Recent Developments In The Clarification Of Oil Field Waters

By JOHN V. SLYKER
Bradford Laboratories Div., Hagen Chemicals and Controls, Inc.

INTRODUCTION

Waterflood operators are in agreement that adequate clarity of oilfield injection waters is essential. Achieving the desired water clarity is another matter and often has been difficult and/or expensive. Recent developments in the field of chemical coagulation for oilfield water clarification have revealed new approaches to the solution of this problem.

Coagulation as a water clarification tool is centuries old. Most municipal water plants and many industrial processes use this technique to remove turbidity. In fact, numerous waterflood projects now use coagulation. The majority of these plants feed conventional coagulation chemicals such as lime and ferric or aluminum sulfate. The use of conventional chemicals is confined, however, in the oil field. Different oil producing areas yield flood waters of widely divergent mineral character and types and amounts of suspended material that must be removed. In the past this has meant that usual coagulants and chemical clarification programs were not too effective in many oilfield waters. West Texas and Eastern New Mexico brines, for instance, are prime examples of such waters.

Development of newer polyelectrolytes as coagulant aids and/or coagulants has broken these coagulation confines and has greatly broadened the spectrum of oilfield waters which can be clarified satisfactorily. As a result, undue burdens that have been placed on mechanical clarification methods can be relieved.

The purpose of this paper is to present the new picture of polyelectrolyte coagulation for the clarification of oilfield waters. This picture includes a framework of What-Why-When-How. This framework will show that polyelectrolytes have brought a semblance of a scientific approach to a field which has largely been art.

DEFINITIONS

Conventional Coagulation

Clarification of coagulation gains removal of turbidity by addition of metal salts (iron and aluminum) to form floc. It involves 3 steps: (1) thorough mixing of chemicals and raw water; (2) slow, gentle agitating which enables floc to grow and entrap suspended matter; (3) providing a period of quiescence for floc to settle. A polished end product can then be obtained by filtration.

Conventional clarifying equipment provides these 3 phases with mechanical mixing and coagulating equipment or baffled sedimentation basins.

High-rate units also use these basic stages. In upflow units, raw water and coagulants mix in a central zone and flow into a gentle mixing zone and then upward through a sludge blanket. Separation of floc and water is a balance of settling and upflow filtering through the sludge blanket. Solids contact equipment functions similarly while providing continuous recirculation of sludge to seed and increase the rate of floc formation in the rapid mixing zone.

Oilfield Coagulation

Oilfield coagulation encompasses the same 3 steps. However, mineral characters of oilfield waters not only can differ substantially from those conventionally coagulated, but they also have quite diverse mineral and gas contents. The outcome is that oilfield coagulation processes are quite different and more complex. Further, some degree of deviation in clarifier design is not uncommon. This deviation may necessarily impart more importance to 1 or 2 of the 3 coagulation steps.

Conventional coagulation chemicals often are not adaptable to such conditions. Also, their application is very limited because of frequent incompatibilities experienced with oilfield waters.

These inherent confines have been broken by the introduction of polyelectrolytes into the realm of oilfield water coagulation.

Polyelectrolytes

Natural polyelectrolytes were used as flocculants several thousand years ago. In modern conventional clarification they have wide application and usage as aids to coagulation. Definitions in this paper will conform to those given by Blakeley: "the term polyelectrolyte has often been used to describe various materials that are both polymers and electrolytes. The term is somewhat misleading when applied to chemicals available to coagulation because many of the materials are mixtures, including some natural or synthetic organic polymer. In this discussion the term 'polyelectrolyte' is used to describe only the polymer. The term 'coagulant aid' is used when referring to compounded materials."[5]

How polyelectrolytes function in the light of chemical reactions is not known. Their action has been likened to those of long interwoven molecular chains, containing charged sites, and extending fingers and tentacles. As floc particles grow they entrap, entangle, and "muscle in" suspended solids.[3, 4, 6]

Though their application covers a wide scope of conditions, no present explanation exists of the fact that certain polyelectrolytes are effective in 1 situation and relatively ineffective in another. Therefore, a fair number of them may have to be tested to derive optimum results.

Polyelectrolytes may perform in 2 coagulation capacities. In combination with weighting agents such as specially processed bentonitic clays, they are used with conventional coagulants to speed up floc formation, growth and settling rate. Here polyelectrolytes are described as being adsorbed onto solids, extending tails and cross bridges. As coagulation proceeds, particles approach one another, bind and coagulation occurs. Thus, they may be considered "binders"[5]

As coagulants per se, both anionic and cationic polyelectrolytes can be used separately or together. Where both are added, coagulation appears to be a coprecipitation phenomenon, again accompanied by entrapment and occlusion of solids.

In whichever coagulation capacity they may function, these unique materials exhibit distinct advantages which make them applicable to the clarification of oilfield waters. They are:

1. Waters of greatly differing mineral character can be successfully clarified
2. Wider swings in solids loadings and the nature and types of solids can be treated
3. More versatile floc properties can be realized
4. They are compatible with oilfield waters
5. Control of pH is less critical, in brines often unnecessary
6. Need for basic feed rate changes is lessened
7. Good uniform water quality can be produced despite fluctuations in raw water quality.

WHY COAGULATE?

The Need

Need for better and more reliable and refined turbidity removal methods is recognized. All too frequently poor waterflood performance is traceable to problems resulting from difficult-to-control characteristics of injection waters. The advent of mandatory produced water disposal and recycling is compounding those problems. The same is true of water shortages in waterflood areas, which necessitate use of source waters having less than desirable mineral, bacterial and suspended solids qualities. The need for better methods of water clarification is evident and will increase in the future.

Many waterflood operators have clarified waters by mechanical methods. Coalescers, oil-water separation equipment, tanks or pits for retention and settling, filters, solvent wash techniques, etc., are usually employed. Experience shows that no one process or any combination of these is wholly satisfactory for solids removal. Natures and types of suspended solids that must be removed explain why.

Oil, free and/or emulsified, is a common flood water contaminant which is difficult to eliminate by oil-water separation methods. It is frequently detrimental to injection programs. It subjects the flood system equipment to continuous fouling and sup-par performance from which injection rates and pressures usually suffer. These effects are particularly noticeable when oil is present with other suspended material, which is usually the case.

Iron sulfide, iron oxide, insoluble calcium salts, barium sulfate, silt, clays, and bacteria are other equipment-fouling and intake well plugging materials. Suspended solids encountered are primarily combinations of these constituents. In oilfield waters these contaminants generally exist as emulsions, suspensions, and colloidal particles which are not entirely removable via physical clarification equipment.

For example, West Texas operators have found oil-iron sulfide problems quite difficult to manage. West and North Central Texas waterflooders encounter many oil-iron sulfide-iron oxide removal problems. Other area flooders experience oil-iron oxide-silt removal troubles. In all areas scale depositions and bacterial aggravations complicate the physical solids removal problems.

The Result

Physical-mechanical clarifying methods would not be expected to efficiently remove such solids loadings, and this is the case. In the past no alternatives have been available. The result has been that the various physical turbidity removal methods have been extended to operate beyond their normal functions and design capacities. Hence, poor efficiency and performance have been the rule.

Retention of water in storage tanks, pits or basins does not assure settling or separation of solids. Such facilities are not usually efficient enough to secure separation of traces of oil.

Filters carry the major solids removal burden, and often are the sole means of turbidity reduction. Oil fouls sand, graphilt ore, and anthracite media used in bed-type filters. When this occurs, operating efficiency is drastically reduced and channeling and cohesion of media particles result. Thus contaminated media needs frequent cleaning. Many times damage is irreparable and beds must be replaced. During all of this, filter performance is poor. Case histories cover these and other side effects of bed filter damage.[1,12] Hence, filters end up being trouble spots, not means of relief.

Cartridge filters can not and should not be expected to handle large solids loadings or smaller oil contaminated loads. With this type of filter, as with most, economy is a factor based on operation within prescribed limits.

Diatomaceous earth filters, as well, will remove solids effectively with certain limitations. Solids loadings should not exceed 30 mg/1. These units will filter oil in not too large amounts, but "squeezing" of oil through them will occur when the filter cake becomes oil saturated. Operation costs rise rapidly as filter cycles are shortened in order not to exceed the "squeeze point". Substantial suspended matter accompanying oil yields short cycles with considerable sluicing necessary to remove an impervious, compressed filter cake.[2] When oil is present, innovations in sluicing must be made to effectively remove adhesive and matted material. Even then, sleeve or screen cleaning must be done periodically, lest remaining gum-like deposits cause imperfect precoat caking and passways for slurry leakage.

Why coagulate? The above discussions point out 1 thing. Costs of gaining solids removal shoot upward and remain high when mechanical means of turbidity removal are pushed beyond their design and functional limitations. Even at that high cost, performance is usually low and the flood suffers because of poor water quality. Coagulation is an answer that can effect better overall turbidity removal and therefore increase physical equipment efficiencies and reduce clarity problems.

Polyelectrolyte coagulation is the means by which this can be done. It affords to the oilfield most advantages of conventional coagulation (except softening). It incorporates wide range treatment, including oil removal and some reduction of bacteria populations.

WHEN COAGULATE?

Water analyses provide information that indicates when to coagulate.[1,7 12] One of the most important tests is the suspended solids determination. Jar testing is the final analytical criteria for deciding when to coagulate.

In general, coagulation should be considered when suspended oil is a problem, and particularly when oil exists in conjunction with substantial amounts of other suspended matter. It is indicated with waters containing large solids loadings and in waters exhibiting significant unfilterable (colloidal) matter. It certainly should be considered wherever mechanical clarification can not provide satisfactory water clarity.

General conditions can be given for a better grasp of when treatment with polyelectrolytes can be most useful:

1. A large amount of suspended material may be best handled with a coagulant aid alone, or with small concentrations of coagulant and aid.
2. Raw water containing a natural coagulant as dissolved iron can provide its own coagulant by aeration. Iron precipitated in the ferric form presents a situation in which an aid alone may adequately and economically clarify the water.
3. Coprecipitation using anionic and cationic polyelectrolytes probably best handles solids containing a major portion of oil. Weighting agents may be necessary.
4. Moderate amounts of finely divided or colloidal solids may use a polyelectrolyte alone, with an aid, an aid alone, or the coprecipitation technique.

Coagulation studies are the only way of determining what type of feeds give the best and most economical approach. Jar testing is the experimental tool with which such studies are conducted.

An example of an initial coagulation study is given in TABLES I and II. Table I is an analysis of the raw water used for this study. Table II gives jar test results. Turbidity and suspended solids of a produced water mixture used for injection in West Texas were moderately high. Conditioning this water with a settling-filtration program was simply not enough to clarify the water adequately. Oil and iron sulfide were major suspended constituents, together with a lesser amount of silica. The iron sulfide-oil combination kept the filter below optimum performance at all times and that was shown by significant post filter deposition in meters and on chokes. Intake well plugging was evident.

Recorded test results are a summary of the best test series. Aids alone did not perform well; neither did single polyelectrolyte additions. Good results were obtained with both -- 1 cationic, 1 slightly anionic -- and the aid containing bentonitic clay as weighting material. During tests it was observed that both free and emulsified oil were coagulated along with other suspended matter and turbidities were substantially reduced. A very small amount of floc floated but was filterable and backwashable.

TABLE I

RAW WATER ANALYSIS

pH	6.4
Temperature	90
Hydrogen Sulfide	500
Turbidity	33
Bicarbonate Alkalinity	900
Chlorides	50,000
Total Hardness	11,200
Calcium	2,600
Magnesium	1,100
Sulfates	1,900
Manganese	0
Iron	1.0
Total Dissolved Solids	90,000
Suspended Solids	40
Oil	22

TABLE II

COAGULATION TEST SUMMARY

Jar Test Series No. I

Polyelectrolyte (mg/1)	Coagulant Aid (mg/1)	Floc Character	Supernatant Turbidity
2	15	Fair	5.0
2	30	Excellent	3.0
3	15	Fair	2.0
3	30	Excellent	2.0

Jar Test Series No. II

Coagulant Aid (mg/1)	Polyelectrolyte (mg/1)	Floc Character	Supernatant Clarity
15	2	Fair	8.0
30	2	Good	0.9
15	3	Fair	2.0
30	3	Excellent	1.0

NOTES: "Floc Character" is a summary expression for separate evaluations of speed of floc formation, its size, settling rate, and tenacity, Turbidity is expressed as parts per million silica. Tests were performed with a Phipps-Bird gang stirrer according to jar testing procedures as given by Blakeley.[5] Order of chemical addition is indicated from left to right.

HOW COAGULATE?

How to coagulate is partly defined by influences already discussed: provisions for some degree of the 3 basic coagulation steps, properties of polyelectrolytes, and, types of solids to be removed.

Further controlling elements include: flood water mineral and gas character, type of system to be used, direction of floc, and confirming jar test studies.

The mineral and dissolved gas character of the flood water will dictate whether the system will be "open" to the atmosphere or "closed". Also it will aid in predicting whether a protective lining or chemical treatment is more economical for corrosion control over the flood life. These factors will point out the most desirable plant clarifier design. The natures of solids will determine floc direction as revealed by coagulation studies. A directional floc may float or be settled depending on chemical dosages.

Equipment must comply with limitations determined by all of the above conditions. Illustrations may be helpful at this juncture.

A very gassy supply well water can utilize a floating floc by virtue of entrained gas lifting the floc. Either an open or closed system can be used, but provisions must be made for skimming the floating floc or "froth". In a closed system, precautions can be taken against atmospheric exposure by maintenance of a low pressure inert gas seal on the precipitation vessel. In an open system, air can be injected into the clarifier influent water to give better floc flotation properties. In fact, this approach can be taken when confronted with flotation of gas or oil.* Results in Table III show how oil can be rendered upward moving with a floc or settled with the same floc, depending on the amount of weighting agent added. In this instance, if equal clarity is gained for either floc direction, the less expensive method is flotation since weighting agent feeds are less or completely eliminated.

TABLE III

SUMMARY JAR TEST RESULTS
FOR DIRECTIONAL FLOC

Polyelectrolyte (mg/1)	Aid (mg/1)	Floc Direction
1	0	UP
1	20	UP
1	30	SUSPENDED
1	40	DOWN
3	10	UP
3	20	UP
3	30	SUSPENDED
3	40	DOWN

NOTES: Supernatant clarities and floc characters varied with amount and order of additions of coagulants. A downward directional floc was determined by the amount of aid, which contained a bentonitic weighting agent.

Most clarifiers other than for the above situations are designed for sedimentation. Commercially available high-rate units or home-made units such as in Figures 1 and 2 are satisfactory provided they are adaptable to the design purpose of the flood system.

Pits are gaining wider usage in floods, and if designed properly, can minimize coagulation and filtration requirements. Figure 3 illustrates a dual pit diagram. Pits and basins, like clarifiers, must be engineered specifically for the flood's defined water problems in order to give good results.

In special instances rapid chemical mixing and filtration can be used without lengthy intermediate sedimentation. Here, floc growth experienced from a source well to a filter may be of such rapidity and achieve a large enough particle size that the solids and floc can be easily removed by the filter. Care must be taken that good conditions for this are met, else serious problems can develop in the filter. If precautions are not taken and test evaluations not performed, the binding action of polyelectrolytes may create an impervious mat on the filter by incorporating this action on media grains.

Jar Tests

Coagulation studies using reliable jar test procedures provide necessary coagulation information. Basic system functions are derived from these tests which, to be of the most value, should be performed on freshly drawn samples at the flood site. Results are used to indicate how best to handle a water, or, if the plant is in operation, tests can be used to duplicate conditions of the plant in order to refine treatments and to achieve optimum clarifier effluent quality.

Figure 4 illustrates a jar test sequence where floc flotation plays the major role in oil removal. Figure 5 shows that settled floc is easily broken up upon reagitation (a) but it will retain settling characteristics if an aid is used (b).

Chemical Dosages

Dosages of aids may extend from 0.25 mg/1 to 40 mg/1. Polyelectrolytes are usually added in the order of 0.5 mg/1 to 5 mg/1.

Economics

Polyelectrolyte feed costs range from a low of 0.1 mill/bbl to a high of perhaps 4 mills/bbl.

A variety of clarifying units are available, as mentioned heretofore. It can be stated that the favorable floc forming characteristics of polyelectrolytes (speed, adaptability), permit clarification equipment to be simple and inexpensive.

Economic considerations must always include the cost of what has not been done with what can be done. In this light the cost of coagulation compares quite favorably with those of replacement of filter beds, replacement of equipment, and injection well workovers.

Interferences

Jar tests are of necessity also in determining adoption of coagulation in waters that may be pretreated chemically.

Coagulation tests have been performed on recycled produced waters where extensive producing well corrosion inhibition programs were in progress. No adverse effects on coagulation were noted. It is conceivable, however, that some types of inhibitors may change flocculation habits.

Scale inhibition programs in producing wells or in oil water separation processes may leave additive residuals. Since many deposit inhibitors are dispersants, such treatments may affect floc character. Literature suggests that small amounts do not,[9] and that the dispersant effect is decreased with increasing hardness. The latter may be compensated for by a small boost in coagulant dosage.[10]

In the flood system itself, chemical addition of 1 to 2 mg/1 of sodium hexametaphosphate for protection against scale deposition in filters is an accepted practice.[8] Such treatment should be located just prior to filters and only after the coagulation process, unless a preconditioning process (aeration) requires scale stabilization.

In any case, jar tests can evaluate pretreatment influences.

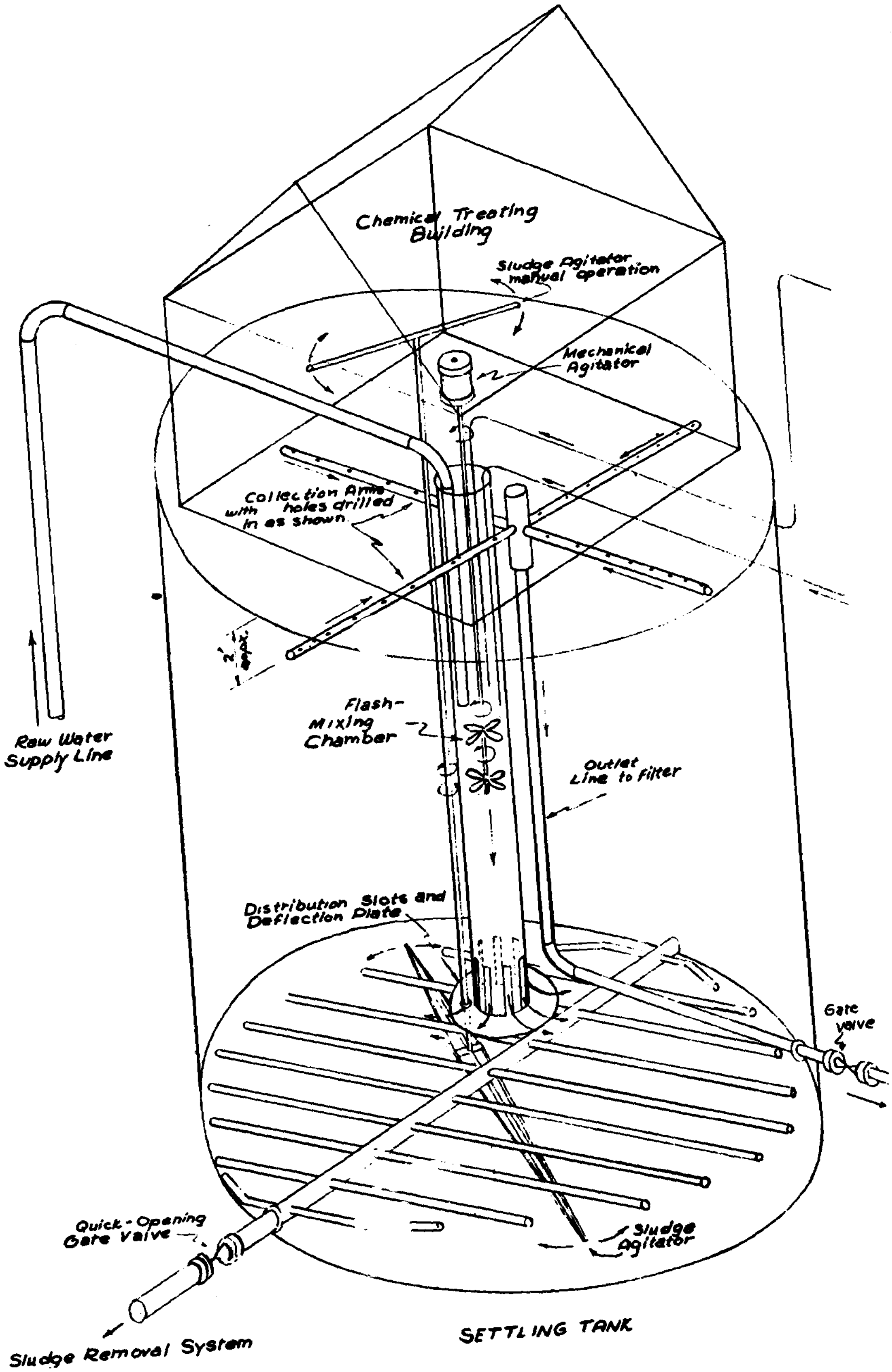


Fig. 1 - A Home-made Flume-type Upflow Clarifier.

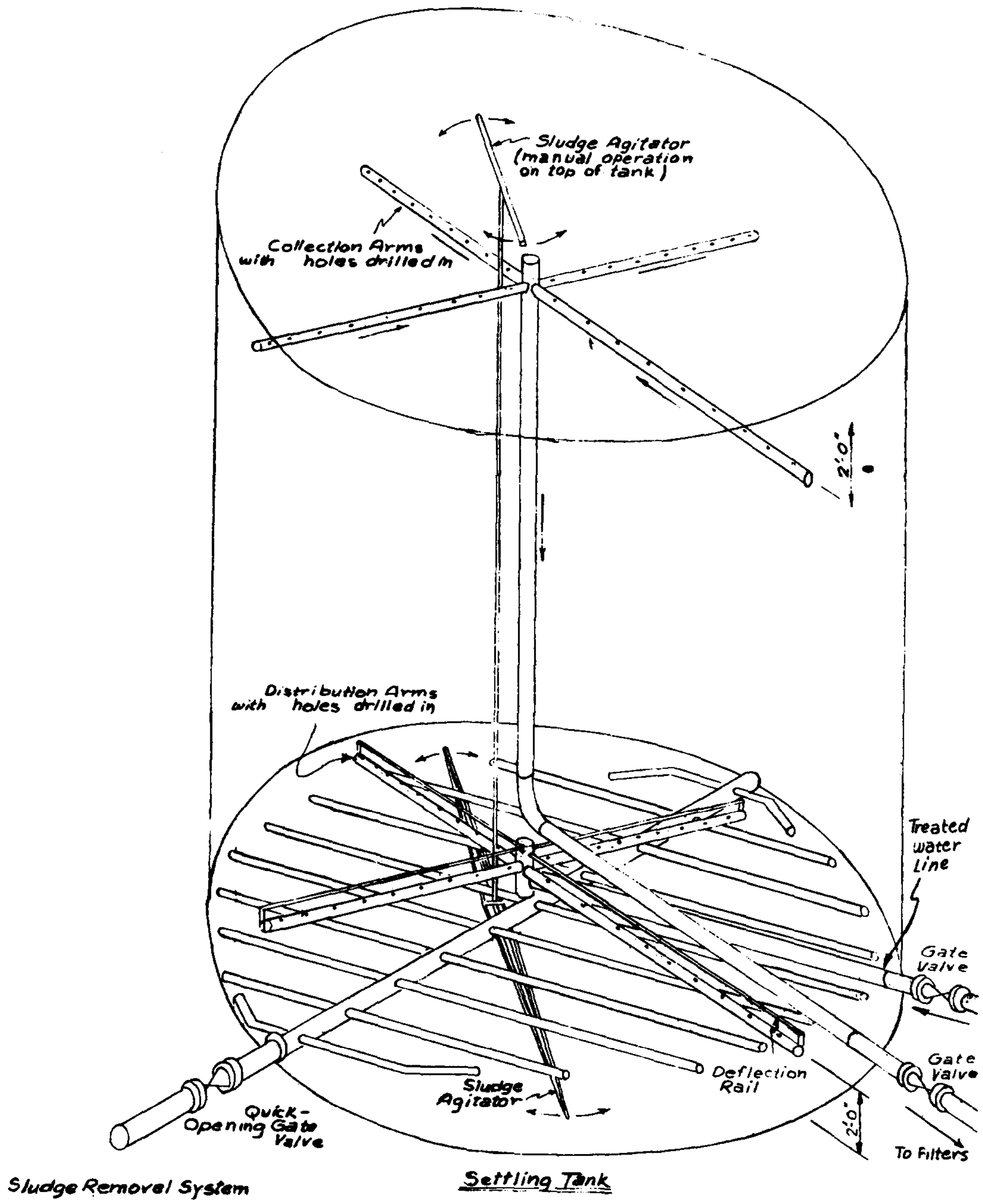
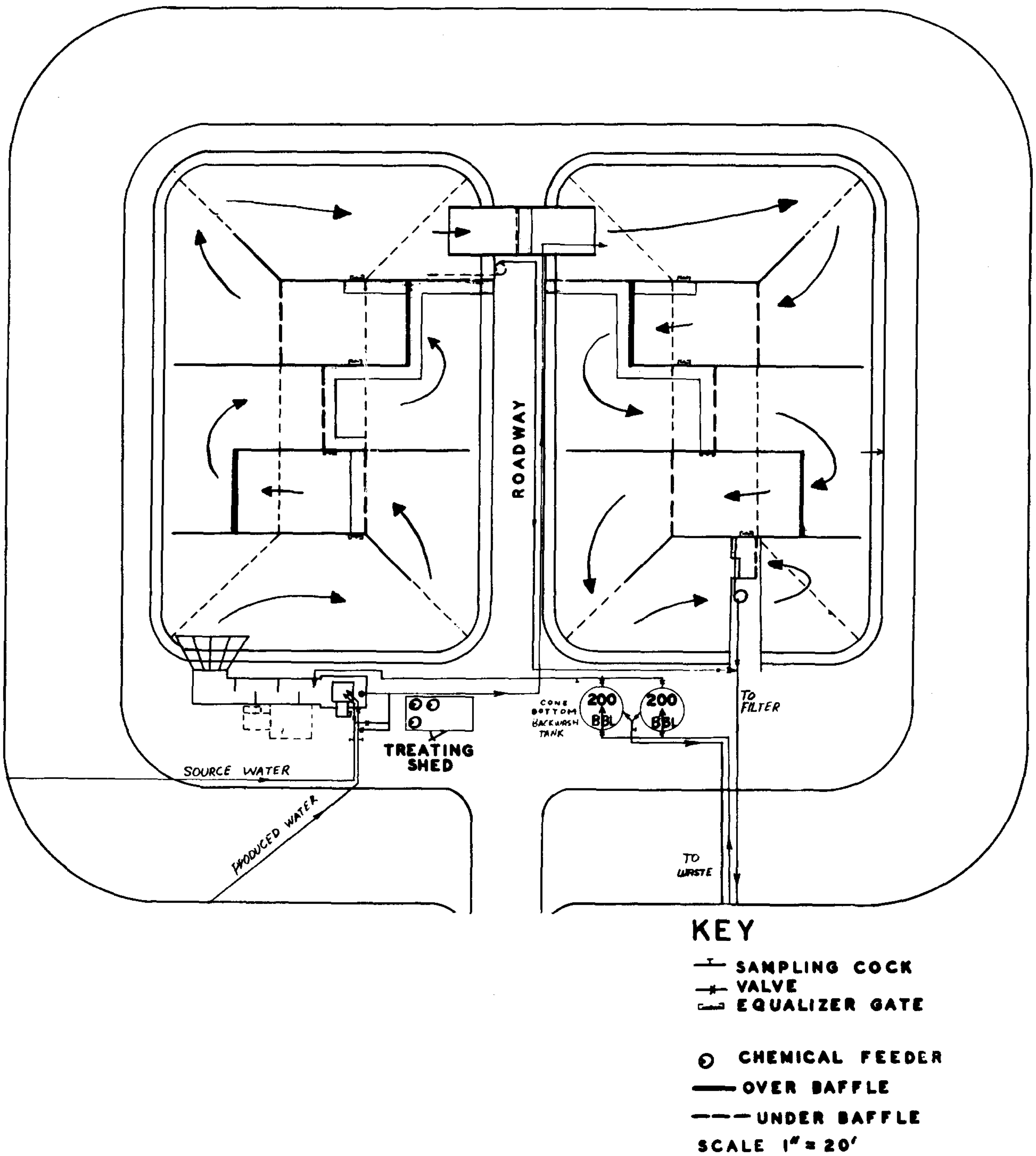


Fig. 2 - A Home-made Upflow Clarifier Emphasizing Proper Distribution And Collection Systems.



ROADWAY
CONE BOTTOM BACKWASH TANK
200 BBL
200 BBL
TO FILTER
TREATING SHED
SOURCE WATER
PRODUCED WATER
TO WASTE
KEY
SAMPLING COCK
VALVE
EQUALIZER GATE
CHEMICAL FEEDER
OVER BAFFLE
UNDER BAFFLE
SCALE 1" = 20'

Fig. 3

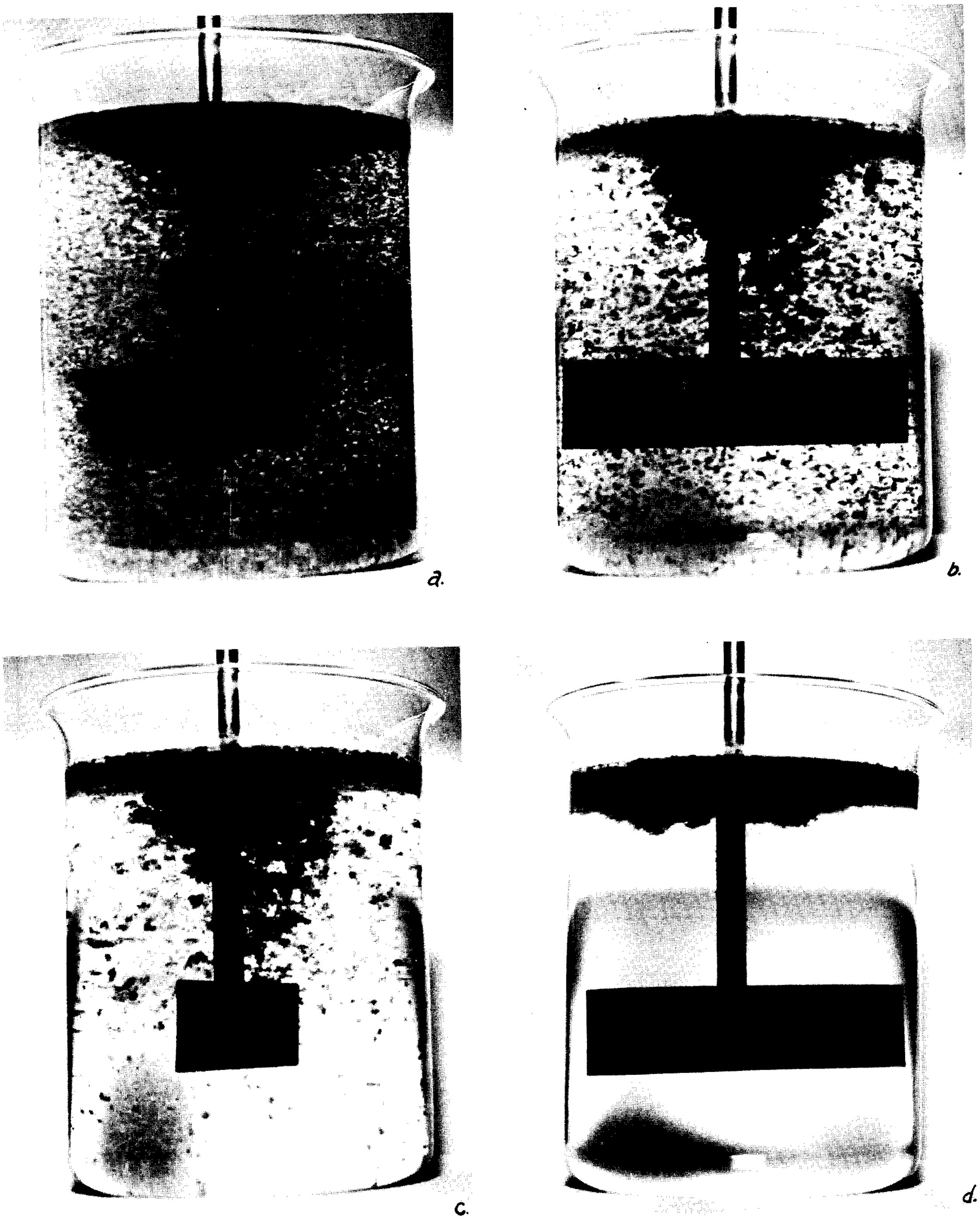


Fig. 4

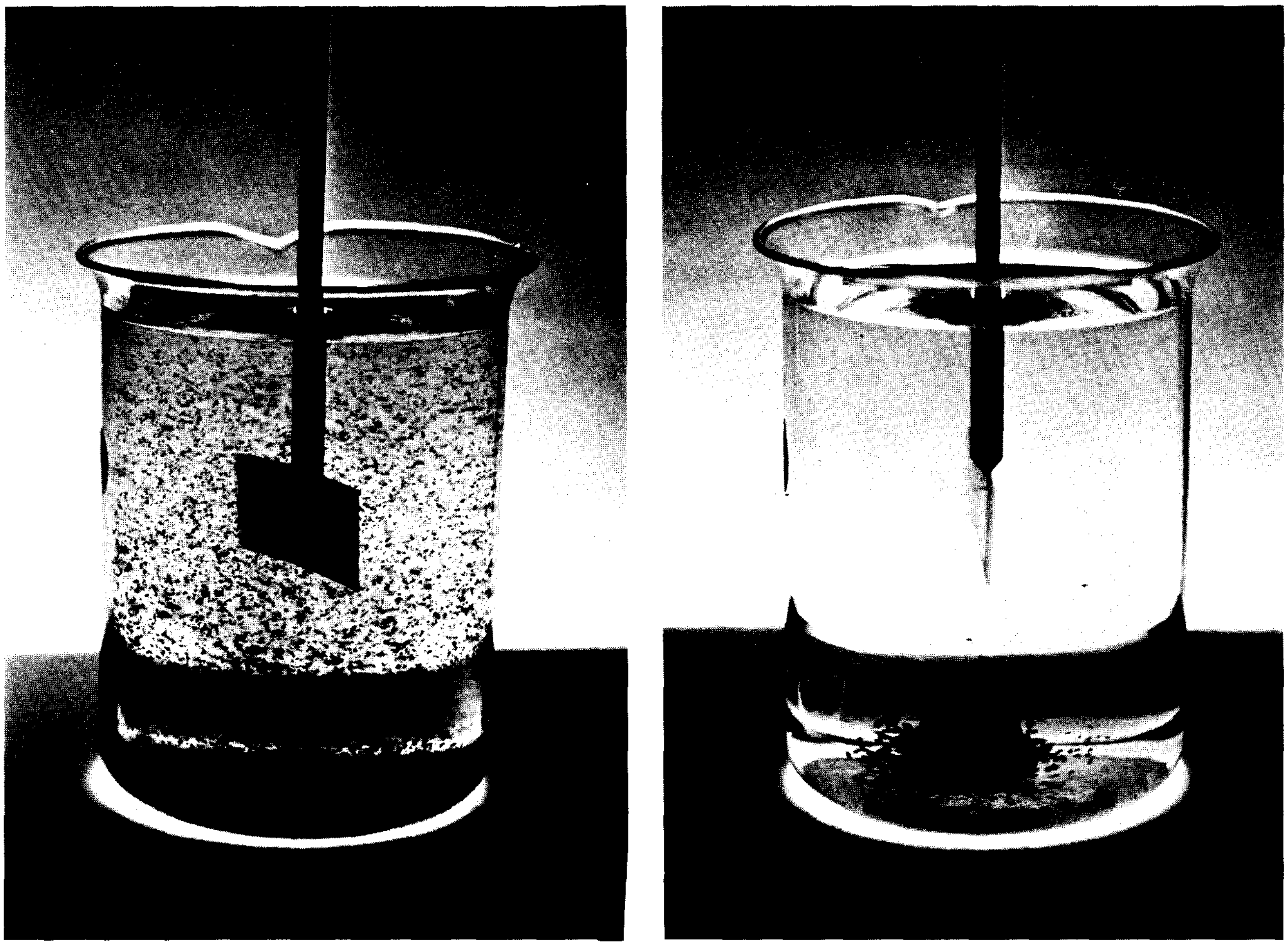


Fig. 5

CONCLUSIONS

Field experience and experimentation indicate that polyelectrolyte coagulation as an oilfield water clarification tool is widely applicable. Economics are attractive and techniques are relatively simple. It is evident that these new products are improving the waterflooder's position in controlling flood water clarity problems. To be derived from this effort are increased injectivities and, ultimately, more oil produced.

ACKNOWLEDGMENT

The author wishes to express his appreciation to fellow co-ordinates of Bradford Laboratories and Hagan Chemicals and Controls, Inc. for their assistance in the preparation of this paper.

REFERENCES

1) A. W. Baumgartner. "Water Analyses--A Basis for the Detection and Prevention of Injection Water Problems," Presented at the West Texas Oil Lifting Short Course, Texas Technological College, April 23-24, 1959.
2) G. R. Bell. "Removal of Oil from Condensate by Diatomite Filtration," Presented at 13th Annual Water Conference of the Engineer's Society of Western Pennsylvania, October 22, 1952.
3) A. P. Black. "Basic Mechanisms of Coagulation," Journal AWWA, (April, 1960).
4) A. P. Black, et al. "Effectiveness of Polyelectrolyte Coagulant Aids in Turbidity Removal," Journal AWWA, (February, 1959).
5) Christopher P. Blakeley. "Old and New Procedures in Water Coagulation"; Public Works, (December, 1959).
6) J. M. Cohen, G. A. Rourke, and R. L. Woodward. "Natural and Synthetic Polyelectrolytes as Coagulant Aids," Journal AWWA, (April, 1958).
7) A. R. Ellenberger. J. H. Holben,; "Flood Water Analyses and Interpretation," Journal of Petroleum Technology, (June, 1959).
8) G. B. Hatch and Owen Rice. "Corrosion Control and Scale Prevention," Industrial and Engineering Chemistry, (August, 1945).
9) James J. Morgan and R. S. Englebrecht. "Effects of Phosphates on Coagulation and Sedimentation of Turbid Waters," Presented at the AWWA meeting in Chicago, March, 1960.
10) E. G. Paulson. "What Synthetic Detergents Really Do," The American City, December, 1960.
11) R. N. Simonson. "Remove Oil by Air Flotation"; Hydrocarbon Processing and Petroleum Refiner, (May, 1962).
12) J. V. Slyker. "Questionable Practices Used in Conditioning Waters for Injection Purposes"; Presented at the West Texas Oil Lifting Short Course, Texas Technological College, April 20-21, 1961.