Solvent removes downhole NORM-contaminated BaSO₄ scale

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A research project in Canada recently demonstrated that a solvent can remove barium sulfate (BaSO₄) scale contaminated with NORM from wells. The solvent dissolves the BaSO₄ scales, and all radioactive material is left downhole, eliminating costly NORM disposal.

Each year, scale precipitation costs operators millions of dollars in maintenance, treatment, and lost production. Scale contaminated with naturally occurring radioactive material (NORM) creates further problems because NORM
scales fall under strict and expensive disposal guidelines.

Highly insoluble BaSO₄ scales can be difficult to treat because radioactive materials often incorporate into the scale as it forms. BaSO₄ scales have had to be removed by mechanical scraping or reaming, which is troublesome and costly. The strict regulations concerning disposal of NORM scale add to the costs of the treatment.

**Scales**

Scale is a solid mineral deposit that forms from produced salt water.1 Because water constantly dissolves and deposits solids, scales can build up wherever water production occurs.

Scaling can cause production problems in primary production wells, secondary wells, injection wells, disposal wells, and pipelines that connect wells to tank batteries.

Scale is caused by a combination of events including:
- Pressure changes
- Temperature changes
- Impurities
- Additives
- Variations in flow rates
- Changes in pH
- Fluid expansion
- Gas evaporation
- Mixing of incompatible waters.

Scale can form quickly or take months to build up enough to affect production levels. Calcium carbonate (CaCO₃) scale builds up quickly but is easy to treat. BaSO₄ scales, on the other hand, build slowly but are difficult to treat.

BaSO₄ scale is highly insoluble (2 mg/L in water) and usually cannot be dissolved economically with chemical agents. In most cases, mechanical scraping or reaming are the only ways to remove precipitated BaSO₄.

BaSO₄ most often is found in deep, hot wells. It is more soluble at higher temperatures and pressures.

Water produced from deep, hot wells tends to have elevated brine and carbonate content, which also increases BaSO₄ solubility. A drop in temperature and pressure as well fluids are produced causes BaSO₄ to precipitate.

For disposal, most operators reinject produced brines, mixing the brine with waters produced from other zones. When the disposed BaSO₄ brine mixes with fresh water, the lower salinity of the mixed water reduces BaSO₄ solubility, forming scale.

When naturally occurring radioactive materials (NORM) incorporate into the BaSO₄ scale as it forms, the scale removal treatment falls under hazardous waste guidelines. The U.S. government categorizes radioactive material by the amount of radiation it is likely to produce. NORM scale is categorized as a potential hazard.

NORM contamination can be found in BaSO₄ scale that clings pipes and equipment and in the sludge from oil storage tank bottoms. The scale can restrict or completely choke production in the tubing, flow lines, at the surface, or in the perforations. Scale also can deposit in fractures and formations that are distant from the well bore.

**NORM contamination**

NORM can occur in the ground, in the air, and in the human body. Natural radioactive substances found in earth formations include uranium, thorium, and actinium.

Uranium products (²³⁵U) cause the most trouble in the oil field. The radioactive contaminant radium (²²⁶Ra), which can occur in some scales such as barites, has a half-life of 1,620 years. Radon decays to radon gas (²²²Ra), which has a half-life of 92 hr. The radon gas generally is trapped in the crystal lattice of the barite scales. Bismuth (²¹²Bi) and a lead isotope (²¹⁸Pb) emit practically all the gamma radiation from NORM-contaminated scale.

Thorium and actinium products are not found in sufficient quantities to be a concern to the oil industry.

**NORM disposal**

Although the health risks from low levels of NORM are considered minimal, disposal of NORM wastes can be hazardous. While radioactivity from oil field scale is low from pipe to pipe, the total radiation level increases when all pipe scale at one site is gathered in one place.

The U.S. government and
individual state regulations control oil field scale disposal, which makes the disposal effort difficult and expensive. As of July 1994, only one site in the U.S. was available for NORM waste disposal. That site, in Utah, charges $300-500/drum for disposal.

The Environmental Protection Agency (EPA) allows some operators to pump NORM wastes underground in regulated hazardous waste disposal wells. Individual states also regulate NORM scale disposal as a solid waste under Subtitle D of the Resource Conservation and Recovery Act (RCRA) under the drilling fluids exclusion.

Texas and Louisiana also have instituted state NORM regulations. Louisiana allows equipment and piping to be used without restriction if the maximum radiation exposure level does not exceed 25 microrem/hr according to the Implementation Manual for Management of NORM in Louisiana.

The Texas Regulations for Control of Radiation, Part 46, limit the maximum contact time to 50 microrem/hr. Other states have implemented the terms of the Texas regulations.

Most oil and gas producing nations have established NORM contamination standards and procedures since NORM became a problem in North Sea wells in 1981.3

**Solvent treatment**

The candidate well for treatment was an injection well that was completed in October 1984 at a total depth of 1,445 m (4,741 ft). The interval was perforated from 1,369 to 1,372 m. In November 1985, the well was converted to an injector. The well had a bottom hole pressure of 10,985 kPa (1,593 psi) and a bottom hole temperature of 53°C (127°F).

The well was treated eight separate times in 10 years. The first treatment, in October 1984, was a gelled acid wash and squeeze with 15% HCl and gelled 28% HCl. Subsequent treatments included a nitrogen squeeze, a series of solvent treatments, and an acid wash and squeeze.

Over the course of 10 years, the well showed a slow decline in the injection rate. The probable cause was scale formation caused by mixing incompatible waters.

**Pretreatment analysis**

To determine the source of the scaling, the project researchers analyzed the produced water and source water for scaling tendencies. The individual waters were analyzed and then mixed in various ratios and analyzed over a range of applicable temperatures.

Table 1 shows the produced water was high in sulfate, and the source water was high in barium. The results suggest that BaSO₄ scale could form if the two waters were mixed.

A scale measurement program (Program 1) was used to analyze the scaling tendencies of the waters. Table 2 shows that the waters had the tendency to form scales of calcium carbonate (CaCO₃), calcium sulfate (CaSO₄), barium sulfate (BaSO₄), and strontium sulfate (SrSO₄) at 24, 38, 52, and 66°C.

According to the program, the produced water had a strong tendency to form calcium carbonate (CaCO₃) scale at 24-66°C, a slight tendency to form barium sulfate (BaSO₄) scale at 24-52°C, and a slight tendency to form strontium sulfate (SrSO₄) scale at 38-66°C.

The program determined that the source water had a moderate tendency to form calcium carbonate scale at 24-66°C and a slight tendency to form barium sulfate scale at 24 to 52°C.

A second scale measurement program (Program 2) calculated the scaling tendency after mixing two waters at various ratios at 24 and 53°C. The well bottom hole temperature was 53°C.

Various ratios of the produced water and source water showed a moderate-to-strong tendency to form CaCO₃ scale and a slight-to-strong tendency to form BaSO₄ scale (Tables 3). The

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**Table 1**

<table>
<thead>
<tr>
<th>Water ratio</th>
<th>Calcium carbonate</th>
<th>Calcium sulfate</th>
<th>Barium sulfate</th>
<th>Strontium sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Produced</td>
<td>Tendency</td>
<td>Tendency</td>
<td>Tendency</td>
<td>Tendency</td>
</tr>
<tr>
<td>Source</td>
<td>Calcium carbonate</td>
<td>Calcium sulfate</td>
<td>Barium sulfate</td>
<td>Strontium sulfate</td>
</tr>
<tr>
<td>At 24°C</td>
<td>Strong</td>
<td>None</td>
<td>Slight</td>
<td>None</td>
</tr>
<tr>
<td>100:0</td>
<td>295</td>
<td>None</td>
<td>7</td>
<td>None</td>
</tr>
<tr>
<td>20:1</td>
<td>187</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>

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**Table 2**

<table>
<thead>
<tr>
<th>Fluid system</th>
<th>% solubility</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% H₂O/50% BaSO₄ scale solvent</td>
<td>75</td>
</tr>
<tr>
<td>40% H₂O/60% BaSO₄ scale solvent</td>
<td>96</td>
</tr>
<tr>
<td>30% H₂O/70% BaSO₄ scale solvent</td>
<td>99</td>
</tr>
<tr>
<td>100% BaSO₄ scale solvent</td>
<td>95</td>
</tr>
<tr>
<td>15% HCl</td>
<td>0</td>
</tr>
<tr>
<td>12% HCl/3% HF</td>
<td>0</td>
</tr>
</tbody>
</table>

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*60°C for 60 hr*
program confirmed that CaCO₃ or BaSO₄ scale was likely to form whenever the produced water and the source water were mixed. Because the well had been treated with conventional acid treatments and still showed an injection rate decline, it was decided that the probable cause was BaSO₄ scale.

Before designing the scale treatment, the researchers performed compositional and analytical tests on the scale to determine the concentration and contact time required for an effective solvent treatment. A scale sample was analyzed with X-ray diffraction (XRD) to identify the minerals. BaSO₄ was the only crystalline mineral present. The scale was also analyzed with a scanning electron microscope (SEM) with an X-ray energy spectrometer to determine the elemental composition of the sample. The results showed that barium (Ba) was the predominant element with lesser amounts of sulfur. The SEM also detected trace quantities of iron, calcium, strontium, and aluminum (Fig. 1).

A gravimetric solubility test determined the maximum solubility of the scale with a fluid system containing 30% water and 70% BaSO₄ scale solvent (Table 4). As predicted, the scale showed no solubility in 15% HCl and 12% HCl-3% HF.

A pretreatment gamma ray spectroscopy log determined the amount and the location of the scale in the well. An earlier gamma ray spectroscopy measurement in the field had discovered uranium in the formation. The perforated interval at 1,369.72 m was immediately below an organic-rich shale containing uranium, which was the source of the NORM.

Treatment results

The pretreatment analysis revealed that BaSO₄ scaling had consistently decreased the injection rate and increased costs to support the waterflood. Difficulty in maintaining injection had resulted in increased gas/oil ratios, which jeopardized the operation of the pool.

The scale had been contaminated with NORM by an organic-rich shale containing uranium located immediately below the perforation interval. Conventional mechanical removal of the BaSO₄ scale would have resulted in radioactive material being circulated back to the surface.

The solvent treatment consisted of pumping 3.5 cu m (22 bbl) of 30% water and 70% BaSO₄ solvent mixture into the wellstring. Matrix rates and pressures were used to squeeze 3.0 cu m of the mixture into the formation.

The mixture was held in the formation for 60 hr. A 5.0 cu m, 15% HCl matrix acid treatment containing two gelled temporary bridging agent diverter stages followed the solvent soak. The scale solvent was bullheaded and displaced, leaving all the radioactive material downhole. The well was then cleaned up and placed back on injection to evaluate the treatment.

A post-treatment gamma ray spectroscopy log shows that the BaSO₄ scale dissolved across the perforations and near the well bore (Fig. 2). The right side of the gamma ray track in Fig. 2 shows the NORM gamma ray signals before and after the well was treated. The black NORM curve represents the scale present before the treatment. The black NORM curve represents the scale remaining after treatment. The gray shading shows the relative amount of scale removed and indicates that 20-50% of scale was removed in the interval from 1,357 to 1,383 m surrounding the perforations.

Near the bottom of the well, as much as 80% of the scale seems to have disappeared. Some redistribution of the scale materials may have occurred, where the black curve is greater than the gray curve. The gamma ray spectroscopy data indicated that the scale removal treatment was successful, resulting in an injection rate of 221 cu m/day (1,390 b/d) at 15,900 KPa (2,306 psi) wellhead pressure. The target injection rate was 60 cu m/day, which was the expected rate after a mechanical treatment.

If only mechanical methods of scale removal were used, an injection rate of 221 cu m/day would have required an additional three wells at a estimated cost of $400,000/well. Therefore, the solvent treatment saved $1.2 million. The treatment also eliminated the NORM scale handling and disposal costs.

References

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