CHEMICAL TREATMENTS FOR PARAFFIN CONTROL IN THE OILFIELD

M. E. Newberry
TRETOLITE Division, PETROLITE Corporation

ABSTRACT

Paraffin deposition during the production and transportation of hydrocarbons prior to refining represents a very real and costly problem. New inroads for chemical treatment have been made during the past few years. These developments have led to a program of preventive chemical treatments which offers a viable alternative to hot oiling or other mechanical remedies for paraffin control. This paper discusses the design of a paraffin treating program using a batch method of application. Topics investigated are sample identification and characterization, paraffin compound testing, program design, chemical application, field performance evaluation, and program adjustments. These topics are presented for practical application.

INTRODUCTION

Paraffin deposition in oilfield production equipment is a widespread, costly and bothersome by-product of crude oil and natural gas production. Virtually every state that produces crude oil (high grade Pennsylvania, high gravity Louisiana gas condensate, high wax content Utah) has wells with paraffin problems. Though severity of the problem brings to light a number of areas such as Northern Michigan, offshore Louisiana and West Texas, the methods of control for these problems can be applied to paraffin deposition throughout the world.

Research is currently underway to find the ultimate paraffin inhibitor. A number of chemical structures demonstrate crystal modification properties, but these are rarely 100% effective. Because paraffin deposits actually consist of a wide spectrum of materials (linear hydrocarbons, highly branched hydrocarbons, resins, asphaltenes, sand, inorganic solids, ice, silt, clay, etc.) they seldom behave in a consistent manner. The picture is further complicated by the wide variety of production techniques and well characteristics. Variations in gas/oil ratio, water/oil ratio, well depths, temperature profiles and wax content result in dramatically variable paraffin deposition tendencies.

Paraffin deposition research using various "cold finger", "cold spot" and "pipe loop" apparatus has indicated a number of trends.

(1) There is no such thing as a universal paraffin inhibitor.

(2) Care should be exercised when choosing an inhibitor.

(3) Most effective crystal modifiers are solids or high pour point liquids such that special handling problems exist with their use.

(4) Generally total paraffin inhibition is economically infeasible.

(5) Some paraffin inhibitors can reduce the amount of wax deposited, but also

make it harder to remove what wax does deposit. This is a result of the crystal modifiers inactivity on the higher molecular weight waxes.

Figs. 1 and 2 demonstrate a carbon number shift resulting from hot oiling and treatment with a partially effective crystal modifier.

Given the fact that paraffin deposition does occur how can we economically treat the problem without aggravating it in the long run. It is our belief that a regular treating program using paraffin removal chemicals is the best approach. While it has been observed that total paraffin inhibition is very difficult and expensive to achieve, periodic removal has proven to be both economical and widely applicable. It is upon this method of application that the following program has been developed.

PROBLEM IDENTIFICATION

The identification of fouling material collecting in an oil producing system can be made through its solubility characteristics. Hot xylene is the single most important solvent to use for material classification. If the deposit dissolves in hot xylene then it is organic in nature and can be treated using paraffin compounds. A great deal of confusion exists in the oilfield concerning foulant identification. Oil wet scale, iron oxides, iron sulfides, clays, drilling muds and bacteria slimes have all been mistaken for paraffin. All of these are insoluble in xylene. Once a fouling material has been determined to be organic then another solvent (pentane) can be used to distinguish between paraffin and asphaltenes. Asphaltenes are insoluble in hot pentane, characteristically dark black, and normally appear hard and brittle like coal. Asphaltene deposits should be handled separately from paraffin treating. These problems will be covered in a subsequent program.

Generally the majority of paraffin problems consist of a mixture of paraffins and low molecular weight asphaltenes and resins. This results in a fouling material that is brown or black with a soft consistency similar to shoe polish or gum.

Samples of paraffin deposits can be gathered from a variety of locations. The rods during a pulling job or directly from a bullplug or valve are excellent locations for fresh samples. A removable flowline test section is also an excellent choice. Valuable information can be obtained by centrifuging an oil sample at successively lower temperatures. An idea of the volume of paraffin capable of depositing from the crude oil can be obtained via this technique. This is especially true where the problem is seasonal and typically located in the flowline.

The amount of paraffin to be removed is often a surprisingly large volume. For example a ¼ inch buildup in a 2 inch diameter flowline will amount to approximately 535 pounds of paraffin per 1000 foot of line. This is well over a ton of wax for a mile of flowline. It's also about 9 barrels of solid wax. Many wells in the field possess the ability to deposit a ¼ inch wax layer in a week or less. This represents a substantial problem to tackle at an economically acceptable chemical rate.

PARAFFIN TESTING

Now that the type and magnitude of the problem has been identified, it is necessary to choose from a wide variety of commercially available paraffin treating compounds. The compound choice normally depends upon the application technique employed to treat the problem. It is generally accepted that the preferred method is a batch application. This is true for the following reasons:

(1) Batch treating guarantees that the chemical is placed in the system at the prescribed amount.

(2) Continuous injection rates of dispersant, inhibitors or solvents have to be so high for 100% inhibition or removal that they are seldom economical. Batch treatment achieves a high chemical concentration for a limited time period at an economical cost.

A surface active mechanism has proven to be very effective for paraffin treating where removal is the prime objective. The combination of selected surface active agents and water produces a treating solution which is ideal for the removal of paraffin. The treating solution provides the necessary contact time to soften, penetrate and remove the deposit and ensure adequate fluid volume to flush the paraffin particles down the system. The production system is then left in a water wet state which is resistant to the establishment of new paraffin crystal-to-metal surface bonds.

The activity of a paraffin compound is determined by the use of a "Flask Test". This test is similar to a demulsification bottle test because it is an attempt to duplicate the treating system employed but the results have to be evaluated subjectively. Basically the test consists of individual jars containing the treating solution and a sample of fresh paraffin. Each jar contains a different chemical except for one which has no chemical and is referred to as the "blank". The chemicals should be soluble or dispersible in the chosen treating fluid. Always watch for flock or gell in the treating fluids. The test solutions are then heated to the formation temperature or to the maximum temperature of the oil at the problem area. The jars are then shaken 100 times every 10 minutes over a one hour period of time for a total of 600 shakes. Each sample is rated for paraffin break-up and dispersion. The chemical that gives the smallest particle size but still maintains the paraffin in a water wet state is judged to be the best. Again, the test is designed to determine chemical performance on comparative basis against the "blank". As with a demulsification bottle test, a number of adjustments can be made to duplicate the system. The chemical concentration of the treating solution can be varied from 100 ppm to 5%. Generally, 2% is tested for cold treating and .1% for hot (180°F) treatment. It should be noted at this time that paraffin compounds are designed to work in hot water. Their activity is greatly reduced under cold treating conditions and this is why higher concentrations of chemical are tested. The fluid used in the treating solution could consist of a number of different solvents (fresh water, produced water, crude oil, diesel, kerosene, gasoline, xylene). Generally water is preferred because of its availability, cost, and ability to form a surfactant solution with paraffin chemicals. The use of water also eliminates problems with high fluid levels of oil in the annular space. The test length and number of shakes can be varied to coincide with the expected "contact time" in the system. A contact time of 2-4 hours is usually preferred for cold treating.

Once the top three compounds have been identified it is best to check the emulsification tendencies of the treating solution. Choose the most active compound that is also nonemulsifying. A bottle test of 2% chemical based on the volume of water should be checked at an oil/water ratio of 90/10, 50/50, and 10/90. This takes into account the various mixtures developed in the production system when batch treating paraffin surfactant solutions.

The above entire procedure should be repeated for each and every underground production zone. All of the various parameters can change greatly from one zone to another. Many fields often require paraffin treatment using different compounds for separate producing zones.

TREATING PROGRAM DESIGN

Once the compound selection has been completed it is now necessary to choose the appropriate program parameters. These include the following:

(1) Chemical concentration

(2) Frequency of treatment
(3) Size of treatment.

All three of the above items should combine together to provide a program which operates within the economic limitations determined from historical data. A realistic cost figure should be targeted based upon historical thermal and mechanical treatments, equipment wear, production losses, man power costs, energy requirements and other related costs.

Previous experience indicates that a 1 to 2% chemical concentration is best for a cold treating solution. This also equates to an easily measured 1 gallon of chemical per barrel of treatment. Hot water jobs require substantially less chemical (1 pint to 1 quart per barrel).

The frequency of treatment is determined by analysis of the historical data detailing patterns of remedial action. These are gathered from "hot oil" or cutting records. A figure referred to as "the half life of well failure" is then assigned. This figure is determined to be ½ the time period between necessary mechanical or thermal treatments to prevent well failure from paraffin accumulation. Fig. 3 is a graph of treating frequency versus the number of weeks between hot oiling. Remedial action in the 1 to 4 week period indicates a relatively severe problem. Chemical treating frequency would be set at ½ the period. An example would be for a well hot oiled once a month we would treat it once every two weeks. A well hot oiled once every week would be treated twice a week. For wells that operate without trouble for 1 to 6 months the frequency is reflected in a sliding scale. This results in a scheduled periodic treatment of once every 3 to 6 weeks. This is important because a treatment in this time period will handle those wells that are seasonal and stay on top of rapid wintertime paraffin accumulations. A separate summer/winter program can be designed for those wells that are identified as seasonal problems. This is particularly true with flowline problems.

The third parameter necessary to fix is the sizing of the treatments. Paraffin chemical treating activity is dependent upon temperature and contact time. The size of the batch treatment provides the necessary contact time to penetrate, soften and remove the accumulated deposits. It is the metered distribution of a small amount of chemical into a dilute treating solution that provides the favorable economics for a successful program. Fig. 4 is a graph of production per day versus size of treatment used to determine the necessary batch size. Note that the production figure consists of total fluids. This graph is designed to provide a 2-5 hour contact time to remove the paraffin. Higher production wells will normally need less contact time because of the presence of a higher velocity component. Low production wells require more contact time because of a low velocity component and less fluid to carry the paraffin through the system. An example would be that a well producing 100 barrels of fluid a day should be treated with a paraffin chemical solution sized at 16 barrels. In all instances a minimum of 4 barrels should be used to provide enough weight to drop against high casing gas presures and high fluid levels.

CHEMICAL APPLICATION

Now that all the treating parameters have been identified it is necessary to apply them to the system. The best method of chemical application is with a pump truck. These units consist of a truck with a 20-40 barrel tank, individual chemical reservoirs and a pump. They are usually set-up to handle 4 to 6 different chemicals and can pump against pressures above 1000 psi. A special feature is the ability to continuously slipstream an even distribution of chemical into the treating fluid or switch from one chemical to another with the turn of a valve.

A standard batch treatment is placed into the annular space at a rate of 1-2 barrels per minute. The treating fluid then contacts the formation face upon entering the well bore area prior to pick-up by the pump. The injection of the treatment at this rate allows for the transportation of the treatment through the system as a slug. The treating solution drops down the casing through any oil standing in the casing and down to the pump where it is picked up and pumped back up the tubing string. This slug movement of the treatment provides the continuous contact time necessary for the removal of paraffin using a surfactant/dispersion mechanism.

When starting any paraffin treating program it is always suggested to start slow. Systems known to be choked with paraffin should be treated in stages. The flowline should be treated first with 1/3 of the allocated paraffin treatment. The remaining 2/3 of the treating mix should be placed down the casing. If economics permit it is usually better to double up on the treatments by treating on two successive days with ½ the chemical amount. This provides a very dilute solution which will prevent too rapid removal and possible plugging from very dirty systems.

TREATMENT MONITORING

Since the ability of paraffin treating chemicals to perform their cleaning function is so dependent upon contact time this critical factor can be monitored by analysis of the returning fluids. Water soluble tracer dyes can be effectively used to study the characteristics of individual wells and formations. A strong solution of green fluorescent dye is placed in the first barrel of treating fluid followed by the remainder of the treatment. A red dye is typically placed in the last barrel of the treatment. By monitoring and sampling the fluids exiting the wellhead over an extended period of time the duration and order of return can be determined. Blowback is a very common problem with wells that make large volumes of casing gas. Obviously a chemical treatment will not handle paraffin deposition in the tubing if the treatment is blown out the offside casing valve following a treatment. If red dye is observed within the first 15-20 minutes following treatment then this problem is occuring and additional water or shut in time is necessary. If the treatment successfully falls downhole then a period of 1 to 6 hours normal oil production will occur until the first dye traces are observed. At this time, some interesting effects can be observed. If the formation is tight then the treating fluid will stack in the casing and the fluid will return in the same order it is placed into the well. Green dye will show first followed by additional treatment and finally the red dye to finish the slug. We refer to this as a "FIFO" (first-in-first-out) return. If the formation is particularly loose then the treatments will be displaced back into the formation and the return order will be red dye followed by additional treatment and finally green dye. This is referred to as a "LIFO" (last-in-first-out) return. Regarding paraffin treating both LIFO and FIFO returns are effective. There is a chance on a LIFO return that the entire treatment will be mixed with the oil in the formation and the slug of treating fluid will be diluted or return more slowly as the formation pressures equalize. Sometimes this may mean a much less concentrated treatment is contacting the paraffin deposit and, therefore, a less effective removal mechanism results with a LIFO return.

The return characterists of a well become particularly important when the wells are treated with a number of different chemicals for various specific problems. Currently wells are treated not only for paraffin, but also for scale and corrosion problems. There is a set pattern of chemical contact that is preferred for well treatments. Ideally, we would like to contact the fouled area in the following order:

(1) Paraffin chemical
(2) Scale chemical
(3) Corrosion inhibitor

The LIFO and FIFO return characteristics become important when this order of chemical addition is necessary for maximum performance. The paraffin chemical should reach the critical area first so that the organic materials are removed to expose the inorganic scale deposits or metal surfaces for inhibitor contact. Laboratory and field testing for both scale and corrosion control indicates that superior performance is observed when organic deposits are removed prior to treatment for this problem.

For a well that returns characteristically in a FIFO order the chemical addition should be the following:

FIFO

(1) Paraffin
(2) Scale
(3) Corrosion

Wells returning in a LIFO order should be the following:

LIFO

(1) Corrosion
(2) Scale
(3) Paraffin

As with any multichemical treatments, the compatibility of the various chemicals should be checked especially in the LIFO return pattern. The LIFO return will typically result in much more mixing of chemicals, treating fluids and produced fluids than a FIFO return. Fig. 5 contains a summary of chemical application and fluid return trends.

ADJUSTMENTS

The previous topics have outlined the parameters necessary to design a treating program. These are considered starting points and as such are subject to change. On a field-wide program it is not at all uncommon for 10 to 20% of the wells to need adjustment. The figures used to establish the "Half Life of Well Failure" are sometimes misleading due to a number of reasons. Down time because of weather, well location, or production allowables results in distorted failure rates.

The failure rate could be either too high or too low and, therefore, need adjustment in order to provide maximum cost/efficiency of the program. Variations in waterflood conditions can have a dramatic effect upon the contact time of a treatment or the temperature of the produced fluids. The most important aspect concerning paraffin treating is flexibility. Once a program has been started it has to be constantly evaluated and adjustment made if necessary. Those wells that are not responding to treatment usually require an increase in contact time and/or an increase in frequency of treatment. Severe paraffin problems may require treatment based upon a "quarter life of well failure" rather than a "half life" interval.

Adjustments to a program should not be considered as the result of failure, but rather as measures to balance the cost/efficiency of a field treating program. Often a few minor changes of frequency, chemical or contact time can mean the difference between a successful or marginal treating program.

SUMMARY

I. Identify the problem
    A. Organic
        1. Paraffin
        2. Asphalt

B. Inorganic
   1. Scale, iron sulfide, rust
   2. Clay, drilling muds

II. Paraffin Testing
   A. Flask Test (break-up and dispersion)
   B. Chemical compatibility
   C. Emulsification tendencies

III. Treating Program Design
   A. Frequency based upon "Half Life of Failure"
   B. Contact time set for 2-4 hours

IV. Chemical Application
   A. Preclean system
   B. Start slow
   C. Slipstream chemical for even distribution

V. Fluid Return Analysis
   A. Sampling
   B. Dye tracers
   C. Identification of LIFO or FIFO returns
   D. Combination treatments

VI. Adjustments
   A. Contact time
   B. Chemical
   C. Frequency
   D. Cost/efficiency analysis

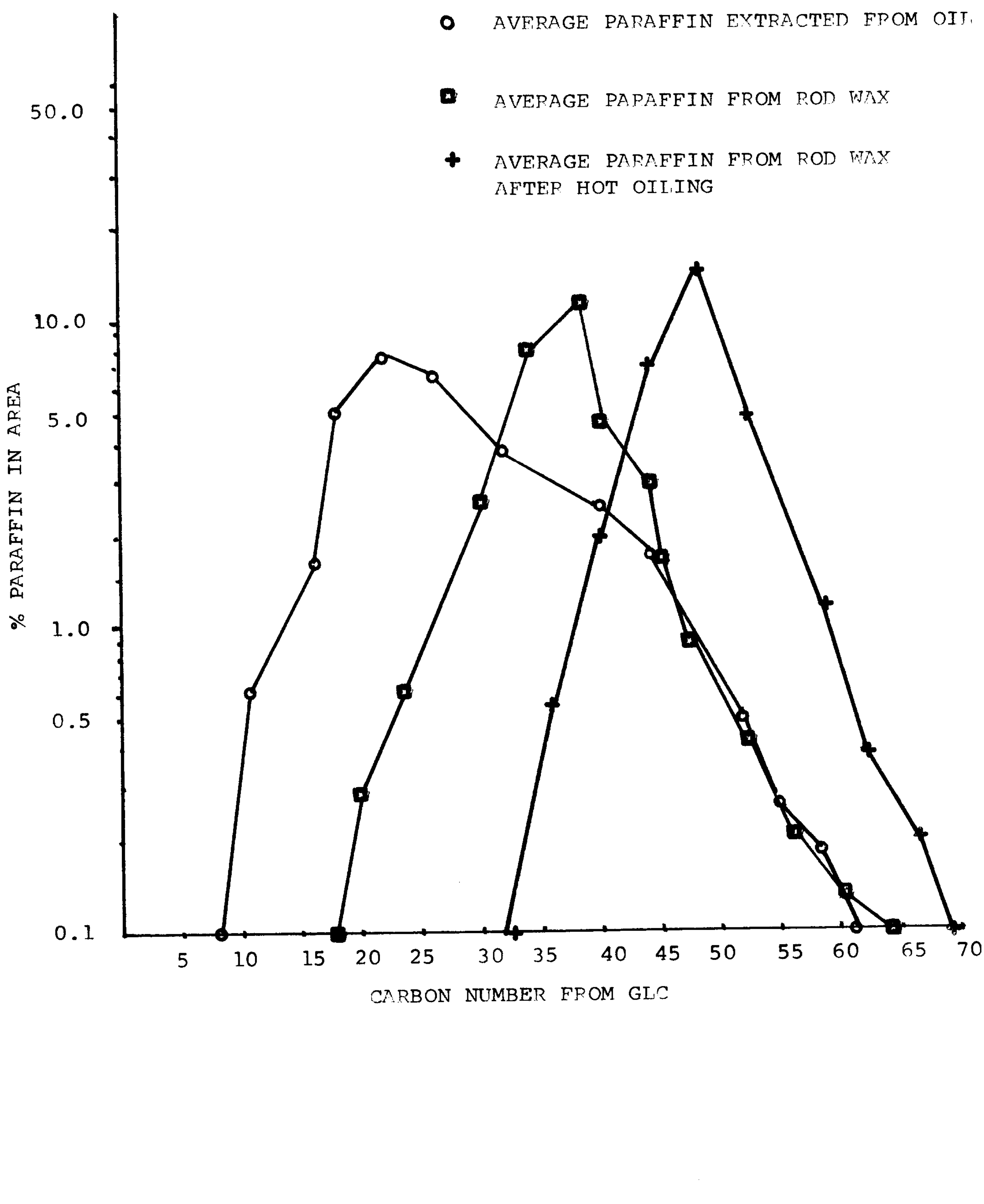

FIGURE 1 CARBON NUMBER vs. % PARAFFIN

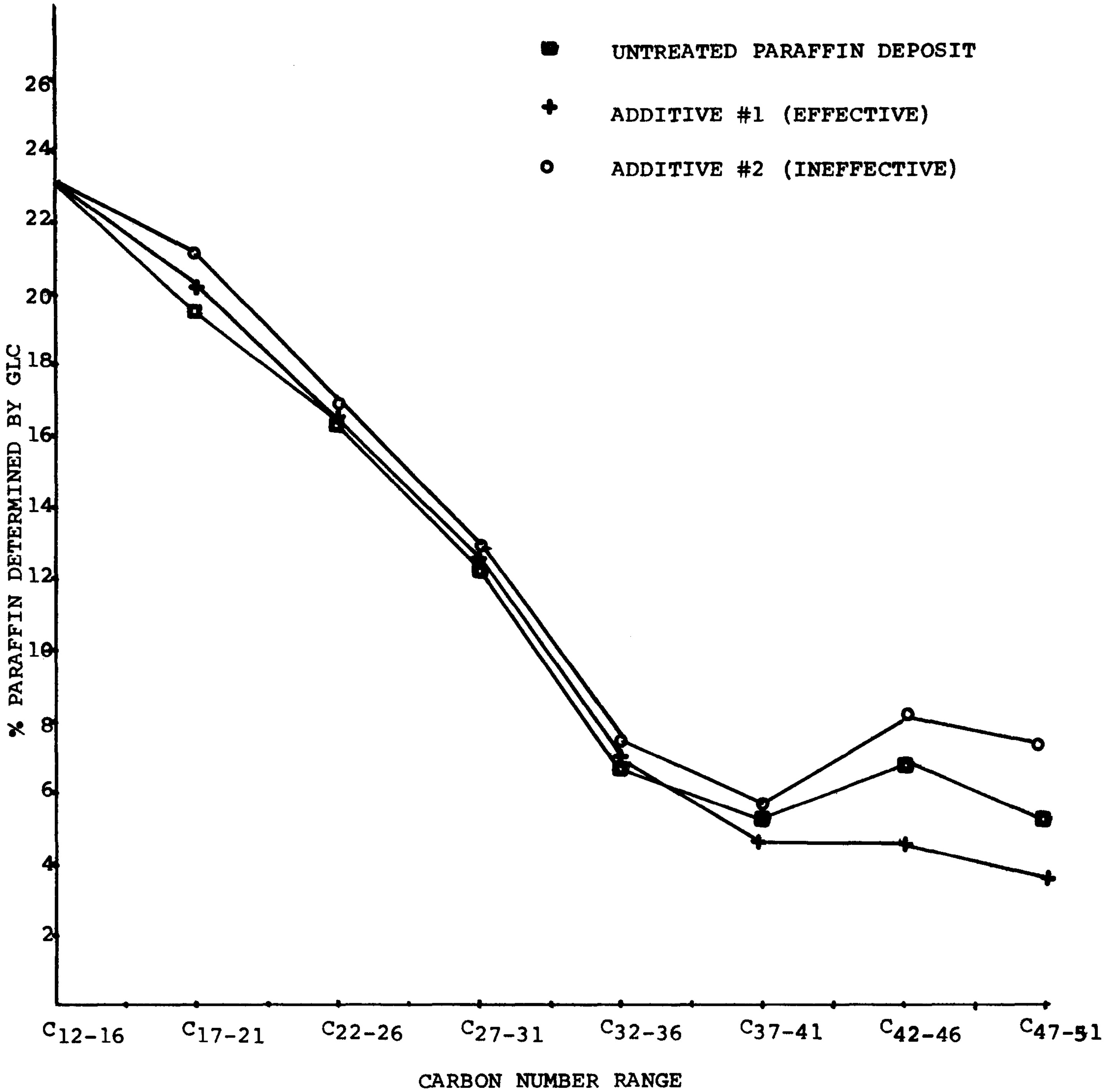

FIGURE 2 % PARAFFIN vs. CARBON NUMBER RANGE

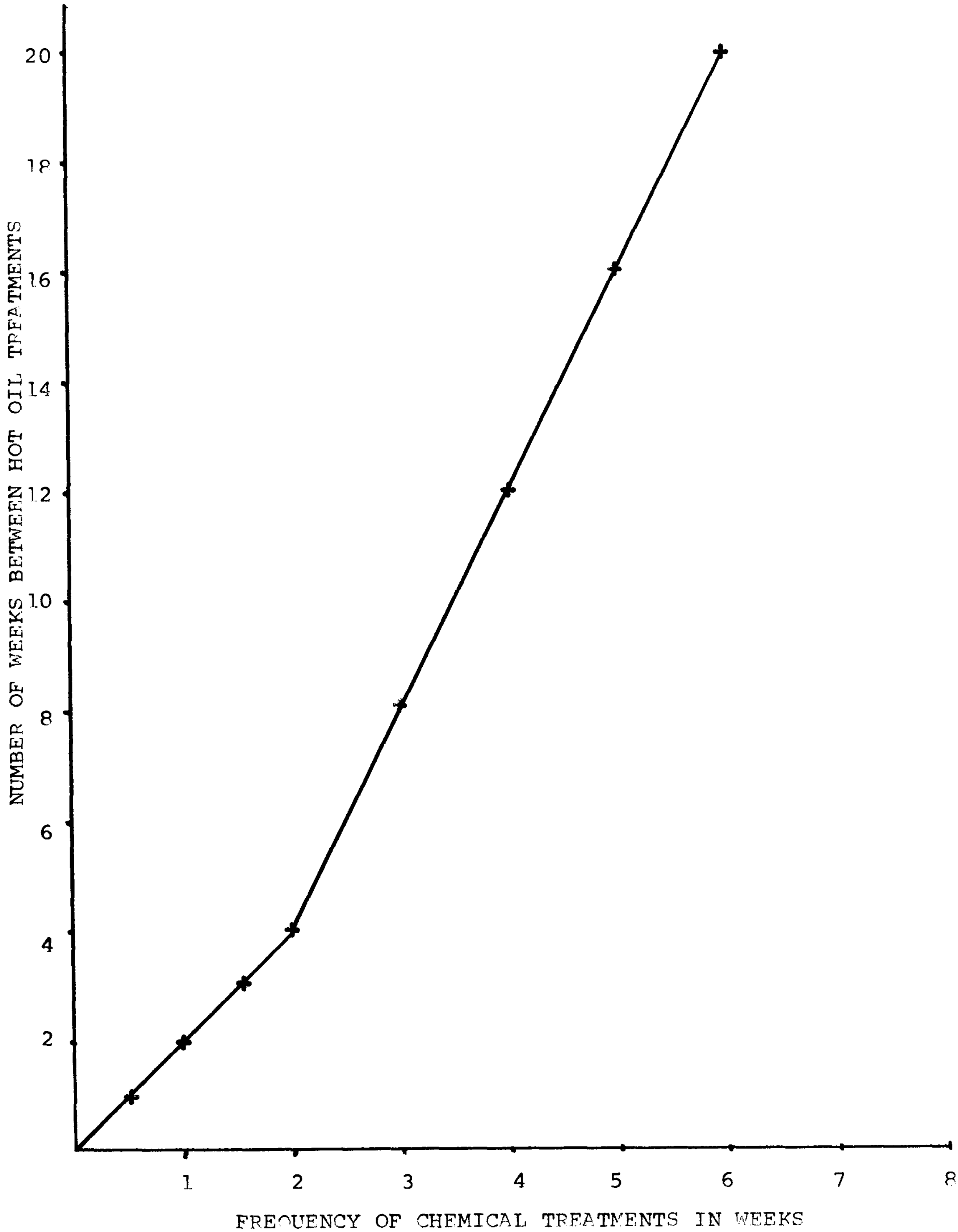

FIGURE 3 CHEMICAL TREATING FREQUENCY vs. HOT OIL PERIODS IN WEEKS

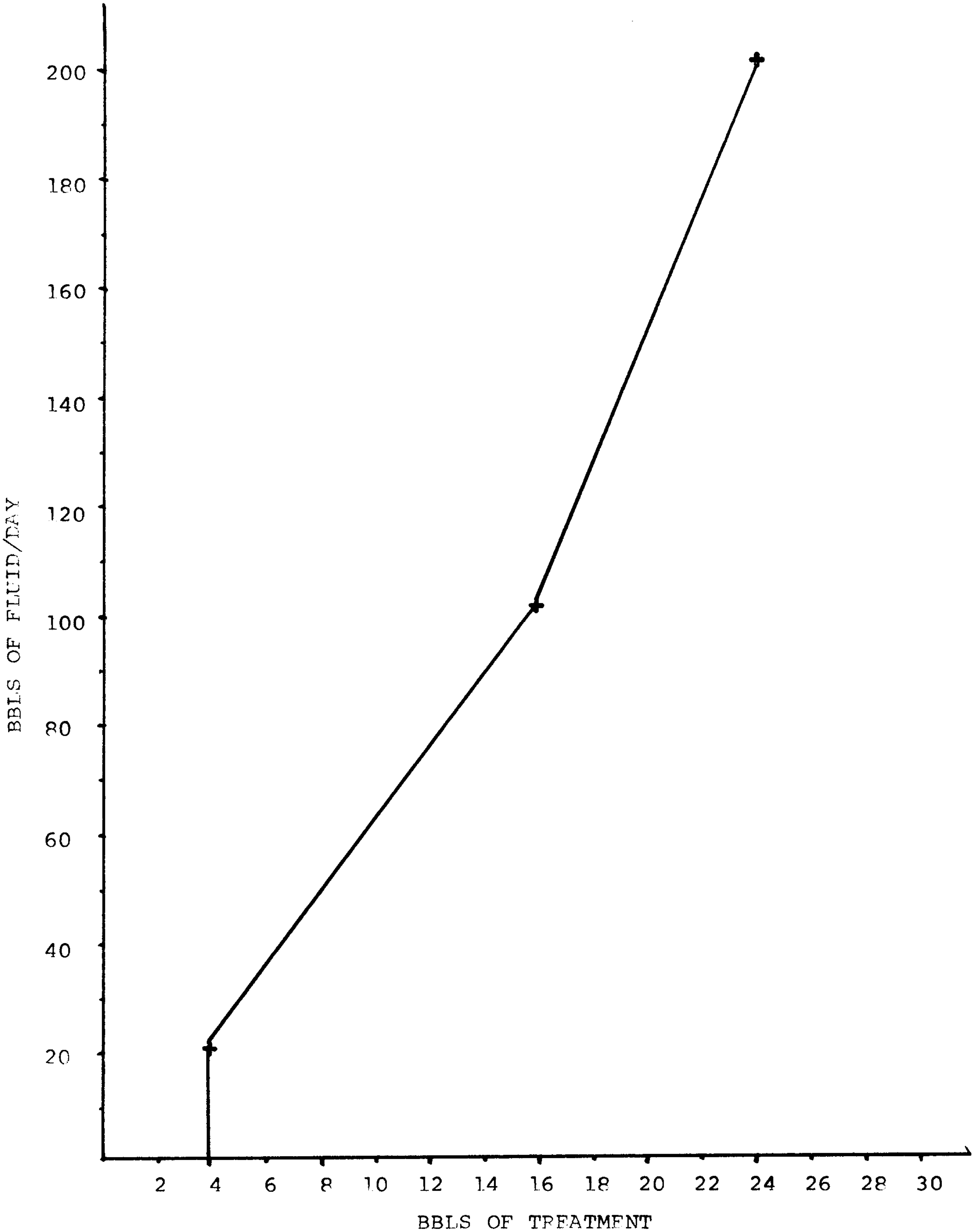

FIGURE 4 PRODUCTION/DAY vs. BATCH TREATMENT SIZE

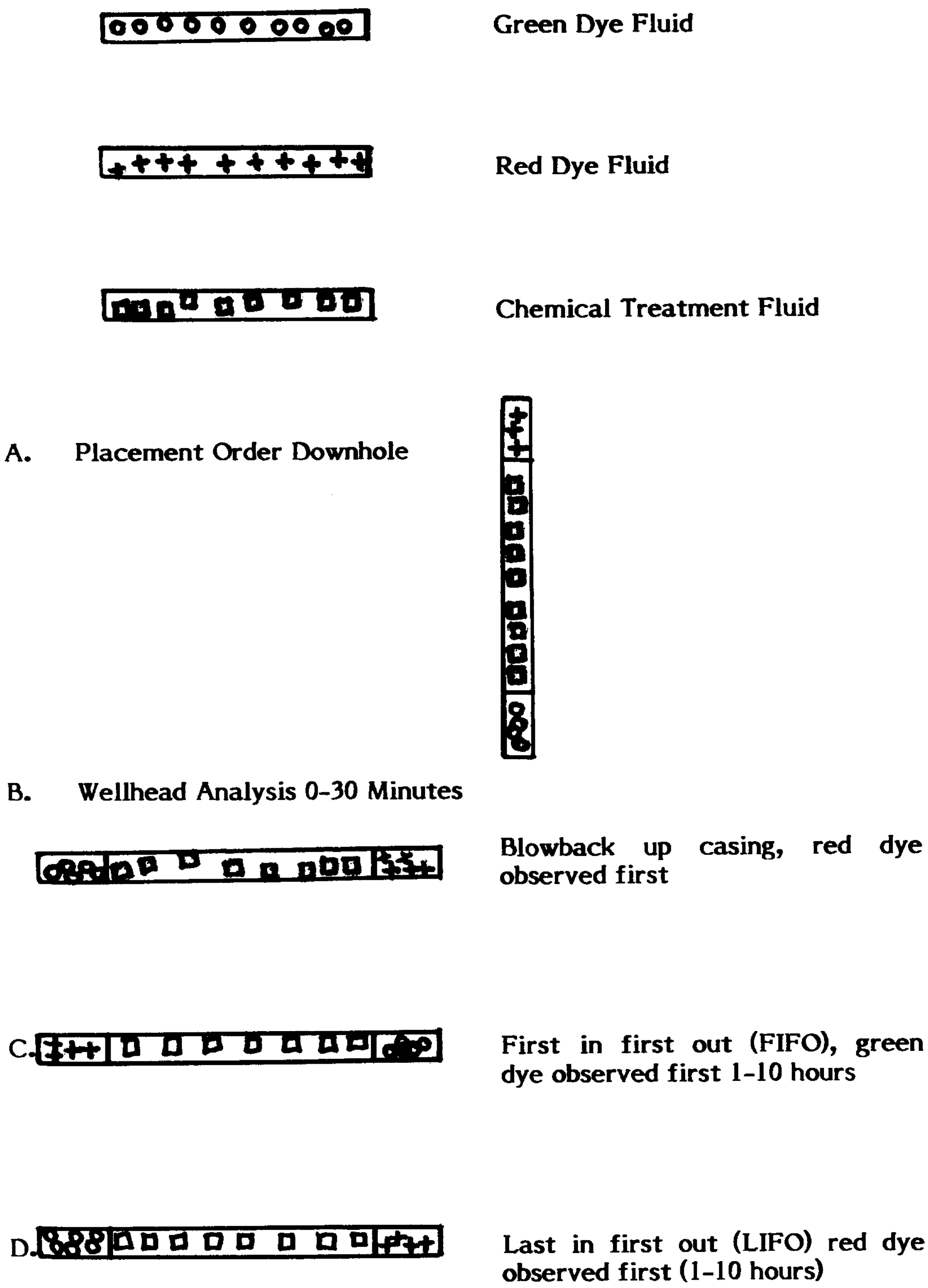

FIGURE 5 WELL TREATING APPLICATION AND FLUID RETURN ANALYSIS