

**STUDY OF SCALE INHIBITOR REACTIONS
IN PRECIPITATION SQUEEZE TREATMENTS**

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ABSTRACT

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The application of chemical scale inhibitors as precipitation squeeze treatments is a common practice to combat oilfield scaling problem. However, the treatment can be costly due to production downtime and inefficient inhibitor placement. An understanding of the scale inhibitor reactions is required to design successful treatments. Aminotri (methylenephosphonic acid) (ATMP), a common scale inhibitor used in the petroleum industry was selected as a model inhibitor. Inhibitor concentration, pH and the presence of salts were found to have a significant impact on the placement of scale inhibitor. Changing the precipitating pH can alter the number of divalent cations attached to the ATMP and results in the formation of precipitates with markedly different properties. The logarithm of the scale inhibitor precipitate solubility was found to vary linearly with the salinity because of the salting out effect, which is consistent with Setchenow theory. ATMP precipitation decreases when Mg is added because of the formation of Mg-ATMP complex in the liquid phase. The competitive reaction among the soluble salts with inhibitor molecule was found to delay the inhibitor precipitation rate. A slow precipitation rate would allow the inhibitor fluids to be transported to the near-wellbore regions without precipitating the scale inhibitor or causing subsequent formation damage. The study of diethylenetriaminepenta methylene phosphonic acid (DTPMP) was conducted and the experimental results suggest potential of shorter squeeze lifetime of DTPMP system than that of ATMP system. In addition, the concept of a critical supersaturation ratio (CSSR) was used to characterize the effectiveness of different types of scale inhibitors, inhibitor concentration, and precipitating solution pH in

order to control the formation of barium sulfate scale. DTPMP and phosphinopolycarboxylic acid polymer (PPCA) were the most effective BaSO₄ scale inhibitors per ionizable proton and the most effective on a concentration basis, respectively. A SEM analysis shows that the higher the scale inhibitor concentration and solution pH, the smaller and more spherical the BaSO₄ precipitates are formed. The results of the particle size distribution of BaSO₄ precipitate reveals that increasing with elapsed time, the scale inhibitor concentration, and precipitating solution pH, all produce a broader particle size distribution and a smaller mean diameter of the BaSO₄ precipitates are obtained.

บทคัดย่อ

วีระภัทร์ ต้นตยาคม : การศึกษาปฏิกิริยาสารยับยั้งการตกตะกอนภายในกระบวนการกักเก็บสารยับยั้งในบ่อน้ำมันด้วยการเปลี่ยนสภาวะสารยับยั้งเป็นของแข็ง (Study of Scale Inhibitor Reactions in Precipitation Squeeze Treatments) อ. ที่ปรึกษา: รศ. สุเมธ ชวเดช และ ศ. เฮซ สกอทท์ ฟอกเลอร์ 104 หน้า ISBN 974-9651-73-1

การประยุกต์ใช้สารเคมียับยั้งการเกิดตะกอน เพื่อการบำบัดแบบบีบการตกตะกอน (Precipitation Squeeze Treatment) ถูกใช้ทั่วไปในการแก้ไขปัญหาการเกิดตะกอนในการผลิตน้ำมัน แต่อย่างไรก็ตามการบำบัดนี้มีค่าใช้จ่ายสูง เนื่องจากต้องหยุดการผลิตในขณะดำเนินการ และตำแหน่งการตกตะกอนของสารยับยั้งการตกตะกอนในบ่อน้ำมันที่ไม่เหมาะสม ความเข้าใจเกี่ยวกับปฏิกิริยาของสารยับยั้งมีความจำเป็นต่อการออกแบบการบำบัดนี้ให้มีประสิทธิภาพ สารยับยั้งชื่อ aminotrimethylene phosphonic acid (ATMP) ถูกเลือกเป็นต้นแบบเพราะใช้อย่างแพร่หลายในอุตสาหกรรมน้ำมัน การศึกษาพบว่า ปริมาณสารยับยั้ง ค่าความเป็นกรดเป็นด่างและเกลือ มีผลกระทบต่ออัตราการตกตะกอนของสารยับยั้ง การเปลี่ยนแปลงค่าความเป็นกรดเป็นด่างมีผลต่อการเปลี่ยนแปลงจำนวนแคทไอออนชนิดวาเลนซีสองที่จะเกาะบนโมเลกุลของ ATMP และมีผลต่อคุณสมบัติต่างๆ ของตะกอนที่เกิดขึ้น นอกจากนี้ยังพบว่าความเข้มข้นสารยับยั้งนี้ในรูปล็อก (logarithm) เปลี่ยนแปลงเป็นเส้นตรงกับความเค็ม ทั้งนี้เนื่องจากผลของเกลือเคลื่อนออก (salting out effect) ซึ่งสอดคล้องกับทฤษฎี Setchenow การตกตะกอนของ ATMP ลดลงเมื่อเติมแมกนีเซียม เนื่องจากการรวมตัวระหว่าง Mg และ ATMP ในน้ำ ปฏิกิริยาแข่งขันระหว่างเกลือที่ละลายในน้ำกับสารยับยั้งมีผลทำให้อัตราการตกตะกอนของสารยับยั้งช้าลง อัตราการตกตะกอนที่ช้าจะช่วยทำให้สารยับยั้ง ถูกพาไปไกลจากหลุมน้ำมันโดยไม่เกิดการตกตะกอนของสารยับยั้ง หรือก่อให้เกิดความเสียหายของโครงสร้างหิน ได้ทำการศึกษาสาร DTPMP (diethylenetriaminepenta methylene phosphonic) และผลการศึกษายืนยันว่าสาร DTPMP ให้ช่วงเวลาที่สามารถบำบัดตะกอนได้ (squeeze lifetime) ที่สั้นกว่าใช้สาร ATMP นอกจากนี้ยังได้ศึกษาการนำหลักการของ Critical Supersaturation Ratio (CSSR) ในการประเมินประสิทธิภาพของสารยับยั้งการเกิดตะกอนชนิดต่างๆ ความเข้มข้นสารยับยั้งการเกิดตะกอน และค่าความเป็นกรดเป็นด่างเพื่อใช้ในการควบคุมการเกิดตะกอนของแบเรียมซัลเฟต พบว่า DTPMP และ PPCA (phosphinopolycarboxylic acid polymer) มีประสิทธิภาพสูงสุดต่อการยับยั้งการเกิดตะกอนของแบเรียมซัลเฟต เมื่อเทียบกับต่อจำนวนโปรตรอนที่แตกออก และต่อความเข้มข้น

ตามลำดับ จากผลการวิเคราะห์ภาพถ่ายอิเล็กตรอนแบบส่องกราด (SEM) พบว่าการเพิ่มความเข้มข้นของสารยับยั้งและค่าความเป็นกรดเป็นด่าง ทำให้ตะกอนของแบเรียมซัลเฟตมีขนาดเล็กลงและทรงกลมมากขึ้น จากผลของการกระจายขนาดอนุภาคของตะกอนแบเรียมซัลเฟต แสดงให้เห็นว่าเมื่อเพิ่ม เวลาของการตกตะกอน (elapsed time) ความเข้มข้นของสารยับยั้งการเกิดตะกอนหรือค่าความเป็นกรดเป็นด่าง จะส่งผลทำให้ค่าการกระจายขนาดอนุภาคและค่าเฉลี่ยเส้นผ่านศูนย์กลางของอนุภาคของตะกอนแบเรียมซัลเฟตลดต่ำลง

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