CHAPTER I
INTRODUCTION

1.1. Formation of Paraffin Deposits

The accumulation of paraffin deposits in sub-sea pipelines is a problem that has been plaguing the oil-producing industry. Typically, when a crude oil containing paraffins flows through pipelines at a comparatively reduced temperature lower than the cloud point of the paraffins, such as in a sub-sea pipeline, the paraffins will start precipitating out of the crude in the form of tiny crystals. As these paraffin crystals fall out of solution, they will adhere directly on the wall of the pipeline if the pipe wall is cooler than the oil. When the temperature of crude oil is further reduced, crystal agglomeration reaches the point at which a loose gel structure starts to form and gradually grows up leading to paraffin deposits. These paraffin deposits vary inconsistency in form from a petroleum jelly to a hard wax, which complicates its removal. Eventually, the effective flow area of the conduit is significantly reduced as shown in Figure 1.1, and hence, cleaning of the pipeline to eliminate the paraffin deposits is desired.

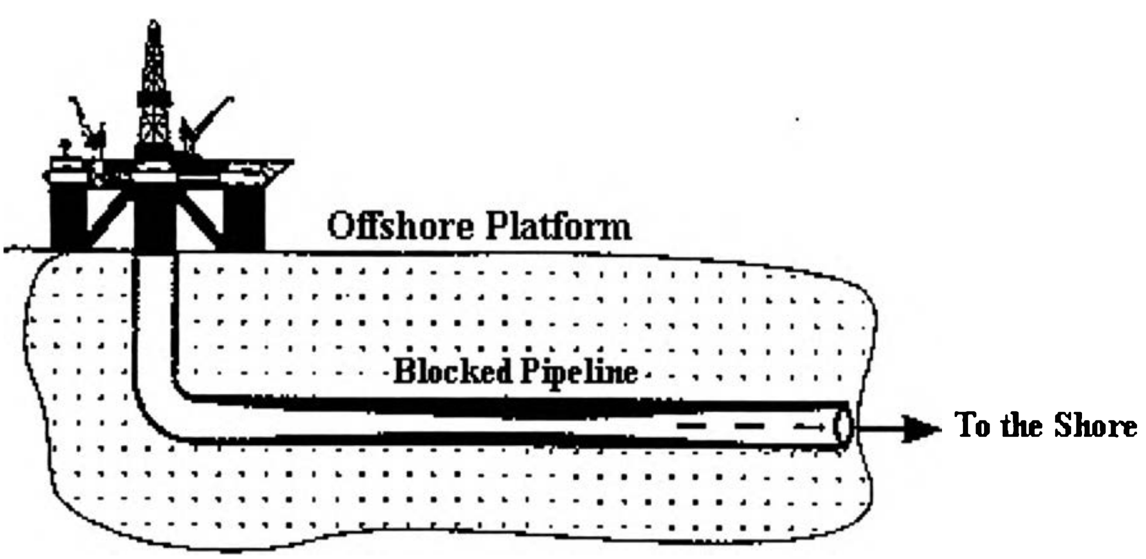

Figure 1.1 Wax deposits blocking a pipeline.

Removal of wax from wells and pipelines have accounted for significant additional operating costs. Prior methods of removing paraffin deposits from pipelines are expensive and time-consuming. The abandonment of an oil field by Lasmo was reported having a cost of over $100,000,000. There is an obvious need, therefore, for a cleaning method that will be both technically and economically efficient. Fused chemical reaction seems to be a very promising method and thus has been investigated and applied using different techniques to delay the release of heat.

1.2. Principles of Fused Chemical Reaction

Fused chemical reaction is a method for removing paraffin deposits from a hydrocarbon pipeline by bringing chemically activated heat and a hydrocarbon solvent into contact with the paraffin deposits. The heat is provided by an aqueous liquid solution of nitrogen-generating reactants selected for generating heat and nitrogen gas at a controllable and significant rate. The aqueous solution is mixed with a hydrocarbon solution containing a solvent selected for its ability to dissolve the particular paraffins in the deposit. Preferably, the hydrocarbon solution further contains a crystalline modifier to produce a minimal pour point for the paraffins involved in the deposit. Either the aqueous solution or the hydrocarbon solution should also contain an emulsifier to maintain an emulsion of hydrocarbon solvents in the aqueous solution (Ashton *et al.*, 1988).

As the chemical reaction proceeds, the treatment solution will be directly heated to a temperature sufficiently high to melt the deposits. The nitrogen fluid or gas concurrently generated with the release of the heat provides an agitation of the heated and emulsified solution to bring the solvent portion of the solution into intimate contact with the paraffins and thus assures the dissolution of the paraffin in the solvent component of the treatment solution. Moreover, the additional incorporation of a crystalline modifier in the solvent solution will effectively prevent the reprecipitation of the dissolved paraffins and permit the removal of the treatment solution from the pipeline for appropriate disposition when the temperature of the solution falls rapidly to the ambient temperature, which, in the case of a sub-sea pipeline, is in the order of 4°C. A desired phase diagram of paraffin deposits during fused chemical reaction treatment is shown in Figure 1.2.

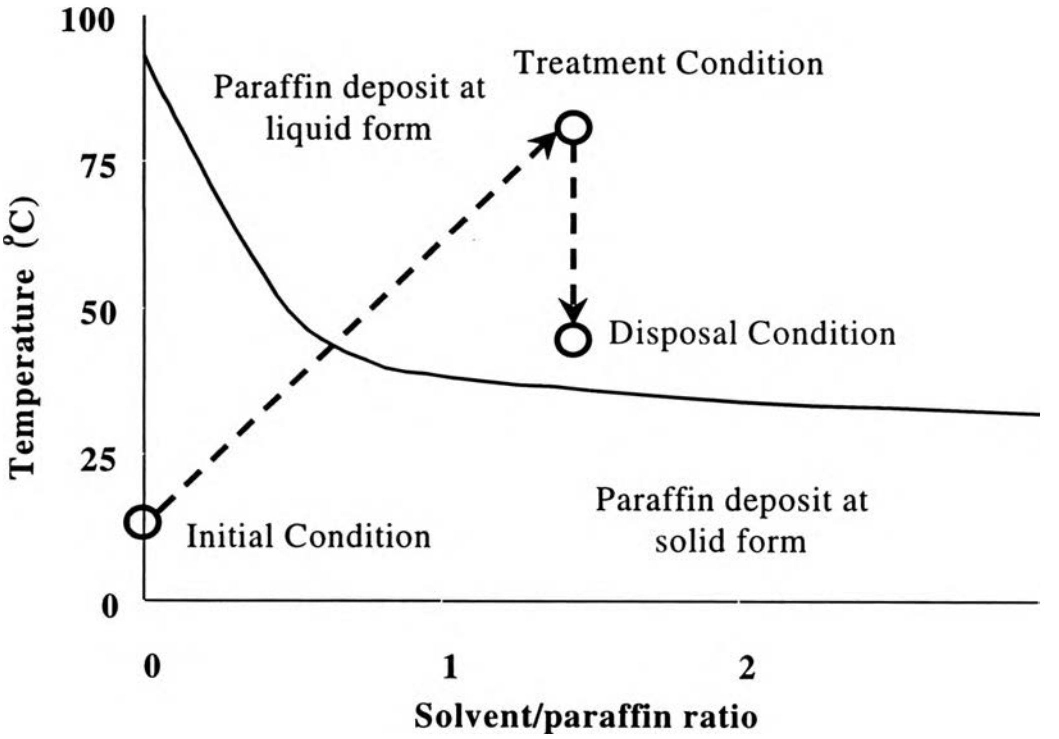

Figure 1.2 Phase diagram of paraffin deposit during the treatment (Khalil, 1997).

The primary challenge is to supply heat to regions further down the pipelines that are more susceptible to wax deposition. The treatment fluid in the vicinity of the paraffin deposits should be heated to a controllable temperature in the range of 50 to 100°C, sufficient to melt the deposits but not too high to adversely affect the internal and/or external coating of the pipeline. Moreover, as shown in Figure 1.2 the temperature of the solution must be maintained higher than the initial crystallization temperature of the paraffin at that treatment conditions until the solution reaches the exit of the pipeline and goes to a paraffin removal complex. Therefore, generally, three criteria to evaluate the effectiveness of a fused chemical reaction are as follows:

1. **The amount of heat generated by the exothermic reaction** is sufficient to raise the treatment fluid to a temperature beyond the melting point of wax deposit for an adequate time. This amount of heat mostly depends on the heat of reaction and concentrations of reactants.
2. **The time that heat begins to be released** is delayed and controlled so that the heat is released significantly only when the treatment fluids are right at or near by the critical region of paraffin deposition in the pipeline. This is achieved through controlling the rate of the exothermic reaction by adjusting the concentration of either one reactant or the catalyst.
3. **The rate of releasing heat** should be appropriate to maintain the temperature of the treatment fluid at a desired value between the two minimum and maximum limitations at least until the solution arrives the paraffin removal complex while still minimize the heat loss to the cold surrounding environment.

With those factors in mind, it is necessary to find a highly exothermic reaction whose rate strongly depends on temperature and/or concentration of reactant(s) or catalyst. Moreover, either the concentration of the reactant(s) or the catalyst (pH-reducing reagent) should be totally controlled. Since the amount of catalyst used is generally much less than that of the reactant(s), controlled release of the catalyst is more frequently applied (Richardson, 1983, Ashton, 1988, and Khalil, 1997).

Techniques for controlling the release of a substance are substantially available, especially in pharmacy industries. Several techniques for controlling the release of heat such as using emulsion, pulse injection, slow protonation have been studied thoroughly in the past few years; the results obtained seem very promising for solving the wax deposit problem in well flowlines and short pipelines. However, as oil wells go further offshore, the need for a controlled release technique that can delay significantly the release of catalyst (therefore, of heat) becomes more and more obvious.

1.3. Encapsulation Technique

Encapsulation is an effective controlled-release technique though widely used in pharmacy industry yet has been applied for fused chemical reactions. This research was conducted to investigate the feasibility of employing this technique to control the rate of the exothermic reaction mentioned above both in a batch reactor and in a pipeline.

The system is comprised mostly of a solution containing two reactants of sodium nitrite and ammonium chloride, which are capable of generating a large amount of heat and nitrogen gas when being mixed together. To control the rate of the reaction, an encapsulation system containing a pH-reducing reagent (citric acid) in enteric polymer-coated hard gelatin capsules is added to the aqueous solution to provide a sufficiently low pH at the desired time in order to trigger the exothermic reaction up to a significant rate. A certain amount of sodium hydroxide is then added to the aqueous solution to provide a rather high initial pH to retard the exothermic reaction so that no significant portion of the reactants could be consumed until the treatment solution reaches the region where more wax deposited.

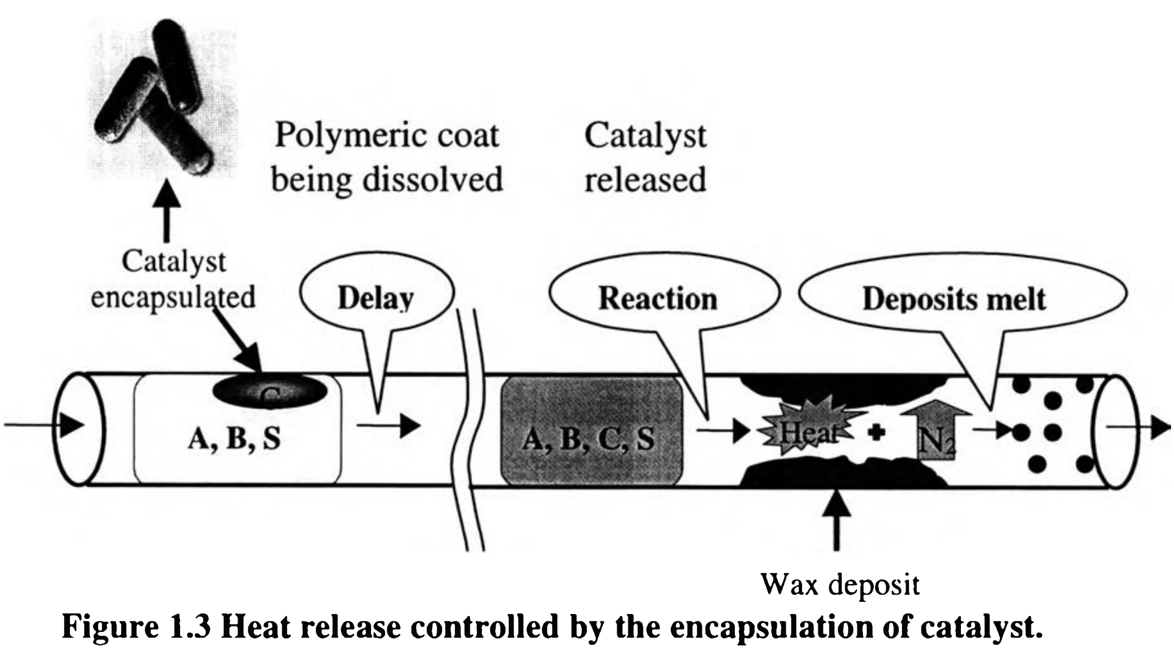

Figure 1.3 Heat release controlled by the encapsulation of catalyst.

The release of the encapsulated catalyst from capsules is essentially delayed by the dissolution of the polymeric coat surrounding the capsules whereas the consequent generation of heat and nitrogen gas is dependent on the kinetics of the exothermic reaction. The overall process is described in Figure 1.3. Therefore, in order to be able to evaluate the potential and feasibility of the encapsulation technique in providing heat to further regions of a pipeline, this research seeks for a more extensive understanding of the reaction kinetics as well as the controlled release of the encapsulated catalyst. Having known those kinetics, a model is then build to predict the temperature-distance profile in a pipeline.

1.4. Objectives

Objectives of this research work were as follows:

1. To formulate the rate law of the exothermic reaction as a function of the concentration of the two reactants, pH, and temperature of the solution.
2. To determine the dissolution kinetics of the polymeric coat and through that, to understand the release of the encapsulated catalyst to the surrounding solution.
3. To model the reactive system with encapsulated catalyst in a batch reactor and compare experimental results with simulation results to verify the kinetics found and the model proposed.
4. Finally, to construct a model to predict temperature-length profiles in a flowloop or a pipeline in order to determine the feasibility of the encapsulation technique used together with fused chemical reaction method to dissolve the wax deposits in a sub-sea pipeline.