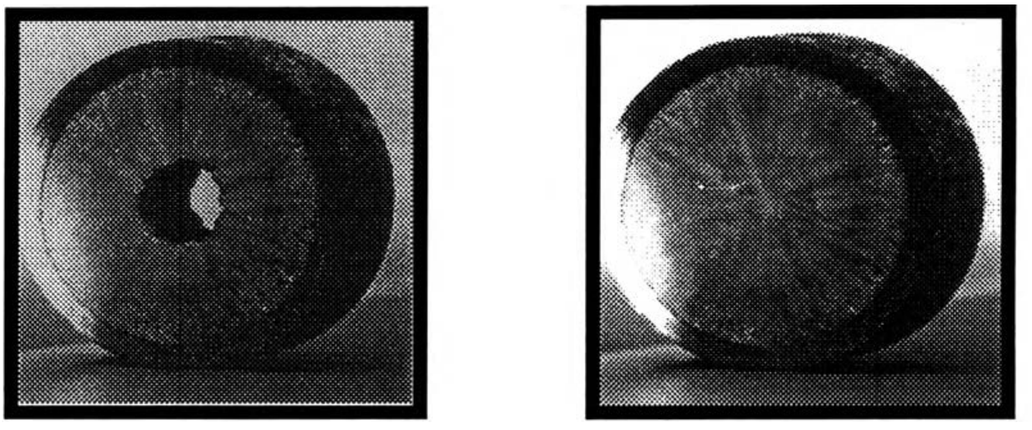
CHAPTER I
INTRODUCTION

Crude oil is a complex mixture of numerous hydrocarbons that are divided into different groups such as paraffins, aromatics, naphthenes, resins and asphaltenes. Among these groups of hydrocarbons, high molecular weight paraffins (i.e. waxes) are responsible for various problems during transportation and processing of these complex fluids. Paraffins, a broad fraction of crude oil, are alkanes of carbon number ranging from 5 to 100 or even higher. One of the main features of high molecular weight paraffins is their low solubility in most aromatic, naphthenic, and other organic solvents at room temperature. At reservoir temperatures (70-150^{o}C), the solubility of these compounds is sufficiently high to keep these molecules fully dissolved in the mixture and the crude oil behaves as a Newtonian fluid with a low viscosity. Once the crude oil leaves the reservoir and flows through sub-sea pipelines, its temperature begins to drop due to the cooler environment on the ocean floor. This decrease in temperature causes waxes to deposit on the wall of the pipeline and results in plugging of the pipeline. (Singh *et al.*, 1999a)

There are two severe problems associated with the wax-oil gelation in an offshore field. The first problem occurs when the crude oil is cooled by the low ocean floor temperature as it flows through the pipeline from the platform to the shore. As a result, the wax in the crude oil starts precipitating and depositing on the pipeline wall as a wax-oil gel. This gel deposition gradually plugs the pipeline leaving a small opening for the flow. Figure 1.1 (a) shows the wax build-up in a cut away view of a pipeline segment retrieved from the sea. A second problem occurs when a production shut down takes place and the entire crude oil in the pipeline becomes gels due to the cold sub-sea environment. Restarting the flow in the pipeline becomes challenging due to the presence of a candle of wax-oil gel in the pipeline. Figure 1.1 (b) shows a cross section of the pipeline filled with the wax-oil gel. These two problems are related in the sense that the restart problem is a special case of deposition problem when there is no flow.



(a) **(b)**

Figure 1.1 Cross-sectional view of pipelines: (a) a plugged pipeline, (b) pipeline filled with wax-oil gel (Singh *et al.*, 1999a)

The solubility of high molecular weight paraffins decreases drastically with decreasing temperatures; as a result, these molecules start forming stable crystals at low temperatures. The crystallization of paraffins leads to the formation of gels with a very complex morphology (Figure 1.2). The gelation is due to the flocculation of orthorhombic wax crystallites that appear in the solution while cooling (Dirand *et al.*, 1998). An observation under a polarized microscope reveals that the crystallites have structures of platelets that overlap and interlock (Holder and Winkler, 1965). Studies on distillate fuels show that only 2% of the precipitated wax is required to gel the fuel (Holder and Winkler, 1965).

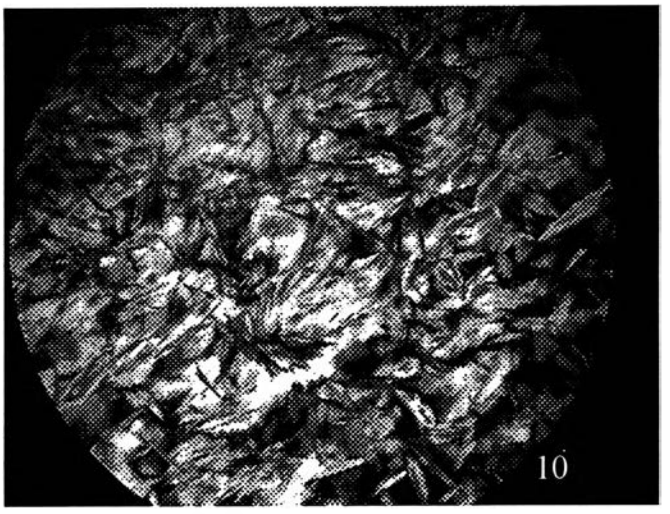


Figure 1.2 Microscopic image of the incipient gel layer deposit (Singh *et al.*, 1999a)

The composition of the gel as well as the rate of gelation depends on the conditions at which the gel is deposited. The wax-oil mixture gels with cooling and the nature of this gel depends strongly on the cooling rate (Singh *et al.*, 1999a). The incipient wax-oil gel deposit contains a significant amount of oil trapped in a 3-D network structure of the wax crystals. Hence, the gel behaves as a porous medium in which hydrocarbons having carbon number greater than the critical carbon number continue to diffuse into the deposit and hydrocarbons having carbon number less than the critical carbon number diffuse out of the deposit. This critical carbon number indicates that there is the counter diffusion of wax molecules into and out of the gel deposit. This phenomenon leads to an increase in the wax content of the deposited gel with time and is called aging of the gel deposit. The aging of the gel deposit hardens the deposit with time and makes the remediation process challenging. (Singh *et al.*, 1999b)

The well understanding of the gelation process will be an invaluable tool for developing methods to inhibit deposition. In fact, once the gelation mechanisms are understood, one can undertake a logical search for inhibitors that will retard or prevent gel formation. The mechanical strength and thermal properties of the deposited gel are important parameters for the selection of the method to remove the deposit. Mechanical pigs can easily get trapped in the pipeline by hard gel deposits. However, thin deposits of soft gels may easily be removed by pigs. Likewise, thermal removal techniques may be most efficient in the removal of deposits having low melting points and low heats of fusion. The mechanical and thermal properties of the gel depend on various factors such as wax/oil ratio, thermal and shear histories of the gel, and the critical carbon number. (Singh *et al.*, 1999b)

This study focused on a physical understanding of the aging process of the gel deposit where there is the critical carbon number indicating the counter diffusion phenomenon of this process. The model systems of wax and oil were used in a series of laboratory cold finger experiments to verify the physics of the aging process of the gel deposits. A thermodynamic model was developed to predict the critical carbon number as well as the cloud point temperature of model oil systems.