绵密的“超临界气泡”,吸附在悬浮石英

砂表面,从而降低支撑剂密度,使其达到在滑溜水压裂液中悬浮的效果。

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## CO<sub>2</sub> Suspended Proppant Technology and Evaluation of Suspended Sand Performance for Complex Fracture Network Fracturing

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**Abstract:** Due to its low viscosity and weak sand carrying capacity, the slickwater fracturing fluid is often unable to meet the efficient filling of proppant in complex fracture networks post-fracture. Based on the theory of bubble suspended sand, a CO<sub>2</sub> suspension proppant technology was proposed and the CO<sub>2</sub> suspension sand effect in slickwater fracturing fluid was evaluated under normal temperature and pressure, high temperature and high pressure, respectively. The results showed that the surface modified coating of suspended proppant could play a stable gas-solid bridging effect. For the surface modified suspended proppant, the adsorption of CO<sub>2</sub> and the bridging effect of proppant could effectively reduce the specific gravity of proppant, significantly slow

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### Microemulsion Stimulation Agent for Fracturing of Low Permeability Tight Oil Reservoir

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**Abstract:** In order to achieve imbibition stimulation of low permeability tight oil reservoirs, a microemulsion additive (ME) for increasing production by imbibition stimulation was developed, based on the integrated construction method of “compression-injection-recapture” and with the goal of improving the performance of fracturing fluids. The major raw ingredients were fatty alcohol alkoxylation sulfate anionic surfactant (SY-1) and methyl 9-octanoate (MS-9). The phase behavior was explored by fitting a ternary phase diagram, and then the formula was optimized using orthogonal tests. Its performance was evaluated by laboratory experiment, and then the stimulation effect during fracturing was tested. The results showed that the optimum formula for preparing ME was obtained as follows: 25% SY-1, 12.5% triethylene glycol butyl ether, 37.5% KCl aqueous solution (2% mass fraction) and 25% MS-9. The average particle size of the microemulsion was 70.5 nm. It could keep stable under the conditions of long standing (180 days) and high-speed centrifugation (8000 r/min). It could also reduce the interfacial tension to the order of  $10^{-4}$ — $10^{-3}$  mN/m. Compared with water, it could reduce the contact angle by approximately 35°. It could maintain high interfacial activity after 8 adsorptions with core powders, indicating strong anti-sorption ability. It had good compatibility with fracturing fluid. When the fracturing fluid without ME was used as blank control, ME could enhance the oil washing efficiency by 54.94 percentage points—61.82 percentage points during the simulated fracturing entry stage. During the simulated fracturing well stage, the imbibition displacement impact might be raised by 15.68 percentage points. Meanwhile, during the flowback stage, it could accelerate the speed and degree of crude oil recovery, and then the crude oil recovery rate could be increased by 32.56 percentage points. The microemulsion had the advantages of small particle size, strong stability, low interfacial tension between oil and water, good wetting improvement effect and strong adsorption resistance. It could increase oil recovery during the whole process of fracturing construction. The effect of increasing permeability and oil displacement was remarkable.

**Keywords:** fracturing; microemulsion; imbibition displacement; interface tension; wettability; low permeability tight reservoir

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down the settling speed of the proppant in slickwater with a reduction of 99%, being of 0.15 cm/min, thus achieving the effect of “low formation damage and high sand carrying capacity”. The performance of CO<sub>2</sub> suspended sand under the condition of normal temperature and pressure was mainly affected by the viscosity of slickwater. The degree of suspension and stable suspension duration increased with the increase of viscosity of slippery water fracturing fluid, but it is basically not affected by sand concentration. Under the condition of high temperature and pressure, carbon dioxide was in a supercritical state (SC-CO<sub>2</sub>), but it could still adsorb on the surface of suspended quartz sand and play a certain suspension role, causing a large amount of suspended quartz sand to be suspended during the stirring process. CO<sub>2</sub> suspension proppant technology can significantly improve the sand carrying capacity of slickwater, and has important practical significance to reduce the risk of sand plugging in complex fracture networks and improve the efficiency of oil and gas well reconstruction by efficient proppant filling.

**Keywords:** fracture network fracturing; slickwater; sc-CO<sub>2</sub>; bridging effect; degree of suspension