Past and present research on Enhanced Oil Recovery is reviewed with emphasis on the surface phenomena involved. The nature of capillary pressure phenomena in porous media has been understood for some time, and much research has been devoted towards the alteration of the surface forces which prevent the efficient displacement of oil by water. Early work often treated surface active agents as wetting agents designed to remove the oil from the solid surface by classical detergent action. More recent work has recognized the strong influence of oil-water interfacial tension on the displacement of discontinuous oil blobs or ganglia. Therefore, surfactant systems are now being developed to produce the lowest possible oil-water interfacial tensions by adjusting the various components and thus, the phase behavior in the total system. In addition to interfacial tension, the phase behavior itself can strongly influence the oil displacement. The surfactant work, current work in blob mechanics, current research in CO₂ flooding, and past results in alcohol flooding all indicate that an expanding oil phase is very important for effective oil displacement. Therefore, much current research is directed toward methods which utilize materials (including gases such as CO₂ and mobility control agents) to dislodge oil blobs, or to prevent their entrapment by maintaining a continuous oil phase and improving sweep efficiency during displacement. The general direction of future research on enhanced oil recovery is predicted.

INTRODUCTION

According to legend, the first successful attempts to force oil from underground rocks by the injection of another fluid
occurred by accident. In the early oil production days in Pennsylvania, wells were often abandoned improperly, and surface water was allowed to enter the productive sand zone (1,2). Actually, the first deliberate waterflood for oil recovery may have occurred in Sweden prior to 1740 when "running water was used to produce crude oil from galleries cut into the rocks bearing strata of 'tar and sand'" (3). Early operators in America feared that water entering the productive zone would "drown" the oil wells and for years, many states had laws which prohibited the injection of water into oil-producing sands. However, the increased production from waterflooding was observed consistently and by 1940, it was considered to be "unquestionably the most efficient method ever devised for increasing oil recovery" (1).

In spite of the enormous effectiveness of waterflooding, the early engineers soon realized that waterflooding still bypassed some oil. A patent was granted in 1917 for the addition of alkali to the flooding water (4), and by 1925 (5), engineers were describing how the surface forces which were responsible for holding the oil in the rock might be altered for better oil recovery. This paper will examine some of these surface chemistry methods and comment on the "state of the art" in enhanced recovery today. Because this is a conference on surface chemistry, emphasis will be placed on methods that alter or eliminate the surface forces which exist between oil and water or between any of the fluids or the fluids and solids which are found in petroleum reservoirs. Recovery methods which depend primarily on heat will not be reviewed.

EARLY WORK ON DISTRIBUTION OF OIL, WATER AND GAS IN THE POROUS ROCKS

From the earliest times, man has recognized that the material called petroleum comes from rocks (3). Although the mechanics of the flow of petroleum, water and gas from these rocks are still being studied, the early petroleum engineers soon recognized that the oil must flow through very small passages between the sand grains, and that capillary forces must be involved wherever interfaces occur between two fluids. The earliest published work on the large resistance to flow caused by a series of bubbles in a capillary was that by Jamin (6) in 1859.

The early oil production experts were well aware of this effect. Indeed, Herold (7), in a comprehensive book dealing with mechanisms of oil production, bases his entire description of Paleozoic production (half of the book) on the fact that oil and gas are distributed uniformly as tiny droplets of oil and little bubbles of gas (he ignores water) which occur in sequence through all pore space within the rock. Just as Jamin (6) found that a series of gas bubbles in a perfectly smooth capillary tube could build up large resistances to flow, Herold (7) pointed out that