

Development of a Squeezable Iron Sulfide Scale Inhibitor for Ultra-Tight Sandstone

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ABSTRACT

Iron sulfide scaling can manifest both downhole and topside in sour production scenarios. Topsides development can be mitigated via continuous strategic application of an appropriate sulfide scale inhibitor package, however downhole sulfide scaling presents a more complex challenge. Continuous downhole application of sulfide scale inhibitors via capillary string and valve, or routed to valve via existing gas lift architecture are two common delivery options available to the operator, but are unfortunately both limited to providing scale control at injection valve depth and up-string. More recent options for sulfide scale control from reservoir to wellhead include chemical impregnated proppant for prop-frack and gravel packed wells, however these approaches present a partial solution, and require topping-up of inhibitor chemical active once the emplaced inhibitor becomes exhausted. Scale squeezing is the industry recognized chemical technology for providing proactive scale control from reservoir to wellhead, however for sulfide scale control scenarios this technology option is currently poorly served as the industry lacks effective and robust sulfide squeeze scale inhibitors.

A new squeezable polymeric iron sulfide scale inhibitor has been developed and engineered with optimum desirable scale squeeze characteristics, and then further tailored for application in high temperature, high salinity sour gas ultra-tight sandstone/chalk formations. The new molecule used the basic structure of an existing novel class of sulfide scale inhibitor, however the sequence and nature of functional groups across the polymer backbone were extensively modified and optimized to improve (i) polymer retention and release character for extended

squeeze lifetime, (ii) thermal stability, (iii) high calcium brine compatibility and (iv) low formation damage potential. Prior to upscaling for bulk manufacture and subsequent field application, the new polymeric iron sulfide scale inhibitor (FeS-SQSI) was formation damage coreflood tested using target well field conditions and ultra-tight sandstone field core. The results of this remarkable coreflood investigation are presented below, where core permeabilities of sub-0.001 mD were the norm. The flood was performed without interruption or issue, and achieved consistent and continuous formation damage data assessment throughout the 5-week post squeeze shut-in flowback period at very low flowrates.

Sulfide scale inhibitor residuals assay observed consistently elevated concentrations of scale inhibitor across the coreflood flowback 'plateau phase' and indicated that the squeeze treatment could generate significant squeeze lifetime, and this is further born out by mass balance performed after deliberate premature termination of the coreflood indicating that in excess of 90% of the injected scale inhibitor remained within the core.

. Monitoring showed sandstone core permeability recovering rapidly following start of backflow, with no evidence of any significant formation damage. Post-flood data indicated no loss of core plug integrity, and mineralogical assay confirmed unchanged material composition. The formation damage sandstone coreflood results clearly demonstrated the suitability and robustness of this new iron sulfide scale inhibitor for squeeze application under extremely challenging squeeze application conditions.

Key words: Chemical Treatment, Scale squeeze, Iron Sulfide Scale, Flow Assurance, Formation Damage, Coreflood, Ultra-low permeability sandstone, Sour Tight Gas formation.

INTRODUCTION

Oilfield sulfide scale formation is peculiar to sour production scenarios, and for many oil and gas fields the issue of iron sulfide scale management downhole presents a major challenge. Historically iron sulfide scaling downwell have featured 'reactive' chemical dissolver interventions to recover well production once sulfide scale has deposited, and operators have published extensively on their experiences i.e. coiled tubing deployed dissolver technologies used in well clean-out treatments (Green, et.al. 2014, Wang et.al. 2017, Wang et.al. 2018, Buali et. al 2014). Unlike common carbonate and sulfate scales, there is no 'proactive' squeeze scale inhibitor alternative for control and management of sulfide scale from the producer well wellbore and up-string / downstream, hence the reliance and dominance of sophisticated reactive chemical dissolver-based interventions, (Wylde, J. 2014, Okocha et. al 2020). There are few sulfide scale inhibitor options available generally to the industry as a whole and this is due primarily to the ultra-low solubility of sulfide scales, and the rapidity with which sulfide scales form and precipitate from solution.

A new and novel polymeric scale inhibitor was developed and introduced to the industry in 2014 (Savin et al., 2014 ; Wylde et al., 2014 Wylde et al., 2015), which gained industry acceptance for topsides and downhole application via continuous injection. Although highly effective and novel in its action for control of all sulfide scales, the polymer coreflood test performance precluded it from being deployed as a standalone squeeze scale inhibitor, however it did excel when deployed downhole as an additive in complex frack treatments in sour wells. In 2017, a joint development initiative focused on re-engineered the original active water-soluble polymer in order to tailor it for squeeze application in hot, tight, gas formations for the prevention of iron sulfide scale. Molecular engineering resulted in the creation of in-excess of 100 viable

iron sulfide scale inhibitor squeeze product variants, and extensive systematic performance ranking studies determined the most suitable scale squeeze product (Petrozziello et. al 2020).

Proof of Concept Formation Damage Assessment

Proactive scale squeezing for control of downhole scaling is preferred to reactive remedial chemical application in the majority of cases, with treatment efficiency, longevity, economics, safety and integrity benefits being cited (Wylde et.al 2009, Okocha et. al. 2008, Jordan et al. 2000; Collins 2001; Nasr-El-Din et al. 2001a; Nasr-El-Din et al. 2001b; Przybylinski 2001b, 2003). In most scale inhibitor squeeze application scenarios, the formation damage potential of the proposed treatment needs to be clearly understood, and will often provide final ranking discrimination between candidates. The three best candidate variants underwent final ranking via their performance in formation damage coreflood tests using outcrop chalk cores. The best performing candidate required ‘proof of concept’ coreflood testing using real field conditions and real field core before it would be considered for upscaling to bulk manufacture and field trial.

Coreflood Study Objectives

The paper describes the ‘proof of concept’ coreflood experiment and the results obtained from application of iron sulfide squeeze scale inhibitor FeS-SQSI into an ultra-tight sandstone field core. The primary objectives were (1) minimal permanent impact on core permeability to gas and oil, (2) significant scale inhibitor retention, and (3) a useful average return RSI during flowback, and (4) potential for useful squeeze lifetime and/or extended squeeze lifetime.

EXPERIMENTAL PROCEDURE

The coreflood experiment is designed to simulate a sulfide scale inhibitor chemical squeeze treatment in field rock material. The formation damage potential of the treatment was assessed by comparing core permeability to oil/brine/gas before chemical pill application and then post shut-in and treatment flowback. The target well is a significant gas and condensate producer therefore gas and liquid hydrocarbon permeabilities were considered key to determining the success or failure of the formation damage coreflood. Reduction in permeability to field brine while maintaining significant hydrocarbon permeabilities was considered to be desirable.

Field Core

Several pre-cut sandstone field cores were generously supplied by the field operator for the experiment, and after intensive mineralogical and integrity screening, one core stub was selected for the ‘proof of concept’ coreflood. The core plug was shorter in length than desired and exhibited permeabilities to liquid and gas < 0.5 mD at 1500 psi, see Table 1, and mineralogical assay in Table 2.

Table 1: Field Core Plug

Confining Pressure (psi)	Pore Volume (cm ³)	Porosity Fraction	Permeability Klinkenberg (mD)	K _{N2} (mD)	Grain Volume (cm ³)	Grain Density (g/cm ³)	Dry Weight (g)	Plug Length (cm)	Plug Diameter (cm)
800	4.246	0.115	0.420	0.606	32.655	2.67	87.166	3.427	3.850
1500	4.070	0.111	0.260	0.422	32.655	2.67	87.166	3.427	3.850

Table 2: Core Mineralogy

Whole Rock Mineralogy Weight %							Clay (Phyllosilicates) Weight %	
Quartz	K-Feldspar	Plagioclase	Calcite	Dolomite	Siderite	Pyrite	Total Clay	Illite & Mica Chlorite
91.9	2.5	0	0.4	0	0.5	0	4.7	4.1 0.6

Coreflood Test Brines

The target well produced water (PW) ion composition was adjusted and simplified to comprise sodium, calcium, magnesium and chloride ions only, see Table 3. NaCl was used to adjust the ion balance. Prior to use, the brine was filtered (0.45 µm) and vacuum degassed.

The FeS-SQSI slug was prepared in 6% NaCl.

Table 3: Brine Ion Composition

Salt	PW (g/L)
NaCl	31.15
CaCl ₂ .2H ₂ O	42.63
MgCl ₂ .6H ₂ O	13.89

Gas

Oxygen free nitrogen (OFN) was used as gas analogue. The gas was humidified via flowing through a bubble cell at test temperature and pressure. Humidification was included to minimize brine evaporation into the gas phase, as this could result in accidental salt precipitation within the core and potentially impact the formation damage assessment.

Oil

Isopar™ was used to represent the field condensate as it was a good viscosity analogue. Measures were taken to ensure that the Isopar™ viscosity was maintained at the supplied viscosity.

PoC Coreflood Test

The PoC coreflood procedure is detailed in Table 4, and test conditions and viscosities in Tables 5 and 6.

Table 4: Coreflood Treatment Sequence

	Action	Medium	Measure	T (°C)	P CP/BP (psi)	
1	Clean core plug and dry	Nitrogen	K_{N_2} / ϕ	RT	2000	
2	Evacuate air from plug and saturate	PW		RT	2000	
3	Load into coreholder, apply CP and BP	--	--	RT	1500 /500	
4	Flow PW at 1 mL/min and increase to TT	PW	ΔP and K_w	140	1500 /500	FWD
5	Flow oil through core at 1 mL/min	Isopar™	$\Delta P K_o@swi$	140	1500 /500	FWD
6	Flow PW through core at 1 mL/min	FW	$\Delta P K_w@sor$	140	1500 /500	FWD
7	Flow PW + tracer at 1 mL/min	FW + [Li ⁺]	$\Delta P PV$	140	1500 /500	FWD
8	Flow PW at 1 mL/min	FW	ΔP	140	1500 /500	FWD
9	5PV of 3% FeS-SQSI in 6% NaCl at 1mL/min	SI Pill	ΔP	140	1500 /500	REV
10	Shut-in for 24 hours		ΔP	140	1500 /500	
11	Backflow PW at 0.1 mL/min for 1000 PV	FW	∇P	140	1500 /500	FWD
12	Flow [oil] at 0.1 mL/min	Isopar™	$\Delta P K_o@swi$	140	1500 /500	FWD
13	Flow PW at 0.1 mL/min	FW	$\Delta P K_w@sor$	140	1500 /500	FWD
14	Clean core plug, dry	Nitrogen	K_{N_2} / ϕ	RT	2000	

*CP = confining pressure **BP = back pressure

Table 5: Coreflood Test Parameters

Parameter	Unit	Value	Comment
Test Temperature	°C	140	Reservoir Temperature
Injection Temperature	°C	140	Injection of Inhibitor slug
Pore Pressure	psi	500	
Overburden Pressure	psi	1500	
Overburden(confining) Pressure	psi	2000	
Fluid Flow Rate	mL min ⁻¹	0.1-1	
Shut-in	Hours	24	