A NOVEL EXOTHERMIC PROCESS FOR THE REMOVAL OF PARAFFIN DEPOSITS IN HYDROCARBON PRODUCTION

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Abstract

The formation of troublesome organic deposits during oil and gas production is a significant cause of decreased production and increased lifting costs. Traditional methods of mechanical and solvent-based removal are time consuming, expensive, and can create additional problems of re-deposition and dehydration facilities upsets. A novel process has been developed to remove organic deposits from hydrocarbon producing wells and equipment by generating an exothermic reaction that melts and disperses paraffin wax and asphaltenic deposits. The reaction product is a powerful paraffin dispersant that prevents re-deposition after the temperature returns to normal. The process is non-aqueous, which does not cause troublesome emulsions or potentially dangerous gas production.

Keywords: paraffin, asphaltene, exothermic, organic deposit, wax

Introduction

One of the most prevalent and troublesome problems facing oil and gas producers is the formation of organic deposits. These organic deposits may be paraffinic or asphaltenic in nature, or a mixture of both, depending on the crude source. Paraffins are defined as saturated alkanes, generally greater than 18 carbon atoms in length and may be linear or branched. Cyclic alkanes are referred to as napthenes and may have paraffinic side chains. Asphaltenes are extremely adhesive, dark, semi-solid amorphous substances that often act as binders between retained oils and hydrocarbon waxes. They consist of condensed aromatic rings with few side chains and have molecular weight ranges from 1000 to100,000. Resins also may be present in organic deposits. They are compositionally similar to asphaltenes but are soluble in pentane and contain sufficient polar characteristics to adsorb onto activated clays. In addition to organic compounds, deposits may also entrap significant portions of inorganic material such as formation fines, iron sulfide and other mineral scales.

Accumulation of organic deposits in the wellbore and near wellbore formation can severely hamper production. Accumulation in tubular goods, production storage and transportation equipment can also decrease production to the point that remedial action must be taken to remove the deposits. Remediation of organic deposits can be accomplished by mechanical or chemical methods. Mechanical methods include scraping and cutting the deposits using knives, scrapers and pigs. These often require extensive equipment such as workover rigs and wireline apparatus. Chemical methods are designed to remove organic deposits into a solvent such as hot oil, hot water wash, or a selected organic solvent. Hot oiling and hot watering may be augmented by the use of chemical additives designed to increase the efficiency of the hot wash. Examples of chemical additives used in hot wash processes include solvent packages, surfactants, dispersants and inhibitors.

Hot wash processes require a dedicated mobile heater unit to drive to the well site, load the unit with either water or solvent, typically lease crude or produced water, and circulate the fluid until the desired temperature is reached. The hot fluid is then pumped into the well, either down the tubing or down the annulus between the casing and tubing. Often the tubing may be sufficiently plugged with deposit to require pumping the heated fluid down the annulus to melt the deposit by convective heat transfer through the tubing wall. A significant portion of the heat content of the fluid is wasted on heating the tubing, casing and a portion of the formation itself. Melted wax and asphaltene deposits can be pushed into the formation where subsequent re-deposition can damage productivity. Melted deposits can also redeposit in surface flow lines and equipment after cooling to temperature below the melting point of the paraffin. Precipitation of deposits in surface equipment can cause significant upsets in dehydration processes and require additional removal processes to be performed in vessels and flow lines.

Exothermic Processes

In recent years new methods of removing organic deposits have been developed which rely on internal heat generation through an exothermic reaction. One such process makes use of a mixture of inorganic nitrate/nitrite compounds in a reduction/oxidation reaction that generates an exotherm, which melts the paraffin deposit and generates nitrogen gas[1]. This process relies on water as the solvent to deliver the reactants to the problem areas, and may require additional chemical components to disperse the melted wax into the water phase. Incomplete dispersion of the melted wax can result in additional problems, which may be expensive to resolve. Aqueous based processes to melt paraffin can result in emulsions that are difficult to break. This can upset dehydration processes and cause shut down of production. Furthermore, gas generating red/ox reactions tend to be self-accelerating, rendering them, at best, kinetically unpredictable and, at worst, explosive. Another method used to generate an exotherm uses a water-soluble acid and base which are mixed together to cause a neutralization reaction. A hot detergent method has been described in the literature where an alkali metal silicate or phosphate is mixed with various solvents and sulfuric acid to generate a detergent compound in an exothermic reaction.[2] These methods both suffer from the same disadvantages of aqueous based methods previously listed.

A novel method of melting and removing organic deposits from hydrocarbon producing wells and associated equipment has been developed based on an exothermic reaction that does not suffer the disadvantages previously described. The key to this new system is that the chemical product of the exothermic reaction is a concentrated solution of an extremely effective paraffin wax dispersant in a hydrocarbon solvent. The exotherm (or heat release) is generated *insitu* by mixing an organic acid compound with an organic base compound or inorganic base to form an organic salt in a neutralization reaction. The salts formed by these types of reactions have long been recognized in the industry as excellent wax dispersing agents. The heat generated by these reactions can result in temperatures in excess of 212 °F (100 °C) which is generally more than adequate to melt most organic deposits.

Examples of organic acids, which may be used in this process, include alkyl-substituted analogs of benzene sulfonic acid and naphthalene sulfonic acid. Various organic amines may be used as the base in the exothermic reaction.
Inorganic bases such as alkali hydroxides may also be used. Amine and alkali salts of sulfonic acids have long been known and used in the industry as effective paraffin dispersants. The solvent system can be crude oil, kerosene, aromatic hydrocarbons, dipentane, carbon disulfide, or any one of a number of polar solvents such as methanol, ethanol and ethylene glycol.

This exothermic method of paraffin removal has three major advantages:

- The heat released is sufficient to raise the fluid temperatures higher than the melting point of most waxy deposits.
- The reactants are carried in a paraffin solvent fluid that is a good solvent at low temperatures, but becomes an excellent solvent when heated to elevated temperatures.
- The by-products of the chemical reaction are exceptionally good paraffin dispersants that tend to sweep through the system to provide total system cleaning.

Laboratory Tests

A laboratory demonstration was performed by assembly of a test unit. A 1000 ml Dewar flask was placed into a ring stand and a large metal stem thermometer was inserted into the vessel. The two components of the exothermic reaction were blended into separate paraffin solvent solutions. Four hundred milliliter aliquots of the two solutions were poured simultaneously into the Dewar, and the temperature rise was observed. Within 15 seconds the temperature of the solvent mixture had risen from ambient room temperature to 218°F. Since the Dewar flask is well insulated, the temperature did not readily drop with time. Four hours later the fluid temperature was observed at 190°F.

To demonstrate the wax removal efficacy of the solution, samples of refined paraffin were coated onto stainless steel screen and were immersed into the hot solution for a period of 30 to 45 seconds. The wax was quickly and thoroughly stripped from the screen. The screen was placed back into the solution and after cooling to room temperature no redeposition of wax onto the screen occurred nor was any deposition of wax observed in the bulk solution.

Yard Pilot Test

In order to simulate a field application, a yard pilot test was performed on a section of paraffin coated flow line removed from an offshore platform. The section was a "U" shaped segment of a 4" flowline which contained six 90° elbows. A flange and connections were placed on each end of the 45-foot test segment, and all were placed on a rack to hold it essentially level. Inspection of the internal surfaces revealed a generous coating of wax. The melting point of the wax was determined to be in excess of 200° F.

Pumping equipment was arranged to pump the two components into a "T" at one end of the line. A temperature probe was mounted in the coupling to measure the temperature of the fluid as it was pumped into the test line. Another temperature probe was mounted at the end of the line to measure the temperature of the exit fluids. The exothermic fluid system was pumped into the line and shut in for 25 minutes or until the temperature dropped. Four successive slugs to monitor the wax removal followed. Each slug was caught and poured through an 80-mesh screen to catch any undissolved wax that may have been flushed from the system.

The first stage did not reach full exothermal because of a poor mix ratio of the pumps. The fluid through the screen was very thin and carried no solids. Adjustment of the pumps in the successive stages achieved the desired mix ratio and higher temperatures were measured. The cooled fluids were poured through the screen and were noted to have a high viscosity. Also chunks of paraffin were retained on the screen. Following the test, the flow line was flushed with water. More chunks of paraffin were flushed from the line. Visual inspection revealed a clean metal surface on the interior of the test segment. A temperature profile is shown in Figure 1.

Field Results

Producing Well: A well was selected for paraffin removal via the exothermic process because it had a history of paraffin problems and usually required an extended downtime for multiple wireline scraping. The paraffin deposition zone lay at approximately 2000 ft. below the wellhead. Approximately 1100 ft. of tubing was selected as the target zone for treatment. A chemical pump system was assembled and set for the proper injection rates. An insulated temperature probe was installed into a valve at the wellhead to monitor the temperature rise. Three stages of chemical were blended and pumped and following the final stage, the temperature was monitored until it returned to normal. After the well was returned to production a full gauge wire line was run to evaluate the treatment. It was found that the majority of the tubing length was completely clean as measured by the wire line caliper and any remaining paraffin was soft and subsequently easily removed by the wire line. The temperature profile is given in Figure 2.

Injection Well: An injection well had been experiencing elevated injection pressures and the injection rate had fallen. Samples taken from the filter cartridge indicated a build-up of a black amorphous solid. Two separate lab analyses indicated this was approximately 90% paraffin with some insoluble iron compounds. There were traces of carbonate, ferric oxide, soluble iron (iron sulfide) and silicates

These analyses clearly indicate a large amount of organic material present. A build-up of paraffin on the injection face can cause a major reduction in injectivity. The removal of paraffin can be approached in several ways, but most applications use paraffin solvents or paraffin dispersants (special surfactants). In addition, elevating the temperature improves the efficiency of the process. For example, many producing wells are routinely treated with hot oil or hot water. This melts the paraffin so it can be dislodged, dissolved or flushed out of the system.

The two components of this solvent-based exothermic system were pumped into a "Tee" at the well head. This produced a paraffin solvent at a temperature in excess of 200° F as it entered the tubing.

Treatment Procedure.

1. The well was back flowed to retrieve as many solids from the injection face as possible. (Samples were caught for the laboratory.)
2. The lines were laid and pressure tested. The annulus was pressured to hold about 58 psi on the backside.
3. The treatment began by spearheading with approx. 3 drums of xylene to adjust the two pumps to pump components A and B at the same rate.
4. Valves were changed to simultaneously pump Part A and Part B. Efforts were made to pump at less than 1 bbl min.
5. The treating fluids were displaced from the well bore with injection water.
6. The well was shut in and the lines disconnected. The treatment was back-flowed to retrieve as much hydrocarbon residue as possible.
7. After the treatment was recovered, 1000 gallons of special HCl was applied. (This dissolved the remaining iron compounds and carbonate scale.)
8. The acid treatment was back-flowed to flush insoluble solids.
9. The well was returned to injection.

Well Performance Results

	Before Treatment	After Treatment
Injection Rates	3000 BWPD 1900 psi	3000 BWPD 1000 psi

Conclusions

The exothermic paraffin removal process does indeed provide a new tool for removal of difficult to treat paraffin deposits. The process not only removes the paraffin deposit and leaves a clean pipe surface, it also helps clean the entire system downstream by dispersing and flushing the entire system. This is accomplished by three mechanisms of wax removal:

- The exothermic reaction develops temperatures that will melt most paraffin deposits.
- The solvent carrier is much more effective at elevated temperatures.
- The by-products act as a dispersant to prevent re-deposition as well as cleaning the system downstream.

References

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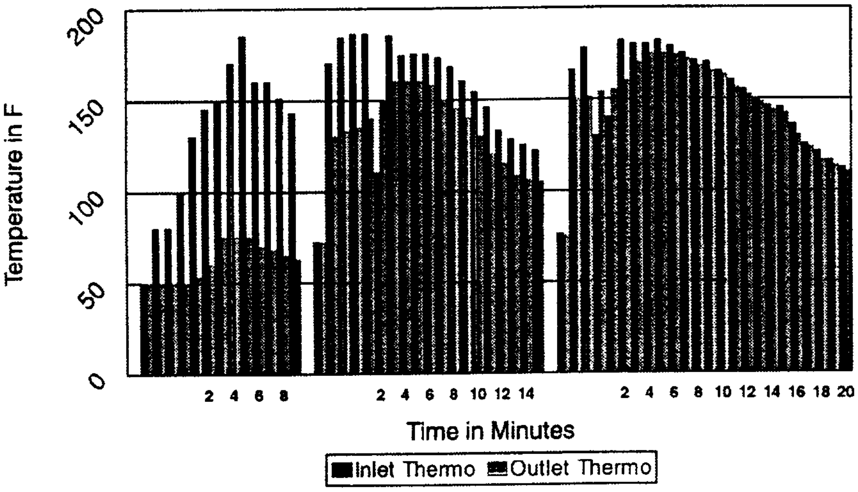

Figure 1 - Exothermic Process
Yard Pilot Test

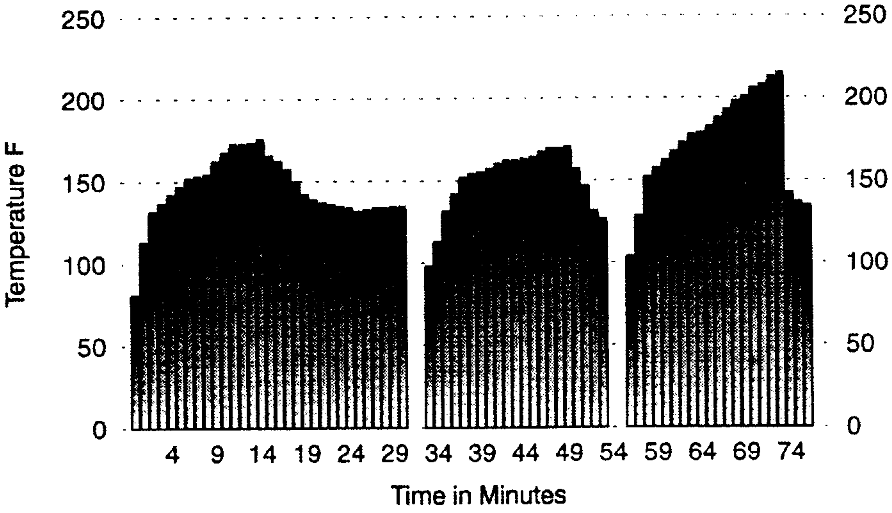

Figure 2 - Exothermic Process
Temperature Rise for 3-Stage Well Treatment