New Understanding on Iron Sulfide Deposition during Acid Stimulation in Sour Gas Wells Using an Advanced Modeling Approach

Dr. Peng Lu, Dr. Tao Chen, Dr. Qiwei Wang, and Dr. Fakuen F. Chang

ABSTRACT

Iron sulfide scaling has been a persistent problem for oil and gas production from sour reservoirs. To study iron sulfide deposition in near wellbore formations, an advanced numerical geochemical method, reactive transport modeling (RTM), is applied in this article to simulate the iron-bearing scale formation — especially during and post-acid stimulation. The code “TOUGHREACT” is used for simulation. The model results allow an insight into the spatial and temporal distribution of iron-bearing scale precipitation, wormhole formation, as well as reservoir pressure and water chemistry evolution.

Results of an acid treatment scenario in a hypothetical high hydrogen sulfide (H$_2$S) carbonate reservoir demonstrate that the scales tend to be concentrated in the wormholes. Pyrrhotite and siderite (FeCO$_3$) are the most abundant iron-bearing scales, however, the latter will gradually convert to the former during the normal production stage. The acid selectively dissolves calcite while leaving the dolomite component largely undissolved. Siderite, as a form of iron-bearing scale, is recognized in this study. This new understanding will contribute to optimizing acid treatment design and formulation for iron-bearing scale prevention in sour gas wells.

INTRODUCTION

Acid stimulation is a frequently used technology to enhance the production rate of hydrocarbons from a reservoir. Depending on the reservoir type — carbonate or clastic — and mineralogical compositions, different fluid compositions and injection schemes are selected to ensure the optimal treatment results. The injected acid dissolves damaged materials accumulated during the drilling or production, and also reactive minerals near the wellbore, e.g., calcite. This increases the permeability and decreases the skin value in the vicinity of the production well.

Carbonate reservoirs demonstrate significant heterogeneity — at different scales — both temporally and geographically in the field. Vertical carbonate facies variations controlled by sequence stratigraphy are dominated heterogeneity at meter-scale. Smaller scale heterogeneity may be present because of: (1) sorting, texture, and chemical composition of grains; (2) diagenesis, e.g., cementation, dissolution and dolomitization, and biological effects, e.g., bioturbation, and (3) geomechanical effects, e.g., fractures and faults. Due to these heterogeneities, dissolution features such as wormholes may form due to the differential dissolution of reservoir rock and formation of selective pathways.

Iron sulfide scaling may impose a significant threat to economic and efficient field operations in the sour carbonate gas wells. The source of iron may come from the corrosion of steel pipes and well completion materials during the stimulation operations. Iron sulfide deposited on downhole tubulars decreased well deliverability and restricted wellbore surveillance. Iron sulfides were also accumulated at the wellhead manifold to cause flow line blockage. In addition, it is suspected that during acidizing jobs, iron sulfide could be formed in the near wellbore reservoir, which renders the effectiveness of acid stimulation and also contributes to the scale problem on tubulars. Due to their thermodynamic metastability, different iron sulfide species can form at different times and well depths; and some are extremely difficult to remove by chemical treatment. Mechanical descaling is currently applied to mitigate the scale buildup on downhole tubing, but it is time-consuming and costly. When precipitated inside the near wellbore formation, scaling is very difficult to be mitigated effectively.

Though extensive research has been carried out to understand iron sulfide scale deposition in sour wells, knowledge of its temporal transformation and spatial distribution is still poor, making the formulation of a cost-effective mitigation strategy difficult. To make a suitable management strategy, it is essential to understand the mechanisms of iron sulfide deposition. In the present study, we constructed a 3D reactive transport model to simulate the iron sulfide scale formation near the production wellbore during a hypothetical well stimulation process to help understand the mechanisms of iron sulfide formation in the near wellbore during acid stimulation. The impact of scale formation on the reservoir and well properties during the stimulation process was evaluated.

MODELING APPROACH

The simulations of the scale formation during acid stimulation for the carbonate formation are conducted with the computer
Table 2. Formation water chemistry used in this study

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mol/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>156.135</td>
</tr>
<tr>
<td>K</td>
<td>64.533</td>
</tr>
<tr>
<td>Ca</td>
<td>28.531</td>
</tr>
<tr>
<td>Mg</td>
<td>5,047</td>
</tr>
<tr>
<td>Cl</td>
<td>780</td>
</tr>
<tr>
<td>HCO\textsubscript{3}^-</td>
<td>0.023</td>
</tr>
<tr>
<td>H\textsubscript{2}O, Y (m)</td>
<td>0.0024</td>
</tr>
</tbody>
</table>

**RESULTS AND DISCUSSIONS**

Figures 2 and 3 display the time series of reservoir pressure and gas saturation distribution for a fractured reservoir, respectively. Note that the variation of the pressure is closely...
related to the flow rate; a higher injection rate will result in higher pressure change. Using the injection rate defined in the present study, pressure was slightly increased from 300 bars — initial reservoir pressure — to up to 321 bars in the vicinity of the well, due to the acid injection in the first 0.5 h. Pressure gradient gradually dissipates away from the well, forming a halo. Subsequently, due to the differential fluid flow rate caused by the wormholes, the distribution of pressure is not uniform; the areas with the wormholes have higher pressures than without. As the injections ceased (sitting period: 0.5 h to 6 h), the pressure returns to initial reservoir pressure. During the flow back period of 6 h to 18 h, a reverse pressure gradient is observed with the pressure slightly lower, 297 bars, in the near well region.

During the acid injection, gas saturation was decreased to 0 — water saturation to be 1 — in the vicinity of the well, Fig. 3. At 0.5 h, the zero-gas saturation zone advances to the wormholes and their vicinities and remains almost unchanged during the sitting period, 0.5 h to 6 h. Although, the gas does invade back to this “zero gas saturation zone” during the flow back period and a halo is formed with the gas saturation decreasing toward the well, Fig. 3.

The model predictions indicate that in addition to iron sulfide, primarily pyrrhotite, siderite can form in the spent acid solution, Figs. 4 and 5, respectively. The formation of siderite

<table>
<thead>
<tr>
<th>Formation Water</th>
<th>ppm</th>
<th>mol/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>28,531</td>
<td>0.7119</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>550</td>
<td>0.023</td>
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<tr>
<td>Na⁺</td>
<td>64,533</td>
<td>2.087</td>
</tr>
<tr>
<td>K⁺</td>
<td>5,047</td>
<td>0.129</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>156,135</td>
<td>4.404</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>780</td>
<td>0.013</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>230</td>
<td>0.0024</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>2,112</td>
<td>0.0241</td>
</tr>
<tr>
<td>pH</td>
<td>6.8 (pH unit)</td>
<td>—</td>
</tr>
</tbody>
</table>

Table 2. Formation water chemistry used in this study

![Fig. 2. Time series of reservoir pressure distribution near the injection well showing the wormhole effects. From left to right are 0.5 h, 6 h, and 18 h, respectively.](image)

![Fig. 3. Time series of gas saturation distribution near the injection well showing the wormhole effects. From left to right are 0.5 h, 6 h, and 18 h, respectively.](image)
is because the high concentration in total dissolved carbon dioxide (CO₂). The carbonate dissolution via acid stimulation increased the total dissolved CO₂ significantly. Calcite is the dominate mineral that dissolves in a carbonate reservoir — with both calcite and dolomite — because: (1) the solubility of calcite (pKₐ = 8.48 at 25 °C) is much larger than dolomite (pKₐ = 17-19 at 25 °C)³, and (2) the dissolution rate constant of calcite at the reservoir conditions is several orders of magnitude faster than dolomite. Furthermore, when both minerals are present, the faster dissolving calcite releases Ca²⁺,
which reduces the driving force for dolomite dissolution —
common ion effects.

The highest volume fraction of siderite, defined as the vol-
ume of a constituent divided by the bulk volume; rock + po-
rorosity, is about one order of magnitude higher than pyrrhotite.

This is likely because the maximum value of total dissolved
CO$_2$ is about five times higher than that of total dissolved sul-
fide, Figs. 6 and 7, respectively. Both pyrrhotite and siderite
scales occur in the wormholes and their vicinities, with higher
concentrations in the wormholes. The spatial distribution of

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**Fig. 7.** Time series of total dissolve carbon (molality) evolution. From left to right are 0.5 h, 6 h, and 18 h, respectively.

**Fig. 8.** Time series of iron (molality) evolution showing the wormhole effects. From left to right are 0.5 h, 6 h, and 18 h, respectively.

**Fig. 9.** Time series of pH evolution. From left to right are 0.5 h, 6 h, and 18 h, respectively.
pyrrhotite and siderite is roughly consistent with that of iron concentration at 0.5 h, Fig. 8. Halos of pyrrhotite, siderite and Fe²⁺ formed around the wormholes, Figs. 4, 5, and 8, respectively; probably due to the diffusion effects of Fe²⁺ from the higher permeability wormholes to lower the permeability matrix.

There are three distinct zones for pH distribution: a low pH zone (< 1) within the wormholes near the well, a median pH zone (~4) in the wormholes and their vicinities and a high pH zone unaffected by the wormholes, Fig. 9. The low pH zone is where calcite is completely dissolved and no buffering remains in this region. The median pH zone is likely to be buffered by the calcite. The high pH zone is likely to be controlled by the equilibrium of the H_2S(g)-H_2O calcite system. The iron distribution in the reservoir reaches its maximum extent at 0.5 h, and its concentration decreases with time after 0.5 h, Fig. 8, due to the continuous formation of pyrrhotite and siderite scales.

Carbonate dissolution and wormhole formation during the acid stimulation are likely to increase reservoir porosity and permeability; however, higher abundances of iron scales are formed within the wormholes. This may decrease the effects of acid stimulation, because permeability could be inversely affected by scale formation in pore throats.

**CONCLUSIONS**

In the present study, we provide a parametric study of iron sulfide deposition during acid stimulation in high temperature gas wells producing from a hypothetical high H_2S carbonate reservoir, using an advanced, reactive transport modeling approach. The potential of iron-bearing scale formation on the reservoir and near well region during acid stimulation operations was evaluated. The following conclusions were made:

1. The modeling results provide dynamic temporal and spatial evolution of reservoir pressure, gas saturation, water chemistry, scale formation, and the formation process of wormholes.
2. Calcite is the dominant carbonate minerals to be dissolved by the acid injected.
3. Pyrrhotite and siderite are the most abundant iron-bearing scales during acid stimulation from model predictions and the maximum concentration of the latter is almost one order of magnitude higher than the former. Subsequently, pyrrhotite is thermodynamically more stable than siderite and the latter could be gradually converted to the former in the H_2S environment.
4. Higher abundances of iron scales can be formed in the wormholes during acidizing treatment. They could partly offset the effects of the stimulation jobs.
5. Our modeling results provide a new understanding that siderite as a form of iron-bearing scale could be present in the subsurface.

**ACKNOWLEDGMENTS**

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**REFERENCES**

Dr. Peng Lu is a Geologist in Saudi Aramco’s Exploration and Petroleum Engineering Center – Advanced Research Center (EXPEC ARC). He is currently conducting research related to carbonate and clastic diagenesis, reservoir quality prediction, and reactive transport modeling.

Before joining Saudi Aramco in 2012, Peng worked as a Geochemist in the Calera Corporation for 2 years, where his work was focused on the experimental and numerical modeling of carbon dioxide reduction through conversion to mineral products.

He has authored and coauthored more than 30 refereed journal articles and several other technical papers, and is a recipient of two U.S. granted patents.

Peng is a member of the Society of Petroleum Engineers (SPE), American Association of Petroleum Geologists (AAPG), Geological Society of America (GSA), Geochemical Society, and American Geophysical Union (AGU).

He received his B.S. and M.S. degrees in Geology from Nanjing University, Nanjing, China, and his Ph.D. degree in Geochemistry from Indiana University, Bloomington, Indiana, in 2010.

Dr. Tao Chen is a Petroleum Engineering Specialist working with the Production Technology Team of Saudi Aramco’s Exploration and Petroleum Engineering Center – Advanced Research Center (EXPEC ARC). His interests are production chemistry and flow assurance in the oil and gas industry, specializing in oil field scale management.

Prior to joining Saudi Aramco in 2014, Tao spent more than 15 years on oil field scale management and worked at Clariant, Champion Technologies, Nalco Champion, and LR Senergy in Aberdeen, U.K.

He has published nearly 70 technical publications about scale management in oil fields.

Tao received both his B.S. and M.S. degrees in Chemical Engineering from Dalian University of Technology, China, and his Ph.D. degree in Chemical Engineering from Heriot-Watt University, Edinburgh, U.K. Tao also received an M.B.A. from Warwick University, Coventry, U.K.

Dr. Qiwei Wang works in Saudi Aramco’s Research & Development Center as a Science Specialist in oil field scale mitigation. Since joining Saudi Aramco in 2011, he has played a key role in all major scale mitigation activities and led the completion of over 40 projects. Before joining Saudi Aramco, Qiwei worked for Nalco Champion as a R&D Coordinator on flow management and as a Senior Specialist on scale management. He has over 25 years of R&D and technical support experience in oil field production chemistry, scale management, and water treatment.

Qiwei is an active member of the Society of Petroleum Engineers (SPE) and National Association of Corrosion Engineers (NACE). He has organized workshops, served on technical committees and chaired several conferences for both organizations.

He has authored and coauthored over 80 publications and nine U.S. patent applications.

Qiwei received his B.Eng. degree in Chemical Engineering from Taiyuan University of Science and Technology, Taiyuan, China; an M.Eng. degree in Material Sciences from Harbin Institute of Technology, Harbin, China; an M.S. degree in Chemistry from the University of Ryukyu, Okinawa, Japan; and a Ph.D. degree in Oceanography from Texas A&M University, College Station, TX.

Dr. Fakuen F. “Frank” Chang is a Petroleum Engineering Consultant in the Productivity Enhancement Focus Area of the Production Technology Team at Saudi Aramco’s Exploration and Petroleum Engineering Center – Advanced Research Center (EXPEC ARC). Prior to joining Saudi Aramco in September 2012, he worked at Schlumberger for 16 years, and he was at Stimlab for 4 years before his Schlumberger career. Frank has developed many products and technologies dealing with sand control, fracturing, acidizing, and perforating.

He is an inventor and recipient of 23 granted U.S. patents and the author of more than 40 Society of Petroleum Engineers (SPE) technical papers.

Frank received his B.S. degree in Mineral and Petroleum Engineering from the National Cheng Kung University, Tainan City, Taiwan; his M.S. degree in Petroleum Engineering from the University of Louisiana at Lafayette, Lafayette, LA; and his Ph.D. degree in Petroleum Engineering from the University of Oklahoma, Norman, OK.