CHAPTER I INTRODUCTION

The precipitation of undesirable scale precipitates or the formation scale causes serious problems in the production of oil and gas. Continuous scale build up in these areas leads to two major problems: a reduction of fluid conductivity in the production system due to the blockage of flow paths by scale precipitates; and the fouling or the damage of the production equipment (Dunn *et al.*, 1999). The most practical and economical method to combat this problem is the use of chemical scale inhibitors as precipitation squeeze treatments. In this treatment, scale inhibitors are injected and retained in the reservoir by precipitation. However, precipitation squeeze treatment can be costly due to production downtime, inefficient inhibitor placement and operating expenditures. An understanding of the scale inhibitor reactions is required to design successful squeeze treatments for various reservoir conditions. Two scale inhibitors, aminotri (methylenephosphonic acid) (ATMP) and diethylentrilopentrakis (methylenephosphonic acid) (DTPMP), used in the petroleum industry were selected as model inhibitors in this study.

Although precipitation squeeze treatments are often used to control scale formation, but their usage is based more on experience than scientific understanding. It is unclear on where and how scale inhibitors retain (precipitate) during the downhole injection of inhibitor solutions. On searching the literature, one finds the scientific explanations for the precipitation of scale inhibitors are not complete. The factors controlling inhibitor precipitation yield as well as the length of time before inhibitors precipitate from solution are still very difficult to predict. Therefore objective of this thesis work is focusing on the precipitation reaction and kinetics of scale inhibitors. In addition, the scale inhibition kinetics was studied as related to the scale inhibitor evaluation. Inhibitor concentration, solution pH and the presence of salts in the produce fluids were investigated their impact on the placement of scale inhibitor.

1.1 Significance of Research

Much of field application research has focused on adsorption squeeze treatments, despite the fact that precipitation squeeze treatments offer longer squeeze lifetimes than conventional adsorption squeeze treatments under comparable conditions.(Carlberge, 1983; Browning and Fogler, 1995; Browning and Fogler, 1996) Precipitation squeeze treatments are used less often than the adsorption squeeze methods due to the concerns of formation blockage and damage caused by the precipitation of inhibitor in the near wellbore region. Our research on precipitation squeeze treatment has been carried out to provide fundamental understanding of the reaction kinetics and mechanisms underpinning this treatment.

In oilfield operation, not only scale inhibitors are delivered into the reservoirs but also a variety of other chemicals such as gel breakers, surfactant during stimulation treatments, corrosion inhibitors, asphaltene deposition inhibitors, demulsifiers, friction reducers, wax inhibitors and tracers (Webb *et al.*, 1999). This study would provide valuable information in designing squeeze treatments of other oilfield chemicals that use in the oilfield.

1.2 Research Objectives

This thesis presents an in-depth investigation of the precipitation of scale inhibitors in oilfield squeeze treatment and elucidates the factors that govern the placement of an inhibitor in the reservoir. This information will aid in designing efficient squeeze treatments with prolonged squeeze lifetimes.

1.3 Impact of this Study on Other Areas

The similar complex precipitating reaction involving the complex formation and acid reaction as scale inhibitors with divalent cations can be found in many different facets of industrial and biological processes for example the precipitation of calcium apatite in human body. An understanding of how scale inhibitors react with cations and how monovalent cations, divalent cations and precipitating conditions affect the precipitation kinetics and precipitates properties would provide valuable information for the development of other complicated precipitation operation.

1.4 Outline of the Thesis

This thesis contains an experimental of the scale inhibitor precipitation in squeeze treatment and a demonstration of the new scale inhibitor evaluation technique. Each chapter is self-contained and represents a document prepared for the journal publication. A summery of each chapter is given below.

Chapter II provides background in an effort to familiarize the reader with the important issues on the topic of scale inhibitor precipitation squeeze treatments. Some of the specific topics covered include: scale inhibitors, scale inhibitor delivery techniques, an introduction to the precipitation and scale inhibitor evaluation.

Chapter III summarizes the chemical and describes, in detail, the experimental and characterization methods used in this study.

Chapter IV presents a study of scale inhibitor precipitation with calcium ions, elucidating factors affecting the process such as solution pH, ionic strength, and the presence of magnesium ions. The important issues addressed in this chapter include: the salting out effect phenomena, the effect of solution pH, ionic strength and the presence of magnesium on the precipitation yield, composition, morphology, crystallinity and dissolution rate of scale inhibitor precipitates. The presence of Mg was found to decrease the effectiveness of Ca-ATMP precipitation.

Chapter V provides an in-depth study of the scale inhibitor precipitation kinetics to identify treatment variables and strategies in order to cause inhibitor precipitation to occur far away from the wellbore. The induction time concept was used to determine the nucleation and surface free energy of Ca-ATMP precipitate.

Chapter VI, the precipitation of DTPMP, a phosphonate scale inhibitor, was comparatively studied with ATMP. The effects of pH and Mg ions on DTPMP precipitation were determined in the batch precipitation system similarly to the ATMP study described in Chapter III. Chapter VII illustrates the application of the concept of the critical supersaturation ratio (CSSR) to study scale inhibition and evaluate scale inhibitor type, concentration and pH effectiveness using the formation of BaSO₄ as example.

Chapter VIII draws conclusions from the experimental results, describes the impact that this study on squeeze treatment procedures and recommends future research topic in this area.

1.5 References

- Browning, F. H. and Fogler, H. S.(1995) Precipitation and dissolution of calcium phosphonates for the enhancement of squeeze lifetimes. <u>SPE Production &</u> <u>Facilities</u>, 10(3), 144-150.
- Browning, F. H. and Fogler, H. S. (1996) Effect of precipitating conditions on the formation of calcium-HEDP precipitates. <u>Langmuir</u>, 12(21), 5231-5238.
- Carlberge, B. L. (1983) Precipitation squeeze can control scale in high-volume Wells. <u>Proceeding of SPE Production Technology Symposium</u>, Lubbock, Texas, USA.
- Dunn, K., Daniel, E., Shuler, P. J., Chen, H. J., Tang, Y. C. and Yen, T. F. (1999) Mechanisms of surface precipitation and dissolution of barite: A morphology approach. <u>Journal of Colloid and Interface Science</u>, 214(2), 427-437.
- Webb, P. J. C., Nistad, T. A., Knapstad, B., Ravenscroff, P. D. and Collins, I. R. (1999) Advantages of a new chemical delivery system for fractured and gravel-packed wells. <u>SPE Production & Facilities</u>, 14(3), 210-218.