



CHAPTER I

INTRODUCTION

Introduction

Oil is an important source of energy and is also used as a raw material in the chemical manufacturing industry. Worldwide oil reserves are being depleted rapidly. Stringent environmental regulations coupled with global economic and political instability are restraining the oil industry from exploration and development of new oil-fields. There is an increasing requirement to recover as much oil as possible from the existing producing oilfields by using different improved oil recovery techniques. Certain water-soluble/hydrogel polymers are especially suited for various oilfield applications including a number of enhanced oil recovery (EOR) processes.

In oil-bearing formations, hydrocarbons are trapped under pressure in the pores of the rock matrix. The pressure and the temperature of an oil reservoir vary from reservoir to reservoir, depending on the depth and the nature of the crude oil (heavy or light) deposit in the reservoir. The pressure can vary from 200 -1500 psi ($1.4 \times 10^5 - 1.055 \times 10^7 \text{ kgm}^{-2}$) and the temperature from 25 to 150 °C. When a productive hydrocarbon formation is tapped, the oil and gas are produced by this natural energy (the pressure differential) of the reservoir. This pressure, which is the driving force for oil and gas to come to the surface, gradually diminishes to the point where pumps are required to lift the oil to the surface. This phase, known as primary

production, accounts for the recovery of approximately 20% of the original oil in the reservoir.

Pressure depletion with time gradually reaches a point where sufficient energy is no longer available to displace oil through the reservoir to the well. So, new injection wells are drilled around the producing wells or suitable producing wells are converted into injection wells to facilitate injection of water or gas in order to restore the original reservoir pressure. This stage of operation is called secondary recovery, whereby injected fluid continues to force the oil out from the rock pores to the producing well. This produces an additional 10-20% of the oil originally in place. However, water tends to pass through the higher permeability zones, fractures or channels leaving a substantial amount of oil behind. Thus, the practice of water flooding becomes uneconomical because of the high cost for lifting and separation of a substantial amount of co-produced water with the produced oil. Polymer-augmented water flooding is a more efficient alternative to just water flooding. This process is known as polymer flooding. Water-soluble polymer, which increases the viscosity of water and thereby reduces its mobility, is used in this process(1). However, full-scale polymer flooding requires the injection of a large volume of aqueous polymer solution. This is capital intensive and often needs a long time to produce results. A popular option is the use of hydrogels prepared by the crosslinking of water-soluble polymers for fluid diversion during the profile control of injection wells or for the treatment of water-coning problems in producing well. These processes require substantially lower costs and shorter payout times than those of full-scale polymer flooding.

Although water-soluble polymers play an important role in a number of oil recovery processes, these polymers may also be used in

other oilfield application such as drilling mud, additives for fluid loss control, shale stabilization, flocculation, filtration control, etc., under harsh conditions of high temperature and high salinity and/or hardness.

Scientific and Technological Rationale

Different kinds of water-soluble polymers can be used for EOR processes. These polymers are classified into three main groups:

- Natural polymers(biopolymers) such as starch, guar gum, xanthan and scleroglucan.
- Chemically modified natural polymers such as starch, cellulose ethers and lignosulfonates.
- Synthetic polymers such as polyacrylamide and synthetic copolymers.

There are several requirements for polymers to be used in the EOR processes. Some of these important and critical requirements are solubility, viscosity and shear stability, compatibility with injection and formation water, crude oil and minerals of the reservoir, corrosion and scale inhibitors, and biocides, etc.; long-term thermohydrolytic stability; injectibility; low adsorption; ease of field handling; and cost efficiency.

Only a few types of polymers have been successful in showing suitable properties to meet these EOR requirements. In particular, the EOR applicability of polymers is determined by the salinity of both the reservoir and the injection water as well as by the temperature of the reservoir.

Polyacrylamide and partially hydrolyzed polyacrylamide are suitable for low temperature and low salinity reservoir conditions. Biopolymer, such as, xanthan gum, are suitable for low to moderate temperature and high salinity conditions. Specially tailored synthetic

copolymers, such as HE polymers (HE is a registered trade mark of the Drilling specialties company for suitable synthetic polymers for hostile environments), are suitable for high salinity and high temperature reservoir conditions. These polymers are also used as drilling mud additives to reduce water loss from the mud, specially in higher temperature applications.

Most of the worldwide polymer-aided EOR projects to-date have been carried out by the injection of fluids containing polyacrylamide and/or partially hydrolyzed polyacrylamide. The polyacrylamides used are very high molecular weight polymers (usually $> 1 \times 10^6$) and, thus, are very effective viscosity building polymers. Polyacrylamides reduce the mobility of displacement water in porous media by a combination of both increasing the water's viscosity and reducing the permeability of the rock matrix to water.

While polyacrylamides are suitable for most reservoirs, they cannot withstand the higher temperature and salinity and/or hardness levels encountered in deeper reservoirs. Polyacrylamides undergo extensive hydrolysis at elevated temperatures. The resulting hydrolyzed polymers precipitate with divalent cations, commonly present in oilfield waters, leading to a substantial loss in viscosity. This seriously limits their use as mobility control agents in high temperature reservoirs.

In recent years, the trend in water-soluble polymer research for EOR applications has been to develop acrylamide-based polymers that are resistant to thermal hydrolysis. It appears that the copolymerization of acrylamide with a co-monomer such as N-vinylpyrrolidone can effectively protect the amide groups against thermal hydrolysis. Thus, the research efforts have produced commercial products based on acrylamide, which can tolerate the hardness at elevated temperatures without precipitation and viscosity loss. Various other acrylamide-based polymer systems,

namely, hydrophobically associating, zwitterionic and ampholytic systems have been reported for their improved solubilities, enhanced viscosities and improved shear stabilities in hard brine solution. However, these systems are yet to be evaluated for high temperature stability.

Objectives

The objectives of this research are the following:

1. To study the suitable method of synthesis for polyacrylamide by gamma irradiation.
2. To study the optimum condition for hydrolysis of polyacrylamide to produce a partially hydrolyzed polyacrylamide(HPAM).
3. To study the suitable method for synthesising the partially hydrolyzed poly(acrylamide-co-1-vinyl-2-pyrrolidone) by gamma irradiation.
4. To study the optimum ratio of the partially hydrolyzed polyacrylamide(HPAM) and 1-vinyl-2-pyrrolidone, which was used in the copolymerization.
5. To characterize the copolymers of partially hydrolyzed polyacrylamide(HPAM)-1-vinyl-2-pyrrolidone by using spectrophotographic and thermal analyses.

Expected Benefits Obtainable for Future Development of the Research

Different kinds of water-soluble polymers can be used for enhanced oil recovery(EOR) processes through its water absorption. Polyacrylamide, in its partially hydrolyzed form(HPAM), has been used in oil recovery processes far more frequently than biopolymer(1). The degree of hydrolysis may be important in certain physical properties

such as polymer absorption, shear stability and thermal stability. However, since the polyacrylamide chain is flexible, it may respond much more to the ionic strength of the aqueous solvents, and its solution properties are suitable to salt/hardness. Copolymerization of partially hydrolyzed polyacrylamide(HPAM) with a co-monomer such as 1-vinyl-2-pyrrolidone can effectively protect the amide group against thermal hydrolysis, which can tolerate the hostile environmental conditions of high salinity and hardness at elevated temperatures without precipitation and viscosity loss(1). Copolymerization of the modified acrylamide with a co-monomer, 1-vinyl-2- pyrrolidone, can be induced by radiation. The benefits for the future development can be:

1. To obtain the method for synthesis of polyacrylamide by gamma irradiation
2. To obtain the method for hydrolysis of polyacrylamide to produce a partially hydrolyzed polyacrylamide(HPAM).
3. To obtain the method for synthesising partially hydrolyzed poly(acrylamide(HPAM)-co-1-vinyl-2-pyrrolidone) by gamma irradiation.
4. To obtain copolymers, which can be used for enhanced oil recovery (EOR) processes through its water absorption.

Preparation Scheme

In order to ease understanding of the entire synthesis process, Figure 1 reveals the preparation of partially hydrolyzed polyacrylamide (HPAM)-1-vinyl-2-pyrrolidone copolymer by gamma irradiation. Further details of which is covered in Chapter III.

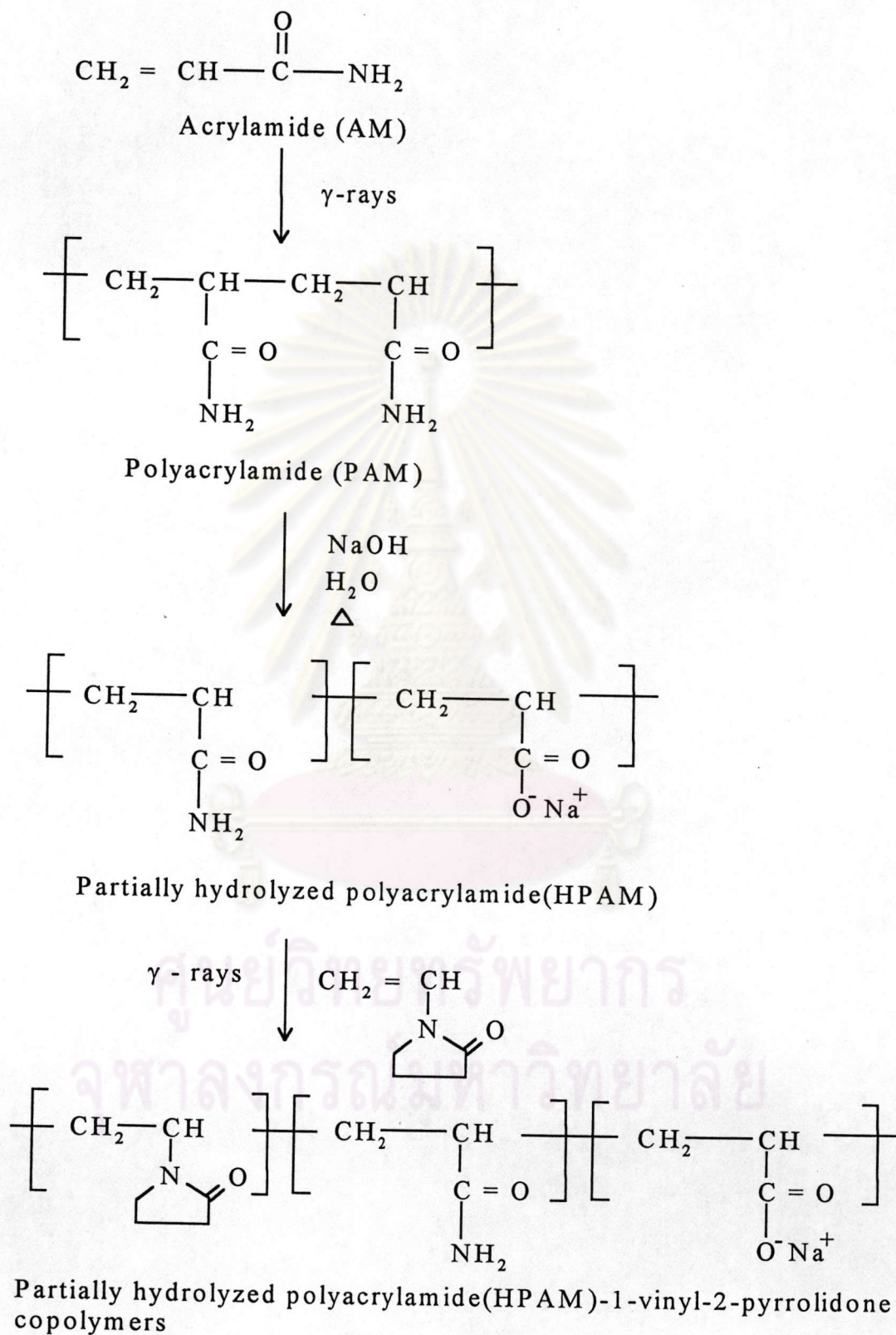


Figure 1.1 Preparation scheme for synthesis of partially hydrolyzed polyacrylamide(HPAM)-1-vinyl-2-pyrrolidone copolymers.

Scopes of the Investigation

In this research, the necessary procedures of copolymerization of partially hydrolyzed polyacrylamide(HPAM)-1-vinyl-2-pyrrolidone by gamma irradiation to achieve the best product is as follows:

1. Literature survey and in-depth study of this research work.
2. Preparing polyacrylamide via gamma radiation by simultaneous irradiation method, by studying the following parameters so as to select the suitable technique and to attain the appropriate reaction conditions:
 - a) The optimum quantity of total dose (kGy).
 - b) The optimum quantity of dose rate (kGy/min).
 - c) The optimum concentration of acrylamide for the polymerization of acrylamide.
3. Hydrolysis of polyacrylamide.

To achieve the degree of hydrolysis, which was suitable to copolymerize with 1-vinyl-2-pyrrolidone, and gave the product that had the highest water absorption value, important parameters on hydrolysis were carried out as follows:

- a) The optimum quantity of polyacrylamide (g).
 - b) The optimum temperature ($^{\circ}\text{C}$).
 - c) The optimum reaction time (h).
 - d) The suitable base for hydrolysis.
 - e) The optimum degree of hydrolysis of polyacrylamide (%)
4. Copolymerization of partially hydrolyzed polyacrylamide (HPAM)-1-vinyl-2-pyrrolidone.

To obtain a good yield of the copolymer with a high water absorption value, important effects on the copolymerization were carried out as follows:

- a) The optimum quantity of total dose (kGy).

- b) The optimum quantity of dose rate (kGy/min).
- c) The optimum ratio of partially hydrolyzed polyacrylamide (HPAM) (g)/ 1-vinyl-2-pyrrolidone monomer (cm³).
- d) The suitable solvent for precipitating the product.

5. Characterization and Testing.

a) Investigation of the functional groups of polyacrylamide, partially hydrolyzed polyacrylamide (HPAM)-1-vinyl-2-pyrrolidone copolymers by infrared spectrophotometry.

b) Determination of the degree of hydrolysis of polyacrylamide.

c) Testing of physical properties: several of which would be tried as follows:

- Studying the absorption capacity (g/g) and wicking time (min) of the partially hydrolyzed poly(acrylamide(HPAM)-co-1-vinyl-2-pyrrolidone) by a newly-invented instrument in the laboratory.

- Testing of temperature stability by thermal analysis.

- Testing of saline stability by measuring viscosity.

6. Summarizing the result and preparing the report.

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