040, though it was slightly delayed at breakthrough, showed the highest peak at 20% of the injected concentration. In terms of surfactant retention in this particular experiment, the levels were: Petrostep 465, 2.7 mg/g rock; Empilan NP9, 1.3 mg/g rock; and Klearfac 040, 0.5 mg/g rock, for a total of 4.5 mg/g rock. These levels are fairly high when compared to the low salanity formulation retention levels of between 0.5 and 1 mg/g rock. Consequently, additional work with sacrificial agents and, perhaps, with less adsorptive materials will be required before commercialization can be realized.

Variations in the arrival time, and adsorption and retention of components clearly show the severity of chromatographic separations that can occur. Due to variations in the ratios of component quantities, many phase transitions of the surfactant would likely occur during the course of the displacement. This aspect is of major concern and can only be addressed by very complete phase behavior and adsorption studies combined with numerical simulation.

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Enhanced Oil Recovery Chemical Needs

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ABSTRACT

A large fraction of known petroleum resources will not be recoverable by conventional methods. Enhanced oil recovery (EOR) is costly, but a significant amount of production is possible at current world oil prices, and additional production is possible at prices equivalent to synthetic alternates. Many opportunities exist for uses of chemicals in EOR. In particular, polymers and surfactants that are effective and stable at high temperatures and high salinities are needed for surfactant flooding to achieve its potential. Potential markets can be large in the 1990s and beyond. Many factors other than improved chemicals will impact on the future development of EOR. Risks to the chemical industry in new product development would appear to be reasonable, as long as oil producers continue a major effort to develop EOR processes.

INTRODUCTION

Enhanced oil recovery (EOR) offers many challenging opportunities for the chemical industry. However, if one does not have a background in petroleum production, the initial challenge is often to understand why chemicals can play such an important role in EOR. The objective of this paper is to provide a general background for those readers who are unfamiliar with EOR. It provides information on the following subjects: what is enhanced oil recovery? Why is so much oil left behind after conventional oil production ceases? What processes are being developed to recover this oil? What role can chemicals play? What chemical properties are needed? Why is the interrelationship between surfactants and polymers so important in surfactant EOR processes? Beyond chemical needs, what other constraints exist on EOR processes that use chemicals? It is hoped this information will suggest areas where the chemical industry can make major contributions to EOR.

BACKGROUND

Enhanced Oil Recovery Targets

In 1981, Welch (1) spoke on the "Status and Future of Enhanced Oil Recovery." In the U.S., as of Jan. 1980, ca. 120 billion barrels had been produced from known resources of almost 500 billion barrels (Fig. 1). Another 30 billion barrels is thought to be producible using conventional techniques. But, over 300 billion barrels, or about 70% of the total known resources, is expected to remain unrecoverable by conventional methods. In the U.S., most of the unrecoverable oil is light and medium oil. Heavy oil comprises only a relatively small fraction of the total U.S. resources.



FIG. 1. Known U.S.A. petroleum resources as of Jan. 1, 1980.

Total world petroleum resources are known with considerably less certainty than for the U.S. Figure 2 summarizes recent estimates of known or "discovered" oil. The ratio of reserves-to-produced oil is higher worldwide than in the U.S., indicative of the later stage of depletion of many fields in the U.S. Here again, a large fraction of the light and medium oil will be unrecoverable by conventional methods. The most striking difference between worldwide and U.S. pictures results from the very large amount of heavy oil, including tar sands, found in Canada and Venezuela.



FIG. 2. Known world petroleum resources as of Jan. 1, 1980.

Conventional producing methods consist of primary production by natural reservoir energy or pumping, and secondary production in which additional energy is supplied. Secondary production usually involves waterflooding, but gas injection is sometimes used.

The main reasons that much of the oil originally in place in petroleum reservoirs is not recovered, despite skillful application of conventional methods, are: (a) some oil is too viscous to flow at economic rates; (b) only part of any reservoir can be contacted; and (c) oil is trapped as isolated, microscopic drops in rock pores. The difficulty in producing heavy, viscous oils is straightforward. However, the other two reasons require some discussion.

A variety of drawbacks, some of which are illustrated in Figure 3, prevent injected fluids from effectively contacting the entire reservoir. The drawing in the upper left corner



FIG. 3. Problems in effective reservoir contact.

illustrates the effect of geometry in reducing reservoir contact. The lines represent the "streamlines," or paths followed by the flowing fluids. The concentration of lines is roughly indicative of fluid velocity. For example, the converging streamlines near the well indicate that fluid velocities are high in this part of the pattern. Fluid velocities are highest along paths more directly connecting injection and production wells and are the lowest near the corners farthest from the wells. The consequence is that injected water moving along the more direct paths breaks through into the production well long before the two nearly stagnant corners of the pattern can be swept clean. Ultimately, declining oil production and the increasing cost of handling produced water cause the wells to be abandoned before the corners are completely swept.

Another, more complicated, inefficiency results when the injected fluid is more mobile, or less viscous, than the oil. This is the situation shown in the upper right corner in which random "fingers" of injected fluid have grown uncontrollably. This leads to premature breakthrough of injectant at the production well and the bypassing of much of the oil. Bypassing can be a serious problem in gas injection EOR projects because gases have such low viscosities. It also occurs in waterflooding of moderate viscosity oils.

Differences in the densities of the oil and the displacing fluid result in gravity segregation, thereby influencing performance. The sketch in the lower right corner of Figure 3 shows the difficulty encountered when oil is displaced by gas. The lighter gas "overruns" the heavier oil, bypassing much of the lower portion of the reservoir.

Most reservoirs are far from uniform. The sketch in the lower left corner of Figure 3 is intended to suggest the sort of vertical homogeneity found in most reservoirs. The effect of vertical homogeneity is preferential flow or "channeling" of injected fluids through the more permeable strata. Large variations in lateral directions, not illustrated in the figure, can also occur.

The combined effects of the difficulties just discussed prevent the displacing fluid from contacting or "sweeping" the entire reservoir. The percentage of the total reservoir which is contacted is termed "sweep efficiency." All of these problems are experienced in real reservoirs, where sweep efficiencies range from less than 25% to more than 85%. Even lower or higher figures are possible for other reservoirs. No matter how efficient the displacement is in the portion of the reservoir which is swept, incomplete contacting invariable reduces ultimate recoveries.

Even in those areas of the reservoir which are contacted, conventional recovery methods leave a substantial amount of oil trapped as isolated, microscopic droplets in the pores of the rock. To show why this is so, we need to look at the reservoir on a much smaller scale.

Rock pores typically are microscopic in size. The total surface area of the walls of the pores within the rock is quite large. For example, the surface area of the pores in 1 m^3 of a typical sandstone reservoir can easily exceed 2 million m². Initially, in an oil reservoir, water coats the rock surfaces, with oil forming a continuous, connected phase winding through these tiny pore passages. As the oil is displaced by water, the oil eventually can no longer remain continuous and breaks up into discrete, microscopic droplets. These microscopic droplets become trapped, held back at pore constructions by surface-tension forces as the water flows past in paths not blocked by oil. Figure 4 is a sketch of such a trapped oil droplet. The droplets are quite small, millions might be trapped in a single cubic centimeter of rock.

Once oil becomes trapped in this form, additional flushing of the rock by water is fruitless and conventional meth-



FIG. 4. Trapped residual oil.

ods are unable to displace additinal oil. Overcoming the "capillary" forces trapping this droplet would require a flowing pressure gradient which is several orders of magnitude greater than that possible in a reservoir. Thus, there is always some "residual volume" of oil, even in parts of the reservoir swept by water. In most reservoirs, the amount of oil remaining as immobile, residual oil ranges from less than 15% to more than 50% of the original oil in place.

Enhanced Oil Recovery Processes

A variety of EOR processes are under development to recover the viscous, bypassed and trapped oil remaining after conventional production. These are summarized in Table I. Note that each of the three major types of processes-thermal, miscible and chemical-may use different approaches.

Thermal. Thermal recovery methods are based on the principle that an increase in temperature can dramatically decrease the viscosity of heavy oils. In the steam stimulation process, steam is injected into a well for a period of a few days to a month. The well is then shut in for a time, after which oil, steam and water are produced from the well. The period of stimulated production can last for several months, and several cycles of steam stimulation are often used.

After a number of steam stimulation cycles, the process efficiency generally falls to a point at which it is more effective to convert to steam flooding. Here, steam is injected continuously into a given well to propagate a heat front toward adjacent producing wells. Here again, reduction of oil viscosity is the dominant recovery mechanism. In addition, however, distillation of the lighter portions of the crude oil at steam temperatures can lead to very low concentrations of residual oil in the steam invaded regions of some reservoirs.

In situ combustion processes involve burning of a portion of the in-place crude oil to generate heat and steam to improve oil recovery. Combustion is used most often with heavy oils. Air or oxygen is injected into the reservoir and the oil is ignited, either spontaneously or artificially. Although the process is simple in concept, it is extremely complicated in practice. Multiphase flows of combustion gases, vaporized hydrocarbons, steam, hot water and oil occur. Water is often injected with the air to recover heat from the region behind the combustion zone, lower the combustion temperature and reduce the amount of air consumed. This also accelerates movement of the combustion front and decreases the project duration.

Miscible. Under the right combination of temperatures, pressure and oil type, carbon dioxide can generate a miscible solvent bank by extracting intermediate and some heavier molecular weight components from the oil. Reservoir pressure is a major factor that determines whether the oil and the enriched CO_2 bank will be miscible. At some minimal pressure, for a particular crude oil, the "enriched" CO_2 can displace essentially all of the oil from the volume of the reservoir which it contacts. This behavior is shown in Figure 5, which is a graph of the results of a laboratory



FIG. 5. Laboratory CO₂ floods.

TABLE I

Enhanced	Oil	Recovery	Processes
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Process	Target	Mechanism
Thermal Steam stimulation Steam flooding In situ combustion	Heavy, viscous oils	Reduces viscosity by increasing temperature
Miscible Carbon Dioxide Nitrogen Hydrocarbon	Trapped oil in waterswept regions	Eliminates interfacial tension
Chemical Polymer Surfactant Alkaline	Oil bypassed by water Trapped oil waterswept regions	Improves sweep efficiency Reduces interfacial tension

experiment using CO_2 to flood crude oil from a test sample that had already been waterflooded. At low pressure, CO_2 was not miscible with the crude oil and did not displace it. At higher pressures, recovery was a function of pressure until, at some pressure, a fully miscible bank was formed and displaced all of the oil. In a few special cases, nitrogen can give the same type of behavior as carbon dioxide.

Hydrocarbon gases can also be used in miscible flooding. However, their increasing value almost rules out hydrocarbon miscible flooding in the U.S. and many parts of the world. Of course, local circumstances, such as remoteness from gas markets, will affect the choice of a miscible agent. Hydrocarbon miscible floods are still viable in some areas, as is emphasized by the fact that two of the world's largest miscible flooding projects—in Algeria and Libya—are hydrocarbon miscible floods. Thus, carbon dioxide flooding is the preferred miscible technique except in special circumstances.

Chemical. The least complex EOR process is polymer flooding, which is shown schematically in Figure 6. Polymer flooding, the injection of water containing polymer, is an improved waterflooding, i.e., secondary recovery, process applicable to some reservoirs containing moderately viscous crude oils. As shown at the upper left of the figure, when the injected water is less viscous than the oil, it has a tendency to channel from injector to producer, bypassing much of the oil. However, if a low concentration of a high molecular weight polymer is dissolved in the injected water, the water becomes more viscous than the oil. This reduces its mobility, and displacement of oil is more efficient as depicted at the upper right. Although polymer flooding increases the volume of reservoir swept, it does not displace any of the trapped residual oil. Thus, if sufficient water can be injected, the ultimate recovery with water alone would be the same as with polymer flooding. However, polymer flooding does enable the mobile oil to be recovered more quickly, and can recover more oil at a limiting produced water-oil ratio, as shown at the bottom of Figure 6.



FIG. 6. Polymer flooding.

Surfactant flooding is a chemical process designed to recovery the trapped residual oil. This is shown schematically in Figure 7. This depicts an idealized cross-section of a reservoir with an injection well at the left and the production well at the right. The top sequence depicts the state of the reservoir after waterflooding. At this point, injection of water results in only water being produced. For good candidates, perhaps half or more of the oil originally present exists as trapped, discontinuous oil ganglia.



FIG. 7. Microemulsion flooding process.

To initiate the process, a surfactant designed specifically to reduce the oil/water interfacial tension to extremely low levels is introduced. Surfactants can be injected in brine, but these usually are dispersions rather than true solutions. An effective way to introduce the surfactant is via a stable microemulsion containing oil, brine and surfactant. The microemulsion mobilizes the trapped oil. The mobilized oil droplets coalesce to form a growing oil bank driven ahead of the surfactant bank.

One would like to inject continuously the microemulsion, but the high cost of the microemulsion bank permits only a small bank size for economic reasons. The microemulsion bank is followed by a bank of polymer-thickened water to effectively push or displace the microemulsion bank through the reservoir. Finally, because the polymer bank is also expensive, we inject ordinary brine. If the process is effective, a significant portion of the trapped oil is mobilized and recovered. Figure 8 shows a 3-D schematic of the process. The importance of good reservoir contacting with these expensive chemicals is apparent.

Alkaline flooding is a process which may be applicable for certain high-acid-number crude oils. Alkaline materials such as sodium hydroxide, sodium carbonate, or sodium orthosilicate are injected to react with acids that are naturally present in the crude oil, forming in situ surfactants. Polymers may also be added, either with or following the alkaline bank, for mobility control. The process is simple in concept, but is complicated and not well understood in practice. While injected fluid costs are lower than for the surfactant process, oil recovery is also expected to be lower. Overall, it is useful only in special cases.



FIG. 8. Surfactant flooding.

EOR—Status and Outlook

Figure 9 illustrates the obvious conclusion from the foregoing descriptions of the various enhanced oil recovery processes: that application of EOR technology must be selective and no EOR process is suitable for use in every reservoir. In the U.S., only about half of the large volume of oil that is unrecoverable by conventional methods is a target for any known EOR process. And of this target, only about 22 billion barrels is expected to be ultimately recovered. Even so, this compares favorably with the remaining reserves by conventional production in the U.S.



FIG. 9. EOR target oil and ultimate recovery, U.S.A.

Table II presents more details on the status and outlook for the various EOR processes in the United States. Polymer flooding is underway. However, it is applicable to only a limited number of reservoirs, and oil recoveries are low. Polymer flooding is expected to contribute about 0.5 billion barrels of additional oil.

Steam processes are now economical for favorable prospects, and are finding widespread application in the heavy oil reservoirs in California. Oil recoveries can be high, since little oil is produced by conventional methods. Steam processes are projected to add about seven billion barrels of reserves.

Miscible gas processes are particularly applicable to those reservoirs with favorable geology located near sources of CO_2 . A few commercial projects are underway. Production could become significant after 1985, when newly constructed pipelines begin delivering large quantities of CO_2

TABLE II

EOR	Status	and	Outlook
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Timing for Ultimate significant Recovery level potential (10° bbl) Process Status production (% OOIP) Polymer Limited prospects _ <5 0.5 Steam Attractive for favorable 7 prospects Now 5-35 Miscible gas Applicable in special After 1985 cases 5-15 6 Surfactant Not yet economical After 1990 10-20 8 In situ Economical for favorable combustion After 1985 5-25 prospects 1

to west Texas from natural deposits in New Mexico and Colorado. Intermediate levels of oil recovery are expected, and ca. six billion barrels of oil production is projected.

Surfactant processes are still in the research stage and will not yield significant production until after 1990. Some of the research challenges are discussed in the next section of this paper. Surfactant processes will be applied in lightto-medium oil reservoirs where conventional methods are most effective. Thus, oil recoveries will fall into a rather narrow range. The upper limit is set by the oil remaining in the depleted reservior, even with high recovery of residual oil, whereas the lower limit is imposed by economics. Surfactant methods are potentially applicable to a large number of reservoirs, and oil recoveries may reach eight billion barrels. Included in this estimate are the relatively small contributions expected from alkaline flooding.

In situ processes currently are economical in some cases. However, the process is technically complex and difficult to control. Severe emulsion and corrosion problems have been encountered. Unless significant technical breakthroughs are made, application is expected to be limited, with ultimate production of about one billion barrels in the U.S.

EOR CHEMICAL NEEDS

Overview

Simply put, the role of chemicals in enhanced oil recovery is to provide assistance in recovering more oil. This aid can take many forms, as summarized in Table III. These may be grouped into three broad categories: (a) chemicals to improve reservoir contact; (b) chemicals to mobilize trapped oil; and (c) chemicals to improve process performance. This paper will focus on water-soluble polymers and surfactants used in the chemical EOR processes. We will briefly outline the other chemical roles in EOR—"foaming" agents and chemicals to improve process performance.

A major need exists to improve reservoir contact in the major EOR processes which use gases—steam and CO_2 miscible. As an example, in laboratory experiments with excellent contact, oil can be displaced with as little as two to three thousand cubic feet (KCF) of CO_2 per barrel of oil. In field projects, CO_2 requirements of 10-15 KCF/bbl are expected, largely due to poor reservoir contact. Similar, but somewhat less severe, problems occur with steam processes. The use of "foaming" agents to improve reservoir contacting is under development for both steam and CO_2 . It may also be possible to directly viscosify dense CO_2 phases with polymers. Two papers (2,3) in this symposium present recent results.

A number of opportunities exist to use chemicals to improve process performance. Additives are used to coun-

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Enhanced	Oil	Recovery	Chemical	Roles
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Objective	Chemicals
Improve reservoir contact	
Steam	Foaming agents
CO,	Foaming agents-polymers?
Polymer flooding	Water-soluble polymers
Surfactant flooding	Water-soluble polymers
Mobilize trapped oil Surfactant flooding Alkaline flooding	Surfactants, cosurfactants, alcohols Inorganics
Improve process performance	
Additives	Stabilizers, oxygen scavengers, biocides, others
Sacrificial agents	Various
Protect equipment	Corrosion & scale inhibitors, water treatment chemicals
Treat produced fluids	Demulsifiers, water classification chemicals
Recover CO ₂	Gas treatment chemicals

teract the harmful effects of oxygen, high temperatures and bacteria on the stability of polymers and surfactants. The need for improved stability will be emphasized in later sections of this paper.

Sacrificial agents may be used in some processes to condition the reservoir and/or reduce adsorption losses of the more expensive surfactants and polymers. A third paper (4) in this symposium discusses this subject.

Oil production chemicals, such as corrosion inhibitors, scale inhibitors, biocides, and demulsifiers, are commonly used in conventional production to protect equipment and treat produced fluids. Problems may become more severe in the EOR processes. For example, emulsions of low gravity oil and fresh water resulting from steam processes can be difficult to break. Emulsions from surfactant processes may become very severe when surfactant breakthrough occurs. Corrosion and scale problems will intensify somewhat in CO_2 miscible processes. Also, as fresh water supplies become limited, use can grow of water treatment chemicals to produce boiler feed water from produced water.

Gas treatment chemicals will be used in the recovery and recycle of CO_2 , due to the expected early breakthrough of CO_2 and the need to minimize the use of purchased CO_2 .

This listing is undoubtedly incomplete, but it does illustrate the large number of expected roles for chemicals in EOR.

As discussed earlier, polymer flooding and surfactant flooding may ultimately produce almost 40% of enhanced oil in the U.S. This can lead to large chemical markets. However, some major product advances are needed if these processes are to reach their ultimate potential. The remainder of this section will focus on needs for better polymers and surfactants.

Polymer Needs

All of the chemical EOR processes-polymer flooding, surfactant flooding and alkaline flooding-are expected to use polymers to aid in good reservoir contact. The conditions under which these polymers must perform are widely varied, and often severe : temperatures to 200 F and above; salinities to above 15% total dissolved solids; long time periods in the reservoir; high shear during surface handling and injection; and varied chemical environments. Commercial polymers available today are all deficient in one or more of these aspects.

The importance of temperature and salinity is illustrated in Figure 10. This plots the distribution of light and medium (<30 CPS) residual oil in the lower 48 states of the U.S. Only about 10% is present in lower temperature (<120 F), low salinity (<seawater) reservoirs, which represents the "easier to recover" oil for surfactant flooding. Over 75% of the residual oil is in reservoirs with salinities above seawater.



FIG. 10. Salinity-temperature distribution for residual oil in U.S.A.

Although many polymers have been tested for EOR, only two have found widespread use-polyacrylamides and xanthan biopolymers. Figure 11 shows laboratory results on the viscosity building properties of these types of polymers as a function of salinity in % NaCl. Polyacrylamide viscosity is high in very fresh water, but falls off rapidly as salinities approach 1% dissolved solids. Xanthan is relatively insensitive to dissolved solids, which is a desirable property.

For polymer flooding, it is sometimes possible to reduce the effects of high reservoir salinity by dissolving polyacrylamide in fresh or brackish water. However, fresh water is becoming increasingly difficult to obtain due to competing demands. For surfactant flooding, it is necessary for the polymer to be effective at or near reservoir salinities, as we shall discuss later.

The need for long-term stability is illustrated by Figure 12, which shows polymer injection and oil production



FIG. 11. Saline dependence of viscosity.



FIG. 12. Polymer and surfactant flood time schedules.

schedules for both polymer flooding and surfactant flooding. Note that polymer flooding may require the polymer to remain effective for over 15 years at reservoir conditions. Surfactant flooding is somewhat less time-intensive, but still requires polymer stability for five years or more. Unfortunately, few reliable data exist on long-term stability of currently available polymers. Available data suggest that polymer stability becomes questionable at temperatures above 60-70 C (140-160 F) at reservoir salinities.

Another stability concern is biostability. Severe biological degradation of xanthan biopolymers has occurred in

TABLE IV

Enhanced Oil Recovery Polymers

	Polyacrylamides	Xanthan
Thermal stability	Questionable	Poor
Salinity tolerance	Poor	Good
Shear stability	Poor	Good
Bacterial degradation	2	Yes
Injectivity problems	Occasional	Frequent
1981 cost (\$/lb F,O.B, plant)	1.50-2.00	2.50-3.50
Availability outlook	Excellent	Good

field tests, and laboratory studies indicate that biological degradation of polyacrylamides can also occur (J.A. Brierly et al., Department of Biology, and Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology, private communication).

Shear stability is still another concern for EOR polymers. Figure 13 illustrates typical points at which EOR polymers experience high shear. Although shear in surface facilities can be minimized by careful equipment design and field operating practices, polymers always experience high shear at the formation face during injection. This is due to the high fluxes required to inject enough fluid to contact a large reservoir volume through the small formation area available at the wellbore. If injection rates are reduced to minimize this shear, the time required for oil recovery becomes uneconomically long. Polyacrylamides have poor shear stability, but xanthan biopolymers are shear-stable.



FIG. 13. Points at which polymers experience high shear.

Chemical environments in the reservoir obviously can be quite varied, and high concentrations of divalent ions are common. These can reduce polymer performance. In addition, ferrous and other multivalent ions can lead to polymer crosslinking, and additives such as oxygen scavengers can degrade polymers.

Table IV summarizes the properties of current commercial EOR polymers. Even if other drawbacks can be overcome or accepted, long-term thermal stability concerns limit polymer applicability to only part of our target reservoirs. This is shown in Figure 14. Polyacrylamides generally are used at lower salinities and biopolymers are preferred at higher salinities.

The need for better EOR polymers is obvious. Critical needs are: (a) acceptable cost-performance, due to the

marginal economics of many chemical EOR processes; (b) thermal and chemical stability; (c) salinity tolerance; (d) shear stability; (e) biostability; and (f) good injectivity, due to the large volumes which must be injected through the small wellbore area. These have been discussed. There are other important needs in the desired EOR polymers; (a) low retention to minimize the quantity of polymer required; (b) surfactant compatibility when used in surfactant flooding; (c) capability to flow through low permeability rock, i.e., the molecules should not be so large as to prevent them from entering rock pores which may contain significant oil; (d) pseudoplastic behavior, which aids high injection rates at the well bore, but still permits good viscosity at low flow rates deeper in the reservior; (e) easy, low-cost handling, because some polymers can be difficult to dissolve and are sensitive to shear; and (f) residual resistance factor-a complex subject, but one that relates to the ability to selectively reduce permeability in order to obtain more uniform reservoir contact,



FIG. 14. Applicability of polymer types.

Unacceptable behavior in one of these areas, e.g., retention, could cause this to be a critical property. However, within reasonable bounds, the EOR scientist or engineer can compromise on these important properties to satisfy critical properties.

Surfactant Needs

A surfactant process must meet several requirements to be successful in recovering residual oil. These are: (a) low IFT between crude oil and microemulsion; (b) low IFT between microemulsion and drive bank; (c) microemulsion mobility less than oil-bank mobility; (d) drive-bank mobility less than microemulsion mobility; (e) maintenance of favorable conditions throughout the flood; and (f) low surfactant retention. Obviously, there must be a low interfacial tension between the crude and the microemulsion in order to mobilize the residual oil. However, we also require a low interfacial tension between the microemulsion and the polymer water to keep the microemulsion from being trapped in small droplets or ganglia like the residual oil. If the microemulsion bank is rapidly depleted by phase trapping, the process effectiveness will also decrease rapidly. The microemulsion bank should have a higher effective viscosity than the oil bank and the polymer bank should have a higher effective viscosity than the microemulsion bank. These conditions are required for an effective displacement-in other words, so that the microemulsion does not channel or finger through the oil-water bank and the polymer water does not channel or finger through the

microemulsion bank. Next, the amount of surfactant lost by absorption on the surface of the rock or through trapping of the microemulsion must be low. The really difficult requirement is to maintain these necessary conditions throughout the flood as the fluid flows through the complex heterogenous reservoir and the fluid banks begin mixing with each other.

These requirements impose constraints on the chemicals used. First, they must meet the basic process requirements. They must also function at the temperature and salinity encountered in the reservoir. This will be discussed in more depth. Mechanical stability also can be important, particularly if shear-degradable polymers are included in the surfactant bank for mobility control. This will affect the surface equipment, and the ability to inject the fluids. Chemical losses to the rock are also significant because they determine the minimal amount of chemicals required. This has a major role in the economics. Also, this can affect the ability to maintain process effectiveness across the reservoir.

In a recent address to the American Petroleum Institute, Holstein (5) summarized factors in surfactant flooding. Figure 15, from his talk, shows a three-dimensional plot of the effect of temperature and salinity on oil recovery. This plot illustrates how expected oil recovery varies with salinity and temperature for one particular surfactant system with a given crude oil. The surfactant system used here was specifically designed for a salinity of 1% (10,000 ppm) and a temperature of 60 C (140 F). Recovery was in excess of 60% of the residual oil at these conditions. Recovery falls off dramatically with changes in either temperature or salinity, or both.



FIG. 15. Factors in surfactant flooding.

Extensive laboratory studies have demonstrated that any given surfactant is effective only over a rather narrow salinity range around an "optimal" salinity. Furthermore, the optimal salinity for a given surfactant varies with temperature. The conclusion is of major importance for surfactant flooding: "For optimum performance, surfactant systems must be tailored to the temperature, salinity and crude oil conditions encountered in the reservoir." Holstein also discussed the applicability of various types of surfactants by salinity and temperature. This information is summarized in Figure 16.

In Figure 16, a rather broad definition of petroleum sulfonates is intended. As used, petroleum sulfonates include crude oil sulfonates prepared by sulfonating specific fractions of produced crudes; petroleum sulfonates prepared by sulfonating selected aromatic streams -such as

APPLICABILITY OF SURFACTANT TYPES



FIG. 16. Applicability of surfactant types.

lube extracts or gas oils, from refinery operations- (usually a rather broad spectrum in molecular weight); and synthetic sulfonates which are typically narrower distribution synthetic alkyl or alkyl-aryl sulfonates.

Within this definition, the commercially available petroleum sulfonates used to date in field tests are effective only at relatively low salinities. Temperature stability is expected to be good, but this has only been demonstrated for a few years in field tests to date.

Figure 16 also shows that it may be possible to extend the salinity tolerance of current petroleum sulfonates using cosurfactants. Both ethoxylates and ethoxy-sulfates have been shown to improve salinity tolerance, although the ethoxy-sulfates suffer from limited temperature stability. A fourth paper (6) at this symposium discusses the use of cosurfactants. Alcohols also are often used to formulate a stable microemulsion system with suitable properties, and can affect optimal salinity somewhat.

Finally, Figure 16 shows that many temperature-salinity conditions will require specially-tailored synthetic surfactants that are not generally available on the market today. In fact, further research will be required to develop materials that are both effective and stable within this region.

For Figure 16, Holstein cautioned that boundaries between the various regions are only approximately located. In most cases, sufficient data do not yet exist to draw hard, fast dividing lines.

If Figure 16 is combined with Figure 14, also from Holstein's address, one can derive the combined applicability of currently available surfactants and polymers shown in Figure 17. Also shown in this diagram are the percentages of U.S. light residual oil in each of the sectors.

The lower sector, representing 25% of the total, is the area where currently available surfactants plus polymers are applicable. Of the remaining 75%, about 30% is at lower temperatures. It will probably be easier to develop stable, new products for this sector than for the higher temperature regions.

Figure 18 illustrates the salinity and temperature conditions of recent industry surfactants where data are available. Shown in the inset at the upper right are the number of active projects over the period 1972-82, as reported in the *Oil and Gas Journal*. The number of projects grew steadily from 1972 through 1978, and have remained in the 15 to 20 range since that time.

Each dot represents the salinity of the formation water and the reservoir temperature for a pilot or large field test. The asterisks show the tests that have been announced as successful, and tend to confirm that currently available



FIG. 17. Combined applicability of surfactants and polymers.



FIG. 18. U.S. surfactant tests.

surfactants are effective over a rather limited range of temperature and salinity.

It is obvious from the distribution that the U.S. industry is testing surfactant technology over a wide range of temperatures and salinities. Most of the high-salinity tests, however, are not true tests of high-salinity chemical systems, in that they generally involve injection of a lowsalinity preflush to reduce the salinity and allow the use of currently available surfactants. Field experience, however, indicates that this type of low-salinity preflush cannot reduce salinity to a uniform level. Thus, the use of a preflush process still requires surfactants with a broad salinity tolerance. As discussed earlier, this is a difficult challenge, since surfactants show optimal performance over a rather narrow salinity range. This has undoubtedly contributed to the large number of failures experienced in field tests to date.

The square on Figure 18 represents a recently reported (7) Exxon pilot test which did use a chemical system specifically designed to be effective at high salinity.

At the 1982 SPE/DOE Third Joint Symposium on Enhanced Oil Recovery, Exxon Production Research Company and Exxon Company, U.S.A. presented the results of a small surfactant flooding pilot test at Loudon Field in southern Illinois. The test used a proprietary surfactant system designed to function at the high salinity and hardness of the formation water-10.4% total dissolved solids and over 4,000 ppm of divalent ions. Xanthan biopolymer was used for mobility control. Although problems were encountered with bacterial degradation of biopolymer and with produced oil-water emulsions, the test is considered to be a technical success. Approximately 60% of the waterflood residual oil was recovered, and the high-salinity microemulsion system functioned well. Further testing is planned. This test is encouraging concerning the outlook for developing surfactants that are effective at high salinities. It also points out the need for polymers that are stable and effective at similar high salinities.

These sections have shown that: improved surfactants that are cost-effective and stable at higher salinities and higher temperatures are needed for reservoirs that represent the majority of surfactant flooding EOR potential; polymers that are similarly effective and stable are also needed in conjunction with improved surfactants; chemical loss by adsorption and phase trapping will have a significant impact on both the performance and economics of surfactant processes. Although losses can be reduced somewhat by using sacrificial agents and/or design of the surfactant molecules, new technology will be required to cut chemical losses dramatically. The results of a recent Exxon test in a high-salinity low-temperature reservoir are encouraging.

NONCHEMICAL EOR CONCERNS

At this point, a chemical industry newcomer to EOR probably is: impressed with the severity of the surfactant and polymer technical challenges which must be met if surfactant EOR is to reach its potential; wondering if overcoming product challenges will make surfactant EOR happen; wondering how long it will take to enjoy some business if new product research is successful. How big will demand be and when? These are reasonable questions and concerns. They cannot be addressed in any depth in this paper, but some major items deserve comment.

Nonchemical Technical Concerns

A major nonchemical technical challenge for all EOR processes, and particularly surfactant processes, is to obtain an adequate understanding of the oil reservoir. If accurate reservoir description data are unavailable for design of the EOR process, the project will almost certainly be unsuccessful.

Among the important reservoir description variables that need to be established are reservoir thickness and areal extent, permeability (and permeability variations), porosity and, of course, the amount and distribution of residual oil saturation. The complex heterogeneous nature of most reservoirs makes this a major technical challenge. Figure 19 is a simplified schematic intended to illustrate one reason why heterogeneities are so important. If a microemulsion is injected into a low-permeability sand, but then encounters a high-permeability zone, it can bypass the target oil zone. Dilution and interactions which affect performance also can occur.

Although the petroleum geologist and reservior engineers have an impressive and growing technology to apply to this problem, the task of determining the characteristics of a reservoir deep below the surface from small diameter holes hundreds of feet apart is a difficult one.

Another area of nonchemical technical concern involves the broad area of process design. Although research has been done in EOR for more than 20 years, additional work is needed to improve the understanding of some of the basic mechanisms involved. Laboratory design methods are undergoing development. There is a need for better mathematical simulators that will include all the complexities inherent in the process. These simulators not only will be a valuable aid in studying basic mechanisms, but can be used to interpret field tests and predict field performance. Finally, and perhaps most importantly, the technology cannot be developed without a significant number of field tests.

Figure 20 shows one reason why field tests are necessary. Note the difference in the dimensional flow patterns between laboratory core tests and this small 0.6-acre test. Then imagine how much more complex a five-acre, threedimensional, heterogenous test would be. Many people



FIG. 20. Lab floods do not model reservoir conformance or mixing.



FIG. 19. Large-scale heterogeneities that affect conformance and mixing in the reservoir cannot be modeled in core floods.

believe scale-up of laboratory and small pilot tests to field-wide or commercial-size projects is one of the most important technology needs, particularly for miscible and surfactant processes.

To summarize, even after 20+ years of research and many field tests, some EOR processes are still very much in the R&D stage. Better chemicals certainly can make a major contribution to improving reservoir contacting and provide stable, effective products, but nonchemical technology advances also must occur.

Economic Concerns

Economic concerns are voiced whenever EOR processes are discussed. Many uncertainties remain in predicting the performance and in evaluating the economics of EOR methods. Any detailed discussion of these uncertainties is outstide the scope of this paper. However, we would like to review briefly two important factors in EOR economics -the cost of injectants and the U.S. Windfall Profits Tax.

It is possible to make reasonable estimates of the volumes and costs of the fluids which must be injected. Data from Welch's presentation are shown in Tables V and VI. For Table VI, direct materials costs are shown for polymer, CO_2 and surfactant floods. For steam stimulation or flooding, costs are for crude oil, coal, or gas for firing the boilers; and for combustion, the costs are those for air compression. A variety of factors other than intectants must be considered in a complete analysis of the economics of an EOR project. However, injectant costs are indicative of the relative economics associated with these processes. For example, polymer flooding and steam processes, which are being applied commercially today, are the least costly. Miscible flooding and surfactant flooding are the most costly.

In the U.S., the Windfall Profits Tax can have a sizable affect on EOR economics. This complex legislation includes incentives for tertiary oil recovery, provided a number of conditions are satisfied. In addition to several very specific conditions, the following must be met: (a) a qualified tertiary recovery (i.e., EOR) method is used, and is applied in accordance with sound engineering principles; (b) a reasonable expectation exists that the project will result in more than an insignificant increase in the amount of crude oil which will ultimately be recovered; (c) the portion of the property to be affected by the project is adequately delineated; (d) the project is properly certified; and (e) the project is one that begins, or is significantly expanded, after May 1979. In brief, the WPT permits qualified injectants to be expensed, tertiary incentive oil (i.e., front-end oil) receives special treatment, and incremental tertiary oil is Tier 3 oil taxed at a 30% rate above a defined base price.

The incremental tertiary oil produced is defined as the excess during any month over the monthly statutory base level amount for that property. The monthly WPT base level is the average monthly production for a six-month period ending March 31, 1979 reduced by the sum of 1% for each month beginning after 1978 up to and including the month of the project beginning date, and 2.5% for each month after the project beginning date month, and before the month for which the base level is being calculated. The project beginning date is the later of the date that injection begins, or the date of certification under WPT provisions.

The foregoing is a very simplified overview of a complex law. Figure 21 is an example case for a hypothetical oil field, with base production having a Windfall Profits Tax rate of 70% above a base price of \$12.70/barrel. The production above the mandated decline rate of 1%/month and 2.5%/month, shown as a dashed line, has a Windfall Profits Tax rate of 30% above a base price of \$16.55/barrel.

In this example, it is obvious that oil fields which have substantial primary and secondary production above the mandated tax decline can receive a tertiary incentive by reducing the tax rate from 70% to 30%. This reduced tax

TABLE V

Approximate Requirements for Enhanced Oil Recovery Injection Fluids

Process	Quantity injected/bbl of oil recovered
Polymer flooding	2-3 lb polymer
Steam stimulation	1-3 bbl steam
Steam flooding	3-6 bbl steam
Miscible flooding (CO ₂)	8-15 kSCF CO ₂
Surfactant flooding	15-20 lb surfactant 2-4 lb polymer
In situ combustion	15-30 kSCF air

TABLE VI

Approximate Costs for Enhanced Oil Recovery Injection Fluids

Process	Cost (\$/bbl oil) ^a
Polymer	3-6
Steam stimulation	2.5-9
Steam flooding	8-16
Miscible flooding (CO ₂)	12-30
Surfactant flooding	15-35
In situ combustion	4.5-12

a1980 dollars.



FIG. 21. WPT calculation tertiary project.

helps offset the costs of the injected fluids, and the risks associated with the amount of increase of oil production that will actually be obtained from the EOR process. This can improve the overall economics of the EOR project.

It is also obvious that the WPT hurts the overall economics of an EOR project if it is applied to largely depleted fields which have little primary and secondary production remaining. In this case, little or no "front-end" crude is subject to reduced taxes. However, the increased oil production from the EOR process now has a Windfall Profits Tax at 30% rate above a base price. Before, this oil was not subject to such a tax.

Unfortunately, most of the better candidates for surfactant flooding are in largely depleted fields. Thus, the Windfall Profits Tax hurts the economics for surfactant flooding. From an oil producer's viewpoint, products from the chemical industry which permit the amount of injectants to be reduced, or which improve the cost-effectiveness of injectants, would be welcomed.

Timing Concerns

Some rather fundamental concerns exist about the timing of EOR. Of course, EOR timing will impact on when chemical EOR markets develop, particularly for surfactant flooding. On one hand, time is needed for commercial development, which must be preceded by technology development, which still requires research and innovation. On the other hand, many reservoirs which are good candidates for surfactant flooding are in advanced stages of depletion. How much time remains before economics force field abandonment?

Consider the timetables for overall process development. The Office of Technology Assessment (8) published an estimate of overall timing shown in Table VII. Some explanation is needed. The reservoir study covers reservoir description and laboratory process design, plus a decision for a technical pilot. The technical pilot consists of one or two five-spot patterns on close spacing. A year of evaluation, decisions of an economic pilot and budgeting occurs. The economic pilot consists of four to nine five-spot patterns on normal spacing. This requires four years. A subsequent year of evaluation and planning permits a decision on commercial development, which takes 10 years. Total elapsed time is 19 years, with 14-15 years lead time before oil production begins. Please note that this scenario inherently assumes that the necessary technology TABLE VII

OTA Reservoir Development Timetable for the Surfactant/Polymer Process

Step	Time (yr)
Reservoir study	1
Technical pilot	2
Evaluate pilot, planning	1
Economic pilot	4
Evaluation & planning	1
Commercial development	<u>10</u>
	19

is already available at year zero.

Opinions differ about lead times before crude production. Probably for easier reservoirs, some economies in the above timetable are possible, particularly if process information is available from another, similar reservoir. However, with more difficult reservoirs requiring new technology development, one can easily speculate lead times of 20 years, particularly if economics hamper decision-making. In any case, there are long lead time processes.

This leads to the question of how much time is available? Let me answer this with a good, firm, I DON'T KNOW. I'm not aware of any in-depth studies in this area. Field abandonment means plugging of wells, removal of surface equipment, alternate use of personnel and relinquishment of lease ownership. Such steps would impose major economic restraints beyond those already discussed. For this paper, I can only suggest that timing constraints must be considered in any long-range planning.

Other Concerns

Other concerns which could impact on the outlook for EOR processes include: (a) political concerns, which cover a wide range of issues. National security and balance of payments both relate to imported oil. Decisions on taxes and incentives can impact EOR economics. Crude supply can obviously be impacted by political developments in the oil exporting nations. Overall, domestic energy policy will set the climate within which EOR must fit versus other energy sources; (b) resource availability, which includes equipment, injectants supply, trained manpower and capital, among others. These appear workable with time and good planning. However, trained manpower is a current constraint for the more complex EOR processes. Near-term oil prices and overall economic conditions obviously can effect the cash flow available to finance EOR projects. Clearly, decisions must be made on alternate use of resources; (c) other EOR concerns would include legal and environmental issues. One legal issue concerns the establishment of operating units for field-wide EOR projects with multiple lease ownership. Environmental issues would include emissions from, e.g., steam generators, fresh water availability and chemical toxicity; (d) alternates to EOR, which include other possible sources of energy and, particularly, liquid hydrocarbons. Although heavy oils, tar sands, shale oil and/or coal conversion offer alternate liquid hydrocarbon sources, they, too, face many constraints. EOR processes, including surfactant flooding, become more attractive when compared to these alternatives.

Overall, many areas of concern and constraint exist which will impact on the future of EOR. The chemical industry can make important contributions to overcoming concerns associated with chemical supply and performance. It should be aware of other constraints which will also affect future markets for EOR chemicals.

EOR CHEMICAL POTENTIAL AND RISKS-A VIEWPOINT

With the foregoing discussion of challenging EOR chemical needs, and of the many complex, interrelated concerns which also affect the future of EOR, why should the chemical industry involve itself in EOR? I suggest three reasons for consideration: potential chemical markets can be large; most of the risk will be borne by the petroleum industry, not the chemical industry; and enhanced oil recovery can help provide future hydrocarbon feedstocks to the chemical industry. In this final segment of this paper, I will briefly discuss each of these reasons.

Future chemical markets will be a function of the amount of crude oil production expected from the various EOR methods. A recent Oil & Gas Journal article (9) estimated 1982 U.S. EOR production. Tomich (10) presented an estimate for the year 2000 in a recent address. Table VIII compares these estimates. It should be noted that Tomich qualified his estimates as follows: "Obviously, estimates of this type may be changed dramatically through unpredictable variations in oil prices, modification of government policies, and unexpected technical developments."

TABLE VIII

Estimated Enhanced Oil Recovery Production Rates	for I	USA
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	Rate (10 ³ barrels/day)		
Process	1982 ^a	2000	
Polymer	2.6	100	
Steam	288	600	
CO ₂	22	550	
Other gases	50	50	
Surfactant	1.9 ^b	400	
In situ combustion	<u>10</u>	<u>100</u>	
Total	375	1800	

^aOil & Gas Journal.

^bIncludes alkaline, other.

Since other papers in this symposium address mobility control agents for steam and CO_2 processes, I will confine my remarks to polymers and surfactants. Chemicals to improve process performance will not be addressed.

To estimate future polymers and surfactant markets, we must take into account: the expected incremental crude production from chemical EOR processes (Table VIII) (note that this applies only to the "Lower 48" United States); the amount of chemicals injected per barrel of oil produced (Table V); the time period between chemical injection and oil production (Fig. 12).

The timing of oil production from surfactant flooding is difficult to estimate, because of all the factors discussed in this paper. However, if we assume that technical and economic conditions permit large commercial projects to begin in the early 1990s, and that production reaches 400,000 barrels/day by 2000, we can also estimate crude production of 100,000 barrels/day by 1995.

Oil production from polymer flooding should develop sooner. The process is economical today, and many large projects have been announced in the U.S. Windfall Profits Tax tertiary incentives also encourage polymer flooding. Again, if we accept an estimate of 100,000 barrels/day by 2000, 1990 production could reach 50-70,000 barrels/ day.

Concerning lead times for chemicals injection, a rough estimate which is suitable for the purposes of this paper would be: (a) surfactant flooding-surfactant slug, four years before oil production, polymer bank, one year before oil production; and (b) polymer flooding-polymer bank, five years before oil production. Of course, these will vary with specific processes, and, at best, are only averages.

With these assumptions, surfactant requirements could reach 500-700 million lb/year by the early 1990s, and could exceed two billion lb/year by the mid- to late 1990s. Cosurfactants and alcohols are included in these totals. The point is that large potential chemical markets exist for surfactant flooding if technical, economic and other constraints are overcome.

Polymers for polymer waterflooding could reach 40-70 million lb/year by the mid-1980s and 70-100 million lb/ year by the mid-1990s. Additional uses of polymers in alkaline waterflooding, near-wellbore control of heterogeneities, and in surfactant pilots would favor the high side numbers. Polymer for surfactant flooding will be small in the early 1990s unless polymer is included in the surfactant bank for mobility control. However, these markets could reach 70-140 million lb/year in the mid-1990s, and 300-600 million lb/year in the late 1990s. Again, potential EOR chemical markets for polymers are large if technical, economic and other constraints are overcome.

My second reason concerns the relative risks of the chemical supplier and the oil producer in EOR. The chemical supplier receives his revenues and profits when the chemicals are bought and injected. The oil producer bears the risks associated with the development of the overall process, the expenses of field facilities, the large expenditures for injectants prior to oil production and the uncertainty of the amount of future oil production.

Today, chemicals used in EOR are largely modifications and extensions of product technology developed for other end uses. Some manufacturing facilities are dedicated to EOR, but almost all facilities are adaptable for use in serving other markets. The difficult decisions will come when existing surplus manufacturing capacity is not sufficient to support near-term demands, but long-term markets are still uncertain. This seems to be some time away.

In considering development of new products, a chemical supplier will obviously face R&D risks. He must also be

TABLE IX

Chemical Enhanced Oil Recovery Process Development

	Time (yr)	Approximate cost (1981 million \$)
Reservior study	1.2	052
Lab process design) Phase behavior screening	1-2	0.5-2
Initial core tests Brea sandstone		
Final core tests Reservoir rock		
Recycle to achieve cost/performance		
Field tests		
Technical pilot Small Close well spacing	2	1 - 4+
Economic pilot 20 to 100/400 acres Commercial well spacing	4-5	10 - 60+
Commercial development Generally stepwise	<u>10 - 15+</u>	Very large
	15 - 25+	

concerned with how to manufacture test quantities of new products for field trials. However, such quantities will be modest for several years. In general, lengthy field tests will be required by the oil producer before commercial decisions are made on major EOR projects. With good planning, ample lead time will exist to install commercial-scale manufacturing facilities. Thus, the risk is largely one of long-term R&D to try to solve some admittedly difficult product problems.

On the other hand, the oil producer faces large development costs. Some rough cost estimates for developing a surfactant flooding process for a specific reservoir are shown in Table IX. These costs exclude base technology development.

Overall, as long as oil producers continue a major development effort in EOR processes that use chemicals, the risks to the chemical industry in new product R&D would seem to be reasonable considering the large potential future markets. Although there are admittedly large differences in size between oil companies and chemical companies, the chemical supplier has the opportunity for large markets with relatively less risk.

My final reason is a brief one. At some time in the future, developed countries must supplement their liquid hydrocarbon supplies from sources other than domestic crude oil. Heavy oils, tar sands, shale oil and/or coal conversion offer alternate sources when oil imports no longer suffice. While some of the more complex EOR processes, such as surfactant flooding, are marginally economical or uneconomical under today's crude oil prices, their outlook will become more favorable when compared to other alternatives. It would seem reasonable for the chemical industry to be interested in helping to develop EOR as one source of future hydrocarbon feedstocks. The time available to do this is not unlimited.

Conclusions

1. A large fraction of known petroleum resources will not be recoverable by conventional methods.

2. Enhanced oil recovery is costly, but: (a) a significant amount of production is possible at current world oil prices, and (b) additional production is possible at prices equivalent to synthetic alternates.

3. Many opportunities exist for uses of chemicals in EOR. (a) In particular, polymers and surfactants that are effective and stable at high temperatures and high salinities are needed for surfactant flooding to achieve its potential. (b) Potential markets can be large in the 1990s and beyond.

4. Many factors other than improved chemicals will impact on the future development of EOR.

5. Risks to the chemical industry in new product development would appear to be reasonable, as long as oil producers continue a major effort to develop EOR processes.

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