CHAPTER II

LITERATURE REVIEWS

A discussion of the nature of paraffin problems, methods of prevention and treatment studied, and the development of controlled release techniques (mostly in pharmaceutical industry) in a substantial amount of literature will be presented in this chapter.

2.1. Wax Deposition Problems

Misra (1995) stated that problems related to crystallization and deposition of paraffin waxes during production and transportation of crude oil caused losses of billions of dollars per year to petroleum industry worldwide through the cost of chemicals, reduced production, well shut-in, less utilization of capacity, choking of the flowlines, equipment failure, extra horse-power requirement, and increased manpower attention.

Wright (1951) remarked that compounds found in paraffin deposits were dependent upon the characteristics of the crude oil. Oil is mostly mechanical trapped in the deposits, held between wax grains. If a large amount of oil is present, the paraffin deposit is hard and less plastic. In this case an increase in temperature does not have much effect on the plasticity until the melting point of the wax is approached. The gums and resins, which are reddish-brown aromatic compounds in solution in the crude oil, normally comprise 10 to 15% of paraffin deposit. The asphalt content of the deposit is normally very small. Essentially, the wax crystal habit was dependent on the crude oil, rate of cooling, and degree of agitation during cooling.

Addision (1984) proposed two mechanisms of wax deposition: molecular diffusion, and shear deposition. The mechanism of molecular diffusion was employed to explain the deposition of wax occurring during production in which the oil temperature is high above the cloud point. Once the warm oil comes in contact with a cold surface, wax will precipitate out of solution and adheres directly to the cold surface. Shear deposition of precipitated wax crystals occurs after the oil temperature falls below the cloud point. The crystals formed are then transported to the wall by the shearing of the oil at the surface of the tubing or flowline. These crystals will deposit on the layers formed by molecular diffusion if it occurs. Shear dispersion is the main mechanism of wax deposition when oil temperatures are below the cloud point.

2.2. Conventional Solutions for Wax Deposit Problems

McClasflin *et al.* (1984) stated that there were many methods of handling paraffin deposition. These can be divided into four categories: mechanical, thermal, chemical, and combinations of these three.

1. **Mechanical methods** Reistle and Blade (1932) showed an impressive list of tools used to scrape paraffin from the tubing. Included were "standard tools" consisting of socket, jar, stem and bit. Wright (1951) mentioned that pigs, the paraffin knife, paraffin hook, corkscrew, porcupine, and swab were in general use. Nowadays, mechanical methods are still in use, and when the paraffin deposits are soft, they are the most effective way to deal with the paraffin problem.

2. **Thermal methods** Hot oiling on a regular basis is recommended by several authors, and several refinements have been developed. Spitser (1987) patented an annular plug which fits on the string. It slows the passage of hot oil down the annulus so that heat is more efficiently transferred to the tubing string. There were also reports that the hot oil process was applied in a field of very high paraffin content near Vernal, Utah. He ran laboratory tests to

compare hot oil, oil with additives, hot water, dispersants, microbial, and solvents. The conclusion was that the preferred technique was the use of hot water without additives.

3. **Chemical methods** They falls into two classes: (1) those in which a solvent is used to dissolve the deposit once it has formed, and (2) those use wax crystal modifiers and/or paraffin dispersants to inhibit wax crystal growth or inhibit its adherence to the tubing wall.

The terms of crystal modifiers, inhibitors, flow improvers, and pour point depressants seem to be used synonymously. McCall *et al.* (1984) defined inhibitors as "generally consisting of high molecular weight copolymers of ethylene and vinyl acetate, which have enough structural similarly to paraffin to enter into the paraffin crystallization process. Paraffin inhibitors function by modifying or blocking the formation of large paraffin crystals." Wax crystal modifiers, when added at a concentration of 0.002 to 0.5%, have been found to modify crystal habits, sizes and crystal/crystal adhesion.

Addision (1984) noted that chemical treating programs (using solvents, paraffin inhibitors, or paraffin dispersants) allow operators to implement very flexible paraffin control methods. Hicks (1990) recommended the use of hot water with a nonionic surfactant to be applied down the annulus to remove paraffin deposits. He also recommended to use hot oil with either a paraffin solvent or a dispersing agent.

4. **Combined methods** Many problems req,uire a combination of these three methods to control paraffin deposition and maintain production. Nitrogen Generation System (described in the Fused Chemical Reactions part below) is one method of the kind.

2.3. Fused Chemical Reaction

2.3.1. Exothermic Reaction

Richardson *et al.* (1983) employed a reaction between a reducing agent and an oxidizing agent to not only generate nitrogen gas but also produce heating of a solvent solution which is introduced into the production zone of a well to affect the dissolution of paraffin and similar deposits from the perforations of the production zone.

Suitable nitrogen-containing gas-forming reducing reactants to use in this process can comprise water-soluble amino nitrogen-containing compounds which contain at least one nitrogen atom and at least one hydrogen atom attached and capable of reacting with an oxidizing agent to yield nitrogen gas and by products which are liquids or dissolve in water to form liquids substantially inert relative to the pipeline. Examples of such nitrogen-containing compounds include ammonium chloride, ammonium nitrate, ammonium nitrite, and ammonium acetate. Ammonium chloride was found particularly suitable for this process and therefore was chosen as a reducing nitrogen-containing agent in this research.

Oxidizing agents suitable for the reaction can comprise substantially any water-soluble oxidizing agents capable of reacting with a water-soluble nitrogen-containing compound of the type described above to produce nitrogen gas and the indicated types of by-products. Examples of such oxidizing agents include alkali metal hypochlorites, alkali metal or ammonium salts of nitrous acid such as sodium or potassium or ammonium nitrite, and the like. The alkali metal or ammonium nitrites are particularly suitable for use with nitrogen-containing compounds such as the ammonium salts.

Reagents for reducing the pH of the aqueous solution and speeding up the exothermic reaction can comprise substantially any water-soluble, relatively easy hydrolyzable materials, which are compatible with the two reactants and their products, and especially for using in this research, are

easily encapsulated. Examples of suitable pH-reducing reactant include citric acid, glutaric acid, ascorbic acid, sodium dihydrogen phosphate, and the like.

A typical reaction which was used in this research is described as follows:
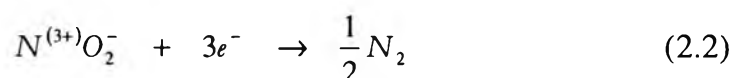
$$NaNO_2 \;+\; NH_4Cl \;\rightarrow\; N_2\uparrow \;+\; NaCl \;+\; 2H_2O \qquad (2.1)$$

where:
$$\Delta H_{rx} = -79.95\,\frac{kcal}{mol} \quad at \quad 25^\circ C$$

$$\Delta Cp = 0.0472\,\frac{kcal}{mol\times K} \quad at \quad 25^\circ C$$

$$Cp_s = 0.334\,\frac{kcal}{mol\times K} \quad at \quad 25^\circ C$$

$$K_{eq} = 3.92E^{63}\,\frac{bar\times mole}{1} \quad at \quad 25^\circ C$$

In this oxidation-reduction reaction, the nitrogen atom in ammonium chloride is oxidized from −3 to 0 while the nitrogen atom in sodium nitrite is reduced from +3 down to 0 in the produced nitrogen gas.

$$N^{(3+)}O_2^- \;+\; 3e^- \;\rightarrow\; \frac{1}{2}N_2 \qquad (2.2)$$

$$N^{(3-)}H_4^+ \;-\; 3e^- \;\rightarrow\; \frac{1}{2}N_2 \qquad (2.3)$$
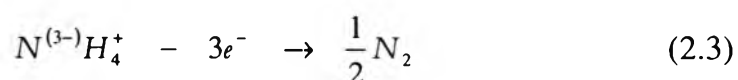
2.3.2. Techniques for Controlling the Release of Heat

Richardson (1987) further described a process for cleaning well casing perforations by injecting an aqueous solution containing nitrogen-gas-generating reactants, an alkaline buffer providing a reaction-retarding pH, and an acid-yielding reactant for subsequently overriding the buffer and lowering the pH in order to trigger a fast-driving pulse of heat and pressure which causes a perforation-cleaning backsurge of fluid through the perforations. This method, however, might produce undesirable stresses if applied to the cleaning

of a pipeline and would not prevent the reprecipitation of the paraffins as the temperature falls, particularly in a subsea pipeline.

Ashton *et al.* (1988) described a process for dewaxing sub-sea conduits which comprised injecting an oil-in-water emulsion of an aqueous solution and a hydrocarbon solution. The aqueous solution contains heat-generating reactants and a pH buffer to delay the delivery of heat up to the chosen point in the conduit where the reaction is to begin. Consequently, sufficient heat is released to melt the paraffin deposits as shown in Figure 2.1. The hydrocarbon solution comprises the necessary amount of a solvent selected for its ability to dissolve the particular paraffins of the deposit, as well as a modifier selected to produce a minimal pour point for the paraffins involved in the deposit. When the action of the emulsified aqueous solution is over, it is pumped off, while the paraffin deposit is withdrawn together with the aromatic solvent. The process has been successfully used in several applications. Nevertheless, they did not provide any field application for the dewaxing of pipes using the suggested process.
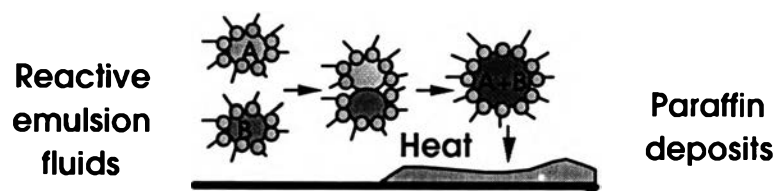

Reactive emulsion fluids   Heat   Paraffin deposits

Figure 2.1 Dissolution of paraffin deposits due to reactive mixture of water/oil emulsions.

Khalil (1997) provided a process and composition for fluidizing and removing paraffin deposits from a pipeline by combining thermal, chemical and mechanical means simultaneously. The treatment fluid is an oil-in-water emulsion between an aqueous-based fluid which contains the reactants and an oil-based fluid which consists of aliphatic and/or aromatic hydrocarbons and their mixtures. The emulsion is stabilized by the addition of a suitable surface

agent, which promotes within the proper period of time the coalescence of the aqueous phase. As a result, there will be a delay time before the exothermic chemical reaction occurs, producing simultaneous and controlled release of nitrogen and heat, which, combined to the hydrocarbon mixture, promote the fluidization and removal of the paraffin deposit. Several de-waxing operations performed at the Campos Basin (Brazil) have confirmed the excellent performance of this process for short pipelines (up to about 20 kilometers). However, using the process for long pipeline is still a challenge as the heat release has to be delayed for a considerably longer time.

Singh and Fogler (1998) developed a simplified computational fluid dynamics model to simulate the pulsed flow of the individual aqueous reactant solutions separated by an inert fluid (pure water). Since the reactants have to disperse through the inert separator before reacting, the generation of heat is delayed. Figure 2.2 shows the system of three pulses just at the entrance end of the pipeline. The movement of these pulses can be seen as a propagation of a temperature wave inside the pipeline.
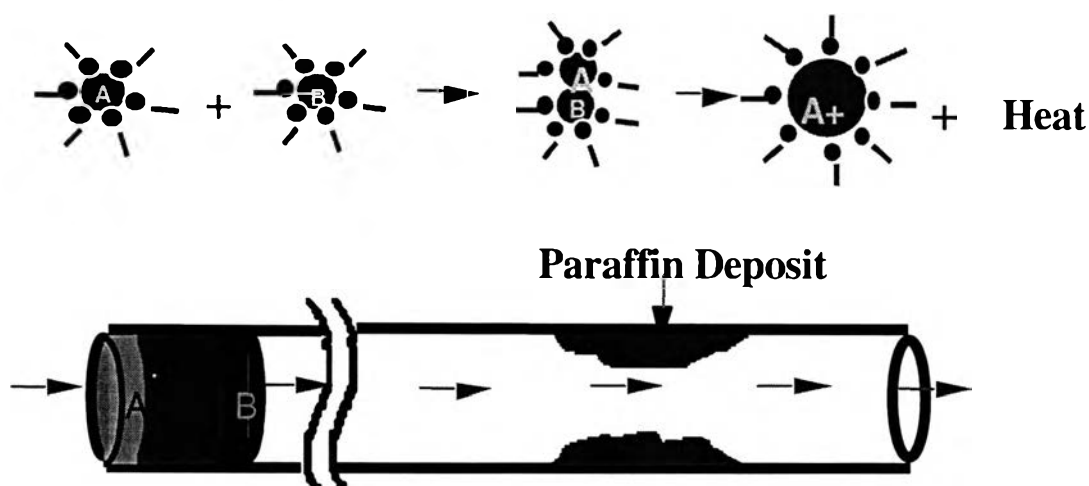

Figure 2.2 Dissolution of paraffin deposits due to separate feed of reactant pulses.

The above set of simulations was also extended to multiple sets of reactant pulses separated by an inert fluid. These simulations show the

feasibility of releasing heat at locations as far as 30km from the entrance of the pipeline.

Heller *et al.* (1978) investigated the kinetics of drug release from a series of partial esters of vinyl acetate-maleic anhydride. These polymers in their un-ionized forms are hydrophobic and water insoluble. But in their ionized forms they are water-soluble. Polymer dissolution is pH sensitive and is limited to the polymer-buffer medium interface. When films are placed in buffered media, they erode (dissolve) at a constant rate that depends on the nature of the polymer and on the pH of the buffered medium. A detailed model has been developed that successfully correlates dissolution behavior and various experimental parameters.

Achim (1996) discussed about the most important features of the degradation and erosion (dissolution) of degradable polymers. Degradation finally leads to polymer erosion and the loss of material from the polymer bulk. The resulting changes in morphology, pH, oligomer and monomer properties as well as crystallinity were illustrated with selected examples. Finally, a brief survey on approaches to polymer degradation and erosion was given. Kao *et al.* (1997) studied the effect of the thickness of the coated polymer on the lag time. Drug release exhibited a lag period followed afterwards by an instantaneous release.

Takashi *et al.* (1998) investigated a new capsule-type dosage form for colon-targeted delivery of drug. The system was designed by imparting a timed-release function and a pH-sensing function to a hard gelatin capsule. The technical characteristics of the system were to contain an organic acid together with an active ingredient in a capsule coated with a three-layered film consisting of an acid-soluble polymer, a water-soluble polymer, and an enteric polymer. It was found that this approach could provide a useful and practical means for targeted (or timed) delivery of drugs.