Chemical Treatment of Oil Field Emulsions

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EVOLUTION OF TREATING

Emulsions in oil production are accepted today as a normal operational condition. The equipment and materials necessary to resolve produced emulsions are usually placed in the field as soon as a well begins to produce water in the form of an emulsion in quantities that exceed pipeline specifications. During the early years of the oil industry neither the knowledge, equipment, nor chemicals were available to treat oil effectively. Early methods of breaking emulsions consisted of settling time, and, in some cases, the use of heat. As a result, emulsion was often drawn off the bottom of tanks and burned as waste.[1]

This practice was undesirable even then but was unavoidable at that time due to the limited knowledge of emulsions and the lack of equipment and chemicals. Petroleum dehydration procedures progressed with the oil industry and some operators found that soap compounds would, in some cases, effectively cause the separation of an emulsion into water and oil. Acid mixtures were also found to be suitable for resolving certain emulsions. With the passage of time, hundreds of materials have been investigated as emulsion breakers.[2]

CAUSES OF EMULSIONS

In modern operations, many of the emulsion problems encountered can be attributed to operational efficiency. Mechanical agitation, which results from present production methods, will tend to intensify the emulsion problem. The gas lift method of producing oil is quite often the most efficient and economical method of producing a well. At the same time, water and oil in a gas lift well are subjected to a great amount of agitation between the point of gas injection and the well head and very tight emulsions may result.

In a pumping well, we have the passage of the fluid through the pump valves while under pressure and the continued agitation while the fluid is lifted to the surface to promote emulsification. In flowing wells, we usually have the produced fluid passing through a choke under pressure to assist in the formation of an emulsion.

It is apparent that energy in the form of agitation is required in some degree for the formation of any emulsion.[3] The actual amount required for any two phase system to emulsify will be dependent upon the amount of materials present that can act as emulsifiers. The produced crude oil may carry the offending emulsifier in many forms. Silts, corrosion products, organic acids, and many other materials that would affect the interfacial tension between oil and water may be present in the crude oil.[4]

When present, these materials are recognized as potential emulsifiers. However, their presence does not guarantee the formation of an emulsion, since the water phase of the system could either counteract the emulsifiers in the oil to prevent emulsification, or be of such a nature as to promote emulsification to any degree of severity. Thus, it is indicated that the produced water must either carry soluble materials or suspended solids to be an active participant in the formation of an emulsion.

The soluble materials will generally control the surface tension of the water and, in turn, the surface tension becomes a component of the interfacial tension between the oil and water of the emulsion when the two are brought into intimate contact. Insoluble solids in the produced water also are instrumental in the formation of an emulsion, either by acting as a nucleus for an emulsion droplet or by collecting at the interface of the two phases of an oil water system to promote emulsification.

TYPES OF EMULSIONS

Oil producers are faced with the problem of resolving many complex emulsions in the normal course of operations, but the emulsion most generally found is of the water in oil type.[5] While we may state that this is the type that is normally encountered, the infinite combinations of emulsifiers, temperatures, and varying conditions are such that each emulsion may be different. In most cases, we find that the emulsions found in an area that is all produced from a common zone will respond to some one demulsifier. This is not always the case, and it is sometimes found that offset wells producing from the same pay will produce emulsions that will not respond to any one demulsifier, economically.

Some operators recognize this condition and may use more than one demulsifier formula to dehydrate the production from a given zone. Others may feel that a loss of economy through the application of one demulsifier would be offset by standardization upon a single formula, would simplify purchasing, and would eliminate confusion in the field. Certainly we can expect production from different horizons in a field to require different demulsifiers. Only in a minority of fields, producing from two or more zones, will one demulsifier be satisfactory for dehydrating all of the production.

To this point nothing has been said regarding the influence of the viscosity of the produced fluid on the formation of water in oil emulsions, or the effect of viscosity on the demulsification of low gravity crudes. Since low gravity crude oils have specific gravities that approach the specific gravity of water, as the gravity of the crude decreases, separation becomes increasingly difficult. Heat is then required to reduce the viscosity of the oil and allow the water droplets in the oil to coalesce, and to aid in the dispersion of the chosen demulsifier in the oil, bringing it into contact with the emulsion interface.

However, we cannot assume that low gravity crude emulsions require more heat than emulsions from imtermediate or high gravity crudes, for heat may be needed to catalyze the oil/water separation and assist in the dispersal of a demulsifier in the oil, regardless of the gravity of the crude.

TREATING COSTS

Normally we find that water in oil emulsions which contain from about 3% to 40% water are the more difficult to treat. As the water percentage increases beyond 40%, the severity of the emulsion will usually be lessened and as the water percentage goes about 85%, chemical requirements are normally very nominal. The amount of chemical required will vary over a wide range and is usually dependent upon the type of equipment available for the dehydration process, the amount of heat that may be used, and maximum agitation possible for dispersing and demulsifier, and the efficiency of the demulsifier chosen.

Treating ratios normally vary in amount from one gallon per hundred barrels of emulsion to as little as one gallon to 5000 barrels of emulsion, with the average being approximately one gallon of chemical to 500 barrels of produced oil. This ratio will result in a treating cost of about 4 mils per barrel: this, however, is chemical cost alone and does not include equipment cost, installation, maintenance, or labor which may be charged to production as dehydration cost.

It is in working with water in oil emulsions that we sometimes encounter overtreated or "burned" oil. These two expressions are used to explain a condition that may arise from the addition of an excessive amount of demulsifier to an emulsion being treated. Actually, overtreated oil can best be described as oil containing a chemically induced emulsion. The emulsion that results from an overtreat will normally be different from the usual water in oil emulsion, to an extent that makes it easily detected by visual observation.

The overtreated oil will have the characteristic brightness or clarity of clean oil, as opposed to a dirty or dull color in a produced emulsion, and the water phase of an overtreat will appear to be finely divided water droplets when observed on clear glass. Since demulsifiers and emulsifiers are closely related chemically, it is not unreasonable to expect that overtreated oil may occur if an excessive amount of chemical is used. It can easily be demonstrated in the laboratory that some materials at low concentrations will act as demulsifiers and at high concentrations as emulsifiers.

The addition of an excessive amount of chemical does not guarantee the overtreatment of the oil in any system, since all demulsifiers do not exhibit this characteristic, nor are all systems subject to overtreatment. Emulsions resulting from an overtreatment are often extremely difficult to resolve. They may be tested to determine a material that would counteract the conditions which caused the overtreatment, or they may be resolved by diluting the overtreated oil with emulsion or bine.

Inverted Emulsions

Oil in water emulsions, which are often called either reversed or inverted emulsions, are usually encountered when the produced water is either fresh or brackish.[6] These emulsions have a characteristic light yellow color and are easily recognized by the fact that they can be diluted with water, or that they will tend to water wet a surface rather than to have the oil wetting characteristics of the water in oil type.

Reversed emulsions require an entirely different class of demulsifier for economical treatment, and most of the materials used for resolving reversed emulsions are water soluble. Reversed emulsions are quite often produced in conjunction with the standard water in oil type emulsion; efficient dehydration of the produced fluid may require the addition of separate demulsifiers for each emulsion. Failure to completely remove the oil from the water will magnify the problem of water disposal by oil welling filter beds or the sand face in an injection well. When oil wetting of this nature occurs, high injection pressures and low injection rates may easily occur.

It is not always necessary for either the produced oil or water to contain emulsifiers for a severe emulsion problem to exist in the surface equipment. Emulsions can be formed in LTX units as a result of inhibition. In many areas, this problem may become so acute that production is interrupted until the low temperature extraction unit is cleared of emulsion. To date, no completely satisfactory correction for this condition has been discovered. Demulsifiers may be added to the inhibitor or injected into the LTX unit to assist in resolving the emulsion, or other inhibitors may be tested to determine whether or not another inhibitor would create the emulsion and at the same time provide adequate protection.

Other troublesome emulsions may result from acidizing or fracturing. These problems are constantly being probed by the service companies and additives are usually placed in the acid or fracturing medium to prevent their formation. In the event that such emulsions do appear, they may be approached in the same manner as other emulsions.

THE TREATING SYSTEM

The type of oil treating system that is employed will usually affect the efficiency of an oil treating compound, and will in this manner have an important bearing on the per barrel cost of dehydration.[7] Most operations would prefer to dehydrate their oil without heat. If this can be done efficiently, the cost of a heater-treater or heater is avoided, as would be the cost of a gun barrel.

In many cases there might be a price advantage to cold treating if the clean production is marginal on gravity breaks and the deletion of heat would increase the price of the produced crude oil. The simplest system for cold treating would consist of a gas separator and production tanks. In such a system, the chemical used for dehydration would be added at the separator inlet or possibly at the well head. Water from the broken emulsion would be drawn from the bottom of the stock tank during filling. After the tank has been filled an additional settling period would be allowed to insure the complete dehydration of the oil.

If a high percentage of water is produced, a gun barrel can be placed in the system to remove excess water and allow settling time for the oil before it reaches the stock tanks. This type of treating is termed as cold treating due to the fact that no heater is used, but such a system will take full advantage of any heat from the produced fluids. This formation heat may often be the difference between treating cold and installing a vessel that will supply heat to catalyze the dehydration.

Many systems that depend upon formation heat are in service across the country. As has been stated previously, the biggest advantage in this type of system is the minimum amount of equipment required. Certain disadvantages are also inherent in a system that depends upon formation heat. We might expect most systems depending upon formation heat to have only the minimum heat requirements for acceptable dehydration available and to be extremely sensitive to cold weather and to overloading.

Since any oil produced that does not meet pipe line specifications may cause lost production, payment of overtime to field personnel, and additional cost in rental or usage of a portable heater, the economy of a system that has only a marginal amount of formation heat available may be questionable. The availability of fuel for any type of heater may make cold treating attractive, even in the face of the conditions mentioned. Each cold treating installation must be evaluated upon the conditions that exist in that given instance.

Gun Barrels

Gun barrels are often used in conjunction with heat and, under these conditions, a stable treating system normally results. In conjunction with a thermostatically controlled water heater or line heater, or with steam coils installed for temperature control, this piece of equipment can be considered both economical and reliable. Temperature control in a Gun Barrel takes full advantage of any formation heat and avoids any troublesome cold weather problems in dehydration. Maintenance costs are usually very low, due to the minimum of moving parts and automatic equipment required for the system to operate efficiently.

Many west coast operators use "wash tanks" which are similar, but much larger than the normal gun barrel; it is quite common to find vessels of this type with volumes as high as 5,000 to 10,000 barrels. The use of treating systems of this size is a result of high production rates and of a treand to centrally treat oil. Heat is controlled by passing steam through coils in the water phase. In general, the operation of wash tanks and gun barrels are the same.

Heater treater systems, which are widely used in the oil industry, have proved to be very effective, and are often used in conjunction with chemical. Some production may possibly be treated with heat alone, but cases where this can be accomplished are in a minority. The automatic nature of a heater treater makes this type of treating equipment particularly desirable when the production is broken up into small leases and the production must be handled separately, due to lease agreements.

With automatic equipment of this type a pumper can handle several leases, making it possible to keep labor costs at a minimum. In actual field operations, the biggest problem normally encountered in heater treater operations arises from a fluid volume overload. This situation results when a lease is being drilled with each well being added to the treating system as it is put on production. A fluid overload will result in both oil contaminated water from the water draw down line and water or B.S. in the oil being placed in stock.

There are other types of treating systems in existence such as retorts and centrifuge systems, which are rate in field operations and are not economical for normal field use. Retorts are found in some areas on the west coast, where the crude gravities are extremely low and the separation of water and oil is almost impossible by the usual treating procedures. Centrifuges may also be used but are even more scarce than retorts. Their value as an oil treating medium is questionable.

THE INJECTION OF CHEMICAL

There are numerous ways of injecting dehydration chemicals into a system to be treated; the most widely accepted method is the chemical pump or injector which is built for this specific purpose. The individual requirements of the systems to be treated will determine the type of pump to be used. Aside from pressure requirements, a choice must be made concerning the motive power for the pump. The motive power may be from electricity, gas or in the case of pumping wells, a beam pump may be used.

The point of injection is normally placed in the system at a point that is a sufficient distance from the treating system to insure adequate agitation and complete dispersal of the treating compound. To insure complete dispersal of a treating compound in an emulsion, it is sometimes necessary to place the chemical injector at the well head. The conditions in the individual systems and the severity of the emulsion to be treated will dictate the placement of the chemical injection equipment.

Placement of the injector at the well head may also be considered in gas lift installations where chemical in the lift gas may prevent the formation of a severe emulsion and result in more efficient treating. In isolated instances, pumping wells are treated by batching demulsifier down the annular space. Both batch treating down the annulus and injecting chemical into lift gas are methods of coping with problem installations. The addition of chemical in this manner is rare as compared to the number of installations where chemical is injected in the vicinity of the gas separator.

THE BOTTLE TEST

The performance of a demulsifier in the field is dependent upon the accuracy of the bottle test by which it was chosen. The field service representatives for most demulsifier manufacturers carry sufficient equipment in their service cars to accurately choose an efficient demulsifier for a given emulsion. Field test equipment will normally exist in the form of a portable laboratory in the trunk of a field car and will contain the pipettes, graduated test bottles, a water bath, a centrifuge, and samples of numerous effective oil treating compounds.

The efficient performance of a bottle test requires accuracy and skill to inusre maximum correlation between the bottle test and the field application of a demulsifier.[8] The proper ratio of chemical to emulsion should be determined through a ratio test before the field service man begins a series of bottle tests to compare the efficiency of a chosen group of demulsifier formulae on the emulsion being treated. Much of the success of a bottle test will depend upon the skill of the service man in detecting small color differentials, evaluating the importance of the water separation characteristics of the various compounds, observing the interface characteristics of the compounds being tested, and making grind outs on the treated oil to determine the percentage of B.S. and W. left in the sample.

Choice Of Proper Formulation

If a compound is outstanding in each of the categories mentioned, the choice of the proper formulation is no problem, but too often the ultimate choice becomes a compromise and more than one compound will be seriously considered. This situation arises due to the fact the one material may excel in water drop properties, a second may impart a desirable color to the oil early in the test cycle, and yet another may afford cleaner oil at the end of the test. Thus, the service man must consider the type of treating system being used, the length of time involved in the treating cycle, and the cleanliness of the oil before a choice is made.

While the bottle test is the tool by which a demulsifier is chosen, the field test is even more important because it is actual proof that a demulsifier will deliver the performance indicated by the bottle test. If a treating compound is being used where the field test is to be run, the field service man should accumulate data which would indicate the minimum chemical requirements for the installation, the temperature range of the treating system, the amount of oil being treated, and the B.S. and W. content of the produced oil.

With this information, a fair and impartial comparison can be made on two or more materials and the comparable costs can be calculated. Calculations based on field data will assist the operator in choosing the demulsifier which will allow the oil to be delivered to the buyer at the lowest possible cost. Without data to be used as a guide in the choice of a demulsifier, an improper choice might be made which would result in reduced efficiency and increased treating costs.

RESEARCH FOR NEW MATERIALS

The search for more efficient demulsifiers is an accepted facet of the demulsifier business. Each manufacturer must constantly search for methods and materials to improve his respective materials. Much of the laboratory research done involves raw materials that have characteristics that are desirable from a cost standpoint, or else have chemical structures that may be of interest.

Before a new material is considered suitable for manufacture and sale, the compound will be prepared in the laboratory, bottle tested in both the laboratory and the field, and plant tested in the field whenever possible. These tests are supplemented by laboratory evaluations concerning pour point, freezing point, and solubility characteristics. The procedures mentioned are empirical in nature and are strong arguments for the statement that the manufacture and sale of demulsifiers is more often an art than a science.

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