BIOLOGICAL PARAFFIN TREATMENT PROGRAMS

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ABSTRACT

This paper discusses the application of biological mixtures for prevention of paraffin deposits in oil wells. Three biological mixtures were field tested. Statistical data on test results in Canada and the United States are presented outlining application parameters. Several case histories are presented including some Thermal Chromatography-Mass Spectrometry (TC-MS) work on treated wells. Theoretical mechanisms of the paraffin control process are discussed.

INTRODUCTION

The terminology "paraffin deposit" is commonly used in the oil industry to refer to a waxy material which is precipitated out of a crude oil onto the surfaces of production equipment. This deposit may consist of paraffins, asphaltenes, oil, water, sand and other debris. The heavier paraffins, C18 and longer, determine the paraffin content of a crude oil. Excessive precipitation of this waxy component on production equipment will cause production problems. Historically oil producers have dealt with the paraffin problem by removing or inhibiting deposition by thermal, mechanical and chemical processes. These methods have various advantages and disadvantages most of which have been covered in the literature.[1][2]

During the last three years Kiseki has treated a large number of wells successfully utilizing biological products for prevention of paraffin problems. This successful approach has also shown significant cost and safety advantages. Three separate product systems were utilized in the treating programs.

PRODUCT DESCRIPTION

It is a well known and documented fact that bacteria will metabolize hydrocarbons. The metabolic pathways of hydrocarbon degradation are not completely understood. However, it is known that alkanes can be oxidized resulting in the generation of several intermediate and end products. Oxidation of the terminal (C1) methyl group gives an alcohol, aldehyde and subsequently a carboxylic acid. To a lesser extent the C2 carbon may be oxidized to give a methyl ketone or the oxidative attack may take place at both ends to give an (alpha) dicarboxylic acid.[3]

In general, paraffinic hydrocarbons are metabolized more rapidly and by more microbial species than aromatic compounds. As a rule long chain hydrocarbons are metabolized more readily and by more microbial species than those of low molecular weight. The susceptibility of petroleum products to microbial oxidation generally increases with the melting or boiling point. For example paraffin wax is oxidized preferentially to gasoline.[4]

The three product systems which were used for the treatment of wells for paraffin problems are comprised of hydrocarbon oxidizing micro-organisms.

The products are proprietary mixed cultures of naturally occurring micro-organisms supplied by three separate manufacturers. The products were purchased from these manufacturers to perform the treatments. Based on the three manufacturers product specifications, the mixed cultures are different from each other.

Product #1 is a mixture of facultative anaerobes produced for sale in a liquid form. Cell concentration was reported by the manufacturer to be 10^6 cells/ml. This product was used in treatments from late 1986 to the spring of 1988.

Product #2 is also a mixture of facultative anaerobes produced for sale in a liquid form. This product was used from the spring of 1988 to the spring of 1989. Cell concentration was reported by the manufacturer to be 10^6 cells/ml increasing to 10^9 cells/ml in the spring of 1989.

Product #1 and #2 have some inherent similarities , both being liquids and mixtures of facultative anaerobes. The products are transported in 55 usg drums containing biological cells, water and nutrients.

Product #3 is a mixture of aerobic bacteria produced in a powder form. Cell concentration is 10^{12} cells/gm. In addition to the powder bacteria this product system includes a liquid bio-catalyst and an inorganic nutrient. This product has been used from the fall of 1988 to the present.

All three product systems are nonhazardous, non toxic, non carcinogenic and non pathogenic and therefore very safe to handle in the field.

TREATMENT TECHNIQUE

Collection of pertinent information about candidate wells is the first step in the treatment procedure. This includes production data, mechanical configurations and a description and definition of the paraffin problem.

On site treating is performed with a small pressure pump. When treating with the liquid products , one to six gallons of the liquid product is pumped into the annular space between the tubing and the casing. This is then followed with an adequate flush volume of brine water to ensure that the product is properly placed at the productive horizon. When treating with the powder product four to ten ounces of the dry material is mixed on location with brine water. This solution is pumped into the annular space of the well followed by an adequate flush volume of brine water containing the bio-catalyst and inorganic nutrient.

The treatment process is simple yet attention must be paid to wellbore conditions. The frequency of treatment for all three products is typically once per month but may vary from once every two weeks to once every two months depending on production volumes and the severity of the paraffin problem.

APPLICATION PARAMETERS

Data has been gathered on over five hundred wells. The length of treatment per well varies from a few months to over two years. Success has been measured primarily by comparison of biological treatment results to the problems encountered on a well before initiation of biological paraffin control. From the fall of 1986 to Jan 31, 1990 the wells used in the data base for this paper represent 133,886 production days. Wells have been treated for 92,617 production days using the liquid products and 41,269 production days using the powder product system. Analysis of trends in well response help guide selection of new treatment prospects and treatment methodology.

A failure is defined as a wax build up causing a well to plug off or return to previous treatment techniques without providing an improved wax inhibition program.

Water Cut

Water Cuts in excess of 1% are recommended. Forty eight percent of the wells treated with liquid products that had a water cut less than 1% resulted in a failure. When utilizing the powder product system 14% of the wells with a water cut less than 1% failed. The bacteria live in the water and it is through surface area contact with the oil that the bacteria are able to metabolize the carbon source povided. Therefore when the water cut is low the function of the bacteria is inhibited. When selecting wells to treat one cannot ignore the importance of water. However this does not rule out dry wells since a treatment approach is possible which combines biological and mechanical, or thermal methods.

Flowing Wells

Flowing wells have proven difficult to treat and should usually be avoided, 87.5% of the flowing wells treated experienced failure. The successful applications did not provide complete wax inhibition but did allow the operator to extended wax cutting frequency and reduce operating costs.

Fluid Level

High fluid levels in the annulus can prevent proper placement of the batch treatment at the productive horizon. Several well failures have been linked to such high fluid levels. This is especially true in wells producing higher density oils as the density differential between the aqueous treatment fluids and the crude oil narrows. A circulation approach to treatment is recommended rather than a gravity feed when fluid levels are high. Better treatment results are achieved by circulation of the biological mixture to the production zone. This can be accomplished by using a pump truck or the on-site pumping system itself. Experience has shown where the fluid level above the pump is in excess of 800 ft (250m) the batch should be circulated to the productive horizon. However one must be careful to place the treatment batch at or near the productive horizon and not circulate it up the production string from the annulus.

Hydrogen Sulfide

Hydrogen sulfide can inhibit the bacterial activity. However, many wells have been treated for over a one year period which have had severe wax build up problems where the H_2S concentration in the solution gas is less than 6%. These wells have a low bottom hole pressure. Limited experience has been gained in treating wells with H_2S concentrations greater than 6%. Caution should be exercised when applying a biological paraffin control technique to wells with H_2S concentrations in excess of 6% in the solution gas. Two wells have been treated where the solution gas H_2S concentration was 10% and 12% Both wells have bottom hole pressures around 1000 psig(7000 kPa). In both cases residual bacteria counts after 60 days were below 10^2 and treatment failures resulted.

Chemicals

The use of scale inhibitors, corrosion inhibitors and demulsifiers may inhibit the bacteria. The toxicity of a chemical to the bacteria is dependant upon the chemical composition of the product. This toxic effect should be tested prior to engaging in a joint treatment program. Many wells have been successfully treated using chemicals for corrosion and bacteria for paraffin. In some cases the use of bacteria may eliminate the need for additional chemical products. However one must understand that joint programs may result in a loss of microbial efficieny.

Manufacturers Recommendations

Manufacturers recommended tolerance levels should be followed. For example, the salinity tolerances for the liquid products are about 10% while the powder product system tolerance is 22%. These tolerances may be stretched by application techniques, however limitations will be met. In Northern Alberta the Keg river formation can have a salinity in excess of 15%. Difficulty was experienced when treating this formation with liquid products but there has been successful projects which are over one year old with the powder product system. Wells with temperatures in excess of 180^0F should be treated with caution. Most oilfield brines have a ph range between 6 and 9 and therefore ph does not usually pose a problem.

RESULTS

A comparison will be made between the liquid and the powder products which were tested. Since some of the products have not been tested in the last year, more recent product enhancements may have occurred which could affect the results presented. Statistics from the two liquid products are treated jointly.

The apparent skew in statistics between the liquid products and the powder product system could possibly be affected by an increase in application knowledge as treatments progressed through time. However it is probable that a significant factor in the statistical difference is the increased cell concentration of the powder product system.

While treating for paraffin with a biological system we have gathered several general field observations. Even though these products act to prevent excessive wax accumulations they can cause the release of slugs of old paraffin deposits from the tubulars. Treatment of a "clean" system will help avoid any large releases of old paraffin. Typically small fingernail size pieces of paraffin will be released from downhole. Operators have reported an increase in paraffin collected from pigging operations for a short period after the treatment process has been initiated. Pigging frequency can be reduced as quantities of recovered paraffin decrease far below accustomed levels. In some cases pigging results indicate no on going flowline buildup. The consistency of the wax recovered will change from the usual tacky material to a vaseline like material.

When the rods are pulled on a treated well they may come out of the hole clean, but usually they will have a vaseline like material on the rods. In severe climates, as in Canada, the top rod may have an accumulation of harder paraffin.

The goal of a preventative maintenance treatment is to prevent the need for mechanical or thermal methods to clean a well. In many cases the need for hot oiling a well, for example monthly hot oil jobs, can be totally eliminated by the use of biological treatments. However a combined treatment process is sometimes required. For example a well with a hot oil schedule of once per month may be treated for eight months biologically to control paraffin and then a hot oil or solvent job may be performed to provide complete control.

On 184 wells in Central Texas producing from the Austin Chalk, Buda, Taylor, and Navarro sands, hot oil cycles were extended significantly by biological paraffin treatment programs. During a total of 2378 production months these wells received biological treatments with either products #1,#2 or #3 . Most of these wells previously required hot oil treatments monthly to keep the rods from hanging up.

Table 1 illustrates the number of remedial hot oil treatments required in Central Texas while using products #1,#2 & #3. Some wells were treated with both liquid and powder products. Fig 1 illustrates these statistics graphically. For the Central Texas wells 52.4% of the wells treated with the liquid products #1 & #2 required remedial hot oil treatments whereas 5.7% of the wells treated with the powder product #3 required hot oil treatments.

An evaluation of 379 wells treated in Canada with the products #1,#2 or #3 showed a similar difference in the results between liquid and powder product systems. Some wells were treated with all product systems. Most wells had continuous on going successful treatment programs. Of 196 wells treated with the liquid product systems 40.8% required a hot oil job sometime during the treatment period. However of 265 wells treated with the powder product system only 12.1% required a hot oil job sometime during the treatment program (see Fig 2)

These results led us to investigate actual oil composition changes in a field test utilizing the powder product system #3. A well in Northern Alberta 13-13-78-12W6 with the characteristics shown in Table 2 was selected as a test candidate. The well 13-13-78-12W6 was first treated Feb 7, 1989. Treatments have continued monthly up to the present time of Jan 31,1990 without any operational problems related to wax. There were no other production modifications during this period. The well had previously been treated with a commercial chemical dewax system. The biological treatment schedule is outlined in Table 2. Treatments were performed by mixing the product system on site and pumping the solution into the well annulus allowing it to gravity feed to the productive horizon. In the summer of 1989 the bottomhole pump was pulled and very little wax was found on the rod string. The workover was performed without any wax related problems. We have concluded that the powder biological paraffin control treatments on this well have been successful.

Samples of produced fluids were collected one day after (GPA60) and seven days after (GPA61) the first treatment ocurred. The samples were analyzed by Ruska Laboratories of Houston utilizing their Pyran System of Thermal Chromatography-Mass Spectrometry. The purpose of the analysis was to identify microbial by-products in the crude oil system. Since the quantity of the micbrobial by-product was expected to be minimal and may not show up in the whole oil analysis, the asphaltene was precipitated out of the oil. From Ruska's previous experience it was expected to more readily find carboxylic acids associated with the asphaltene. The asphaltene was analyzed for the presence of microbial by-products. Table 4 is a summary of these findings. Table 4 lists specific ratios of individual compounds in an attempt to distinguish oils before and after treatment with bacteria. The n-paraffins used are C17, C18 and C27, PR is pristane, PN is the aromatic phenanthrene; and C14A is a carboxylic acid. Most significant is the appearance of the C14 fatty acid and the large increase of this acid in oil sample

GPA61. It also appears that phenanthrene (PN) increases relative to C18 as bacterial degradation progresses which is the expected trend as phenanthrene (PN) is not as readily degraded as the n-paraffin C18. The C17 to C27 ratio shows a significant increase. The increase in the ratio of PN/C18 and C17/ C27 would indicate a reduction in the n-paraffins C18 and C27. More analytical work of this nature is scheduled.

It is postulated that the mechanisms of paraffin control is the generation of minor quantities of microbial by-products such as fatty acids (surfactants) and changes in the properties of some heavy paraffins which increases the solubility of the remaining heavy paraffins in the crude oil system.

CONCLUSIONS

1. Biological paraffin control programs are effective in reducing paraffin related problems.
2. This paraffin treatment technique may be used as a stand alone process for long term control or may be combined with more traditional systems such as hot oiling to provide a control program.
3. Individual well parameters affect treatment success. The parameters of key importance are: water cut, fluid level, H_2S concentration, bottomhole temperature and brine salinity.
4. Different products are available in the marketplace and they provide varying results.

RECOMMENDATIONS

Prior to commencing a biological paraffin control program review treatment candidates carefully to ensure operating conditions meet successful treating parameters and manufacturers product specifiations.

REFERENCES

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3. Davies, June A and Hughs, D.E., 1968 The Biochemistry and Microbiology of Crude Oil Degradation, The Effects of Oil Pollution on Littoral Communities pg 139-144
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Table 1

Central Texas Hot Oil Treatments while using Biological Paraffin Control

Number of Hot Oil Treatments per well	During Use of Liquid Products		During Use of Powder Products	
	#of wells	%of Total	#of wells	%of Total
0	71	47.7	66	94.3
1	32	21.5	0	0
2	34	22.8	1	1.4
3	10	6.7	1	1.4
>3	2	1.3	2	2.9
	Total 149		Total 70	

Table 2

ALBERTA 13-13-78-12W6 WELL CHARACTERISTICS

Field	: Pouce Coupe South
Formation	: Boundry B
Production Depth	: 1820m (5970ft)
Daily Oil Production	: 2.6m^3/d (16.5 bopd)
Daily Water Production	: <0.5%
Fluid level	: pumped off
H2S %	: Nil
BHT	: 70°C. (158°F)
OiL Gravity	: 41° API
Water Salinity	: <5%

Table 3

BIOLOGICAL TREATMENT SCHEDULE WITH POWDER PRODUCT #3
ALBERTA 13-13-78-12W6

Date	Bacteria Quantity		Nutrient Quantity		Bio Catalyst Quantity		Flush Volume	
	(oz)	(gm)	(oz)	(gm)	(usg)	(l)	(bbl)	(m3)
Feb 7/89	16	453	4	112	2	8	1	0.3
Mar 7/89	16	453	4	112	2	8	1	0.3
Apr 4/89	8	226	4	112	2	8	1	0.3
May 2/89	4	113	4	112	2	8	1	0.3
May 16/89	4	113	4	112	2	8	1	0.3
Jun 13/89	4	113	4	112	2	8	1	0.3
Jul 11/89	6	170	4	112	2	8	1	0.3
Aug 8/89	6	170	4	112	2	8	1	0.3
Sept 5/89	8	226	4	112	2	8	1	0.3
Oct 3/89	8	226	4	112	2	8	1	0.3
Oct 31/89	8	226	4	112	2	8	1	0.3
Nov 28/89	8	226	4	112	2	8	1	0.3
Dec 22/89	8	226	4	112	2	8	1	0.3
Jan 23/90	8	226	4	112	2	8	1	0.3

Table 4

RUSKA LABORATORY PYRAN SYSTEM
THERMAL CHROMATOGRAPHY-MASS SPECTROMETERY RESULTS
ALBERTA 13-13-78-12W6

Sample#	C17/C27 ratio	PN/C18 ratio	C14A/PR ratio
GPA 60	4.076	0.090	0.009
GPA 61	11.130	0.172	0.027

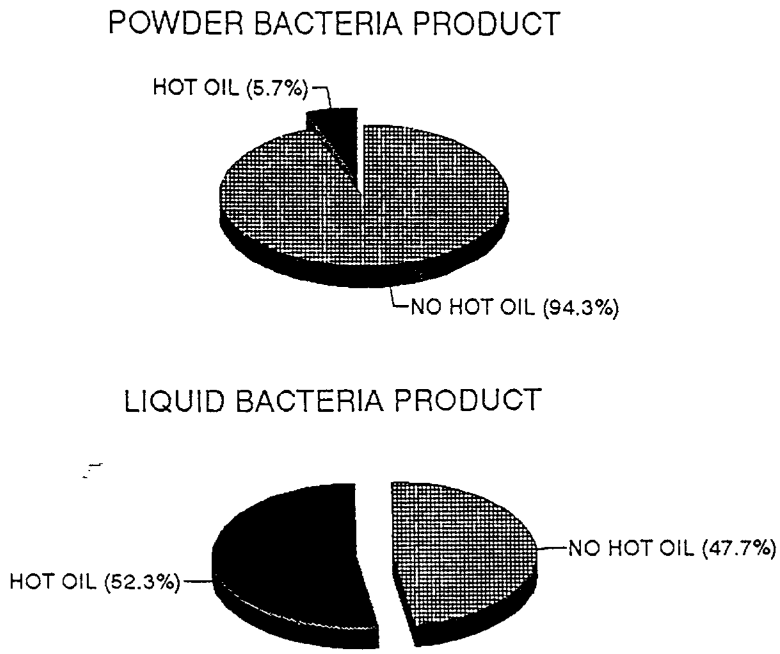

Figure 1 - Central Texas treatment success

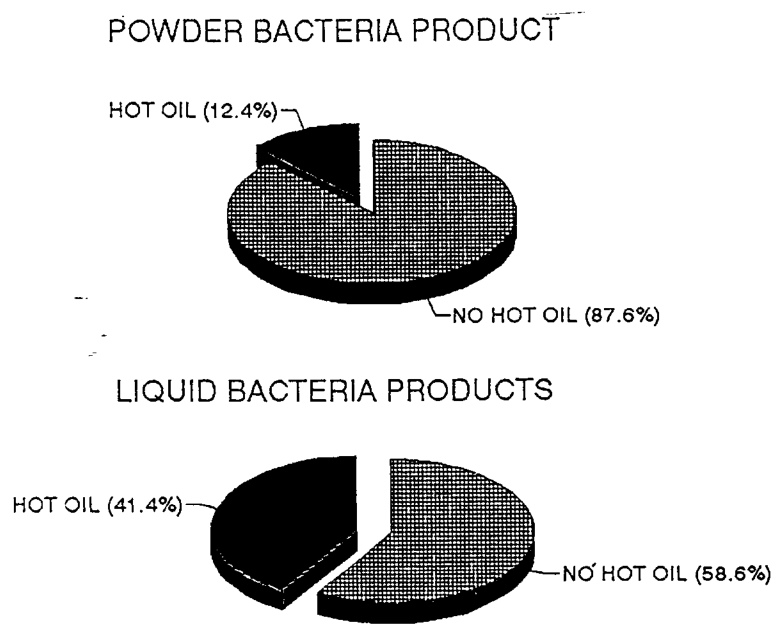

Figure 2 - Alberta treatment success