THE USE OF BIODEGRADABLE PARTICULATE DIVERTING AGENTS IN HYDRAULIC FRACTURING AND REFRACTURING: AN EXPERIMENTAL STUDY

by

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ABSTRACT

The success of stimulation treatments highly depends on the stimulated reservoir volume. Stimulation fluid tends to take the path of least resistance including toward zones with high permeability and low stress as well as perforation clusters that have already been stimulated. This causes stimulation fluids to bypass zones that could benefit the most from the treatment. The use of particulate diverting agents helps overcome this issue.

Particulate diversion methods work by pumping particulates into the wellbore where they temporarily block the path of least resistance by creating a barrier inside perforation tunnels or inside fractures in the near-wellbore and the far-field. Conventional particulate diverters work through permeability reduction of the diverter-pack that cause flow resistance into these zones. This resistance aids in redirecting (diverting) the fracturing fluids to other zones and perforation clusters to maximize the stimulated reservoir volume. The particulates must stay intact during the stimulation treatment and later degrade to allow flowback from the plugged regions.

Although many field and lab studies show successful results with the use of biodegradable particulates, many operators question their effectiveness for hydraulic fracturing and refracturing operations due to inconsistent results. In this research, an automated permeability plugging apparatus is used to investigate the effect of different testing conditions and different physical characteristic of polylactide biodegradable particulates on their plugging performance.

Results from this work show that biodegradable particulates behave differently than conventional diverters. They have a significant advantage due to their ability to deform and undergo a phase transition from rigid to flexible above the glass transition temperature (T_g) creating a plug capable of sealing perforations and fractures while using significantly lower amounts of diverter. It was also found that different shapes and sizes of

biodegradable diverters (above T_g) behave in a way that is contradictory to the behavior of conventional particulates. Not accounting for this difference in behavior can lead to undesirable field results including low stimulation efficiency and low stimulated reservoir volumes. Recommendations and design guidelines are provided for the use of biodegradable particulates above T_g.

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LIST OF ABBREVIATIONS

Automated permeability plugging apparatus . . . . . APPA

Degradable particulate diverting agent . . . . . DPDA

Distributed temperature sensing . . . . . DTS

Glass transition temperature . . . . . T_g

Gram . . . . . g

Lost circulation material . . . . . LCM

Melting temperature . . . . . T_m

Polyglycolide . . . . . PGA

Polylactide . . . . . PLA

Pound . . . . . lb

Pounds-per-gallon . . . . . ppg

Resistance temperature detectors . . . . . RTD

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To my guardian angels in heaven mom dad and big sister

To my guardian angels on earth uncle Basel and auntie Alia

CHAPTER 1
INTRODUCTION

The success of stimulation treatments, such as hydraulic fracturing, refracturing, and acidizing, is highly dependent on delivering the treatment fluid to the zone of interest and maximizing the contact area with the reservoir. Stimulation fluids tend to take the path of least resistance. This path of least resistance can include intervals with high permeability and low stress, zones and perforation clusters that already been stimulated, and zones that are naturally fractured. This in turn can cause the treatment fluid to bypass zones that could benefit the most from the stimulation. To overcome this obstacle and to maximize the stimulated area in the reservoir, create complex fracture systems, and increase hydrocarbon recoveries, diversion methods are crucial. Diversion methods work by creating a barrier over these areas of least resistance to redirect the stimulation fluids to other areas of the reservoir and maximize stimulation performance. This in turn, can have a significant impact on the overall well economics and productivity.

Diversion methods used in stimulation of oil and gas wells can be broken down into three distinct categories. These categories include mechanical diversion, rate and pressure diversion and chemical diversion. Mechanical diversion includes the use of mechanical tools such as packers, plugs, and perforation ball sealers. Rate and pressure diversion include methods such as limited entry and modified limited entry techniques. Meanwhile, chemical diversion includes the use of particulates or fluid diverting agents. The work of this study is focused on particulate diverters in the chemical category, and specifically biodegradable particulates that are made from polylactide (PLA) resins.

Biodegradable particulate diverters have many advantages over other methods; they are environmentally friendly, made from renewable resources, self-degrading, non-damaging to the formation, and have lower cost as compared to other diversion methods. To perform

effectively, these particulates must remain intact throughout the fracturing operation to create the desired barrier. Later, they completely degrade after the operation is complete to permit flowback from the areas plugged and allow production. Biodegradable particulates can be manufactured to have different physical characteristics including different shapes, sizes, and surface roughness as well as different mechanical properties to meet the different criteria as required by the operation.

The effectiveness of particulate diverters in general has long been questioned in the petroleum industry. The slow degradation rates observed with biodegradable diverters in the field have also been a problem; having to wait for weeks at times before production from the plugged intervals can commence. However, field and laboratory data to date indicate that biodegradable particulate diverters perform better than conventional particulate diverters. This work is aimed at understanding the plugging performance of biodegradable diverters. Specifically, to study how the different physical properties of biodegradable particulate diverters such as their shape and size can affect their plugging performance. The objective of this research also includes understanding the role that different testing conditions, such as temperature, pressure, and time have on their plugging and diverting capabilities. This in turn can help determine whether these particulates can be effective at temporarily plugging perforations and large fractures during stimulation operations. Additionally, this work is intended to find the parameters and conditions that cause the most effective plugging performance, and to understand the flowback potential within a 24-hour period.

A series of laboratory tests were conducted using an Automated Permeability Plugging Apparatus (APPA). The APPA equipment is used to test the plugging performance of different material against slotted discs with different geometric openings to simulate a fracture and a perforation. A total of 56 different tests were completed using seven testing variables including: temperature, differential pressure, heating duration, pressurization duration, different APPA slotted discs, diverter samples with different shapes and sizes, and

finally, the mass of the diverters used. The variables were compared to the testing results, and pictures were taken to document critical observations made during and after testing.

1.1 Research Objective

The goal of this project is to perform lab-based experiments using APPA equipment to understand which parameters govern the effectiveness of PLA diverters. This understanding in turn, can help improve the design criteria for optimal performance of biodegradable particulate diverters. This is accomplished by understanding how the physical characteristics of those diverters along with different testing conditions effect plugging performance. The specific objectives of this research are:

1. Determine the effect of temperature on the plugging performance of biodegradable particulate diverters. The following temperatures are evaluated:
    - 70°F (at room temperature and below the glass transition temperature of the diverters)
    - 150°F (above the glass transition temperatures of the diverters)
    - 200°F.
2. Determine the effect of differential pressure on the plugging performance of biodegradable particulate diverters for the following pressures:
    - 50 psi
    - 200 psi
    - 500 psi.
3. Determine the effect of different heating duration on plugging performance for the following time intervals:
    - 10 minutes

- 30 minutes
- 60 minutes.

4. Evaluate the effect of particulate shape on plugging performance for the following diverters:
    - Coarse flake
    - Coarse bead
    - Blend (a mixture of flake and powder).
5. Determine the minimum amount of diverter required to plug a fracture with 0.12 in. width.
6. Determine the minimum amount of diverter required to plug a perforation with 0.4 in. diameter.
7. Determine the length of time it takes for the different diverters to start plugging a perforation or fracture.
8. Determine if flowback is possible within 24 hours at 200°F using the different diverter samples of beads, flakes, and the blends.
9. Evaluate the plugging performance effectiveness of particulate diverters for four hours under 200 psi differential pressure. These times are within industry averages for an actual stimulation treatment.
10. Determine which parameters have the most effect on plugging performance.
11. Develop a list of recommended design criteria that needs to be considered to design a successful diverting treatment that is optimized.

1.2 Background

Polylactide (PLA) particulate diverters are referred to by many names in the oil and gas literature. Some of the names include biodegradable diverters, degradable particulate diverting agent (DPDA), PLA diverters, engineered diverters, degradable diverters, and self-degradable particulates (SDP). PLA particulates are biodegradable, made from renewable sources such as corn and beets, have minimal carbon footprint, and thus are environmentally friendly.

The molecular formula for PLA is $(C_6H_8O_4.C_6H_8O_4.C_6H_8O_4)_x$ (EPA 2022) and they are known with their EPA CAS identifier number (DiverterPlus 2018a). PLA is a biodegradable polymer from the aliphatic polyester group. Polymers in general have many properties, including phase behavior changes, solubility, physical properties, and mechanical properties. The phase behavior and solubility of polymers, including PLA, depends on the glass transition temperature (T_g) of the polymer. T_g is the temperature at which the polymer will transition from solid (rigid) to a flexible (rubbery) state and eventually to fluid. This process that polymers go through is known as hydrolysis. Other properties that polymers have include mechanical properties, such as toughness and Young's Modulus (Qin 2016).

Aliphatic polyesters, which are biodegradable polymers, include polylactide (PLA), polyglycolide (PGA) and many others. The use of aliphatic polyesters in diversion is not new to the petroleum industry. PGA for example have been used in diverting stimulation fluids since the 1980's but in the form of perforation ball sealers. However, the use of aliphatic polyesters in the form of particulates is more recent and was introduced to the petroleum industry in 2006.

PLA degrade through the process of hydrolysis with time and temperature, changing their form from a solid state and into clear fluid state (Burg 2014). Therefore, there is no need to inject additional fluids or intervene mechanically to remove them from the wellbore. PLA hydrolyzes into polylactic acid and has a glass transition temperature of

around 55°C (131°F) for poly(D,L-lactide), and 63°C (145°F) for poly(L-lactide) (Burg 2014). Meanwhile, PGA hydrolyzes into glycolic acid, has a melting point greater than 200°C and a glass transition temperature between 35-40°C (95-104°F) (Qin 2016).

Aliphatic polyesters, including PLA and PGA, can be engineered to have different physical and mechanical properties. They can be manufactured into different shapes and sizes, including bead, flake, fiber, and fine powder. The manipulation of mechanical properties, such as toughness and impact strength, can be achieved through mixing the polymer with additives. Additionally, the manufacturing process can be used to manipulate other properties, including the glass transition temperature and the melting point temperature. This is done by "altering the degree of branching or cross-linking in the polymer or by the addition of plasticizers" (Qin 2016).

Particulate diversion methods in general work by pumping diverting particulates into the wellbore where they block the path of least resistance to create a barrier over fractures and high permeability zones. In the application of hydraulic fracturing, such diverters block the areas with low stress and high permeability. They form a barrier on certain areas thus diverting the fracturing fluids to the perforation clusters where they are needed to increase the stimulated reservoir volume and achieve maximum stimulation performance.

PLA particulate diverters have been used in many applications in the stimulation of petroleum reservoirs. They can be used to divert in acid treatments, as well as hydraulic fracturing and refracturing operations. They can be applied near-wellbore to bridge on perforation tunnels and inside the near-wellbore fractures. They can also be used in the far-field for hydraulic fracturing to screen-out the tip of the created fractures. This is used to either control the fracture growth to mitigate interference with nearby wells or nearby faults, or to obtain a more complex fracture network around the created main fracture. Usually, powder diverters or a mixture of bead particulates with proppants are used in the far-field application. An illustrative image of how particulate diverters work in near-wellbore and far-field to create complex fracturing systems can be seen in Figure 1.1

(Gomaa et al. 2015).

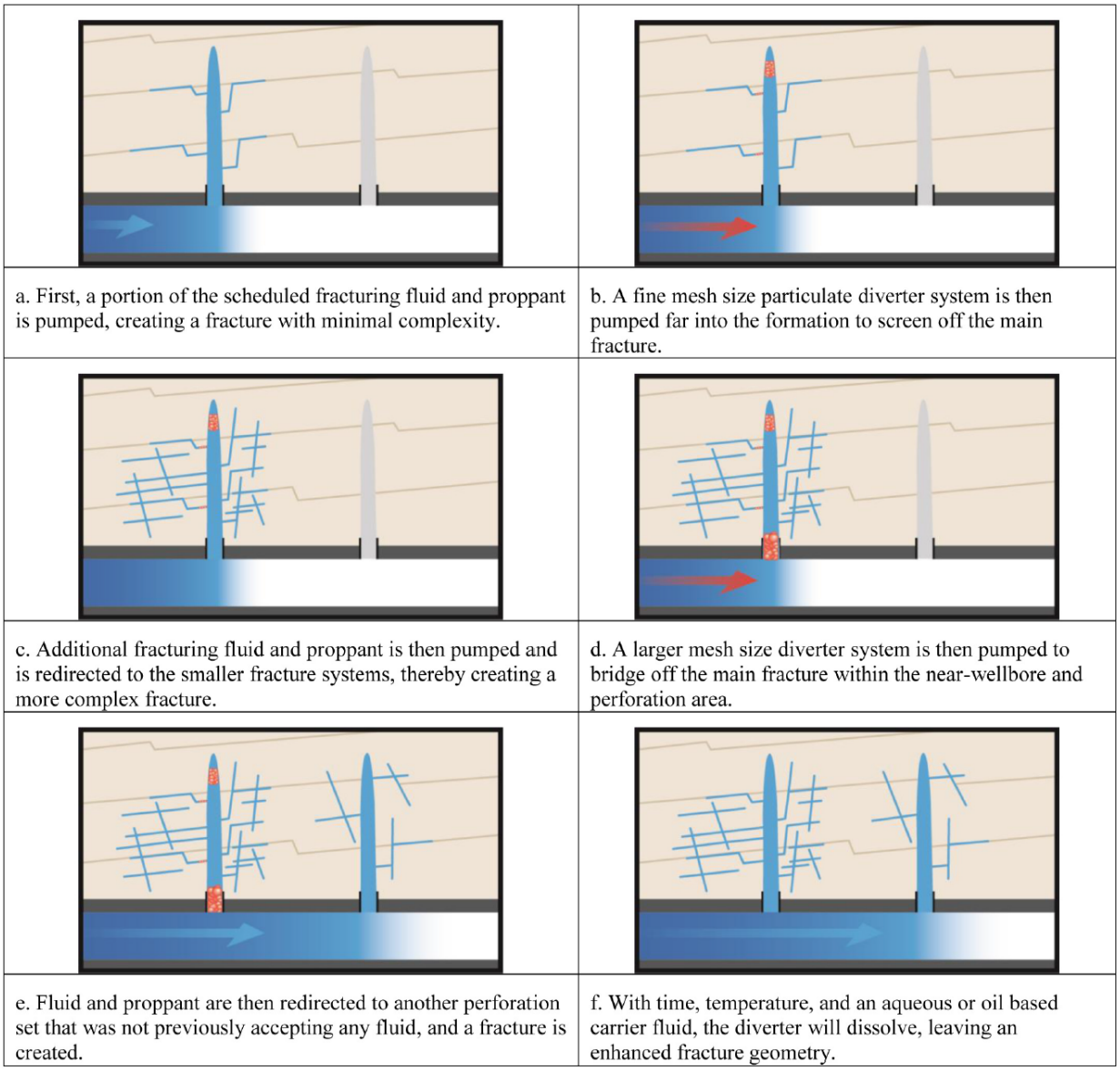

Figure 1.1 An image illustrating how particulate diverters work to help achieve a complex fracture network in far-field and near-wellbore applications (Gomaa et al. 2015).

Diversion methods in the petroleum industry date back to the 1930's. However, conventional particulate diverters started to lose popularity in the 1970's. This loss in popularity was due to many reasons including the difficulty to place particulates in the desired zones. In addition, most of the particulates used at that time dissolved too quickly,

which in turn require a large volume and large particle size to have an effective diversion. Additionally, some of these particulates were difficult to clean-up and completely remove after the stimulation operation is over. In the meantime, fluid diverters were much easier to place downhole, and easier to remove after the stimulation operation is complete. Furthermore, it was easier to pump fluids through gravel pack completions, where particulates were not able to make their way through.

However, particulate diverters still have many advantages over fluid diverters. For example, particulates can be more effective in areas with high stress, where fluids are not as effective in diverting. Moreover, some of the disadvantages of chemical diverters, including both fluid diverting agents and conventional particulates, is the possible formation damage and fluid incompatibility.

Other diversion methods that stayed popular include mechanical diversion. Mechanical diversion methods have always been the most effective type of the three diversion categories. However, mechanical diversion tools, although highly effective, are expensive because they require a rig on site to place them inside the wellbore. Additionally, there is always an inherit risk in mechanically intervening in a well, especially if the well has already been producing for a while. Moreover, the number of mechanical plugs that can be used in a single well has a physical limit. This limit, for example, can be problematic especially in multiple thin-layered formations. All these reasons in turns, translate into the need for effective particulate diverting agents.

Aliphatic polyesters, in the form of particulates, were first introduced to the petroleum industry in 2006 for the application of diverting acid treatments. Particulate diverters made with aliphatic polyesters (including PLA) eliminated many of the major problems associated with conventional particulates and other chemical type diverters. Since they are self -degradable, they do not require the use of additional chemicals to remove them from downhole. Unlike other chemical diverters, they are a much better option for the environment and do not result in formation damage. In addition, they don't dissolve as

quickly as other particulates, such as salt and benzoic acid flakes. These particulates are not limited to be used with a certain carrier fluid such as oil or salt; they can work with any type of stimulation fluid. Moreover, they don't alter the pH of the treatment fluid as other chemical diverters do, making them compatible with both, stimulation fluid and reservoir fluid. All these advantages of PLA and other aliphatic polyesters made them a much more appealing alternative over conventional particulates that were previously used in the industry.

The introduction of biodegradable particulates to the oil and gas industry coincided with the US shale boom that started in the 2000's. Shale formations, such as the Bakken, Eagle Ford, Haynesville, and Niobrara shale require horizontal drilling and multistage fracturing. The use of horizontal drilling and multistage fracturing technology helped transform and unlock these unconventional plays. Although biodegradable particulates were first introduced for diverting acid treatments, they soon started gaining popularity for wider applications, including hydraulic fracturing and refracturing of horizontal wells. This was the case especially since these diverters were strong enough to withstand the high pressures associated with these large-scale hydraulic fracturing jobs that are currently used to stimulate shale formations.

Some of these long horizontal wells are divided into more than 100 stages, by mechanical diversion methods, to hydraulically fracture each stage. These mechanical methods include plugs and sliding sleeves system. Each stage can contain multiple perforation clusters. However, studies show that usually only few of the perforation clusters end up receiving the majority of the stimulation fluid treatment, leaving behind substantial volumes of untapped potential.

To achieve complete coverage and increase the number of stimulated perforation clusters, the aid of particulate diverters can be of critical importance. These particulates can temporarily plug these main dominate fractures and help divert stimulation fluid to the other perforation clusters. In addition, particulate diverters can be used in the far-field

where mechanical methods cannot be applied. Far-field diversion works by pumping the particulates far into the reservoir, usually with the proppants. This helps to screen-out the fracture tip and achieve a much more complex fracture system.

One of the limitations of unconventional shale plays is the high and exponential initial production decline rate. This initial production decline rate can be as high as 90% in the first year. This in turn, coupled with poor initial diversion, make these types of wells great candidates for refracturing operations to help restore production rates and unlock additional pay. The restimulation of some of these wells can even be necessary for the overall well economics. However, to have a successful restimulation, the previously fractured and depleted zones need to be isolated to divert the treatment to new areas of the reservoir. Although mechanical diversion is the most effective method used in the industry today, there is always an inherit risk in using mechanical intervention techniques, especially for wells that have been producing for a while. This in turn makes the use of particulate diverters for refracturing applications even more appealing.

1.3 Research Motivation

Biodegradable diverters, including PLA particulates, are environmentally friendly, made from renewable resources, have a significant lower cost as compared to other mechanical diversion techniques, and can possibly replace mechanical diversion methods in some applications. Additionally, they can increase stimulation efficiency, increase hydrocarbon recovery, maximize the stimulated reservoir volume, and improve the well's overall economics. Even a slight increase in hydrocarbon recovery can have a substantial impact in determining whether a well is economic or not. This is especially important during economic downturns that are periodically experienced in the petroleum industry, where low hydrocarbon prices can make many petroleum fields economically unfeasible.

In the petroleum literature, various laboratory tests and field case studies have been conducted using degradable diverters including PLA particulates. These studies show that these particulates can be applied effectively and successfully for wide range of applications

including hydraulic fracturing and refracturing. Additionally, degradable polymeric particulates were found to be the most effective for diverting treatments in horizontal wells.

Despite the extensive published work that presents evidence of successful and effective application of biodegradable particulates, many operators still question their effectiveness. This is the case especially in hydraulic fracturing and refracturing of horizontal wells. The problem with long degradation time, sometimes up to weeks seen in the field, is another significant issue associated with using biodegradable particulates. Other concerns that operators have include possible ineffective placement of these diverters. Although surface pressure responses indicate effective diversion, operators are concerned that the diverters are possibly plugging some of the perforation clusters that need stimulation. All these reasons are causing many operators to move away from using particulate diverters for both hydraulic fracturing and refracturing applications and reverting to the use of only mechanical methods to divert near-wellbore.

There appears to be few contradictions between the extensive published work on biodegradable diverters and what is experienced by many operators in the field. These contradictions include inconsistencies in placement, pressure responses, and the overall effectiveness. Additionally, there are contradictions in degradation rates and the potential of fast flowback time. For example, the degradation rate in lab studies show quick degradation rates that can happen within few hours, while many operators are experiencing slow degradation rates in the field that can take up to weeks.

The literature review done revealed that current guidelines assume that all particulate diverters behave in the same manner, including biodegradable and conventional particulates. These guidelines include determining the volume of diverters, the shape, and size to use, as well as the required particulates concentration in the carrier fluid. This has resulted in recommendations that usually assume that the effectiveness of biodegradable particulate diverters, like conventional particulates, is based on optimizing the particle size distribution to lower the permeability of the diverters-pack and deliver the appropriate flow

resistance to achieve diversion. The effect of temperature on plugging performance of biodegradable diverters has not been previously studied nor accounted for. This includes the effect of temperature on the plugging performance of different shapes and sizes of particulates.

This work is aimed at understanding the plugging behavior and performance of biodegradable particulates under different conditions. Tests were conducted to understand how different parameters and conditions including pressure, temperature, diverter shapes and sizes effect their performance. This in turn can help develop some recommendations in selecting the appropriate parameters to consider when designing the diverter pill in order to optimize the particulate's plugging performance. The results of this research will help in addressing some of the concerns that many operators have regarding the particulate effectiveness and inconsistent results, as well as the longer flowback times experienced. In addition, to shed some light and offer explanations behind the contradictory results between field operations and the literature.

1.4 Research Contribution

Contributions from this work include the following:

1. Present laboratory data that help in understanding the plugging behavior of biodegradable PLA diverters under different testing conditions.

2. Demonstrate that biodegradable particulates do behave much differently than conventional particulates. Failing to take this difference into consideration can lead to negative and detrimental effects during field operations.

3. Demonstrate that PLA diverters and other aliphatic polyesters do have a significant advantage over conventional particulates in certain applications. This notable advantage stems from the ability of the different particulates to deform above their glass transition temperature. This deformation causes the particulates to bond together and achieve an effective seal under minimal differential pressure.

4. Demonstrate how this advantage along with the particulates plugging behavior below and above their glass transition temperature can have significant effect on how to design the most effective particulate diversion pill.

5. Provide some design recommendations, which include selecting the appropriate diverter shape, size, grade and volume.

6. Provide data and explanations concerning degradation times and flowback potential. This includes explanation on why flowback can take longer than expected in the field.

7. Demonstrate how faster flowback potential can be achieved by designing the appropriate diversion pill.

8. Provide a summary of conditions and parameters that have the most effect on the biodegradable diverter's plugging capabilities and ideas on how to utilize this information and use them for field applications.

9. Last, provide recommendations for future work concerning particulate diverters to understand their behavior during field operations.

Understanding the plugging performance and behavior of degradable particulate diverters can result in better design and better field application. By correctly designing the diversion treatment and correctly applying them in the field, effective diversion will result. This effective diversion in turn can increase stimulation efficiency, maximize the reservoir stimulated volume, increase hydrocarbon recovery, and unlock the vast untapped reservoir potential to improve the overall well economics.

CHAPTER 2
LITERATURE REVIEW

The literature review done for this work includes a historical overview of how the use of diversion techniques in the oil and gas industry evolved over the years. In addition, a more extensive review has been done on degradable particulate diverters specifically. This extensive review includes a summary of literature on laboratory experiments conducted on degradable particulates as well as field case studies. Moreover, the literature review includes a summary of theoretical models and industry guidelines that have been proposed over the years regarding optimum particulate diversion designs.

Based on the literature review done for this research, it was observed that most particulate diverters, including biodegradable particulates, were developed, or introduced for acidizing applications and for vertical wells. However, these particulates were later tested with encouraging results in horizontal wells and for hydraulic fracturing and refracturing in the near-wellbore and the far-field applications. Moreover, it was observed that current guidelines for particulate diversion designs assume that biodegradable diverters behave in a similar manner as conventional particulates. These design criteria usually consist of achieving a particulate pack permeability that is low enough to generate the required flow resistance and allow the stimulation fluid to be diverted to other zones and perforation clusters.

2.1 History of Diversion

The first documented use of a diversion technique in the petroleum industry utilized chemical diverters. The need for a diverting agent came about after the industry started using hydrochloric acid for stimulation purposes in 1932 (Harrison 1972). Haliburton Oil Well Cementing Co. was granted a patent in 1938 for a calcium soap solution for the use of diverting acid treatments. This calcium soap solution is insoluble in water but soluble in oil

and forms a precipitate upon reacting with calcium chloride. This solution in turn can help in plugging water zones to divert the acid treatment to the oil-bearing zones that require the acidizing treatment and to prevent acidizing the water-bearing zones (Clason 1938).

During the 1930's and early 1940's, most wells were shallow wells drilled up to 5,000 ft deep and were open hole completions. The main use for diversion was to avoid acidizing into water zones in water drive reservoir systems. Additionally, most wells drilled in the USA at that time were targeting carbonate reservoirs in the Permian Basin. These reservoirs were usually treated with low volumes, averaging 2,000 gallons of acid (Harrison 1972).

Haliburton and other service companies started to develop and use different material for the purpose of diverting acids in shallow open hole wells. Some diversion material included sulfuric acid, calcium chloride solutions, locus bean gum, and emulsions. However, many of these materials did not become popular. For example, sulfuric acid was believed to cause permanent formation damage. Additionally, material made from locus gum required the use of a breaker after the treatment was completed, to lower the viscosity of the diverter (Harrison 1972).

In the 1940's, new stimulation techniques were introduced. The use of hydraulic fracturing as a stimulation technique was invented in 1947 and first documented in a paper written in 1949 by Clark et al. This new stimulation method included the injection of large volume of fluids at a pressure higher than the formation fracturing pressure. This injection of large volumes of fluid at high pressures creates fractures in the formation. After creating these fractures, an injection of fluid with sand is required to keep the fracture open and allow more formation fluid to flow into the wellbore. The paper written by Clark in 1949 also introduced a multiple fracturing technique, which is known today as multi-stage fracturing. This technique utilizes the use of packers to separate the well into different zones or stages to divert stimulation fluid and achieve multiple fractures around the wellbore (Clark 1949).

This new stimulation technique proved to be very successful, and many operators utilized it in unlocking pay that was not previously accessible. After the introduction and utilization of this new and successful method of stimulation, the use of packers for diversion to achieve multi-stage fracturing proved effective and became popular (Harrison 1972). However, packers are expensive to use, especially since their installation and removal require more operation time and the use of a rig. This higher cost associated with using a rig can make the utilization of packers uneconomical in certain wells. Therefore, there was a demand for new diversion methods as well as diversion chemicals that are compatible with hydraulic fracturing fluid.

As deeper wells were drilled and higher volumes of stimulation fluids were used, there was a need for diverting agents that can withstand higher formation temperatures and pressures. One such material was naphthalene. In 1954 naphthalene, also known as mothballs, started to be used as a diverting material especially for acidizing. The advantage of naphthalene is that it only sublimes at temperatures higher than 175°F. In addition, naphthalene is oil-soluble, making it easy for cleaning up the diverters once the wells are put into production (Harrison 1972). However, some of the disadvantages of naphthalene is that it is highly soluble. Therefore, the particulates need to be large enough so that some material is still available by the time the diverter is delivered downhole. Moreover, naphthalene tends to shatter under stress, making them ineffective in hydraulic fracturing (Watanabe 1967).

This demand for chemical diverters for the use in different applications contributed to testing various materials in the 1950's. Some of these materials included crushed limestone, gilsonite, sodium tetraborate, and rock salt. Soon after, rock salt became the most popular diverting agent as it was inexpensive, readily available, safe to handle, and easy to use (Harrison 1972).

As the industry started to move from open hole completions and toward perforated casing, additional methods to divert fluids in perforated wells were introduced. Ball sealers

are one example of such methods. In 1956, the Western Co. introduced the use of rubber ball sealers to divert stimulation fluids in perforated wells. The ball sealers have a spherical shape and come in different size diameters. They are used to seal off perforations inside the casing. However, the perforation must be in good condition for the ball sealers to sit on the perforations and successfully seal them. If the perforations are slightly damaged, diversion cannot be achieved (Harrison 1972). Another important advantage to using ball sealers is that they can be used in multi-stage fracturing (Kastrop 1956). The use of ball sealers in multi-stage fracturing helped decrease the cost associated with using packers that were necessary to space out the fracturing stages.

In the 1960's, there was significant progress made in diversion techniques. A new method that uses pressure and rate variation was invented and tested by Shell Oil Co. A new mechanical diversion technique called frac baffles was also introduced. In addition, a myriad number of chemicals, including particulates and fluids, were tested and applied in the field, including swellable polymers, wax-polymer mixes, benzoic acid flakes and foams.

In 1960, Lagrone and Rasmussen from Shell Oil Co. introduced and tested a new diversion technique. The new method, called the limited entry technique, uses pressure and rate variation to achieve diversion. Diversion through this technique is achieved by "(1) limiting the number of perforations in a well and (2) providing sufficient injection rate to require the restricted flow capacity of the perforation to divert the treatment to a greater portion of the perforated interval". This technique helps in breaking down multiple perforations resulting in multiple fractures. In this study, Shell Oil Co. preformed this method on 363 wells between 1960 and 1963 and used gamma ray tracers to quantify the effectiveness of the technique. The results of this new limited entry technique showed an improvement in stimulating additional pay. However, this technique has some limitation. The inventors noted that the stimulation fluid did not reach all the pay zones in the targeted reservoir (Lagrone and Rasmussen 1963).

In 1962, DOW Chemical Co. introduced a synthetic polymer in a dry solid form. The particles from this polymer can swell up to 40 times their original volume when submerged in hydrochloric acid. The polymer, once it absorbs the acid, can deform and seal off fractures, allowing additional acid to divert to other areas. The polymer was effective as a fluid loss additive as well as a diverting agent in acidizing treatments due to its pliability. Furthermore, the polymer deteriorates with time, allowing the absorbed acid to slowly disperse, which in turns allow the acid to penetrate deeper into the formation (Carpenter and Ernst 1962).

Along the progress made in chemical diversion, new mechanical diverters were also being introduced in the 1960's. For example, Haliburton filed a patent in 1963 on an invention called frac baffles, and the patent was granted in 1966. This method is one of the very few diversion methods invented specifically for the purpose of achieving multiple hydraulic fractures (Schell et al. 1966). Figure 2.1 shows an image of a frac baffle, which is used to shut off an entire lower zone after fracturing it. This will then help to divert fluids to an upper zone to fracture it, which limited their application capabilities to successive zones (Harrison 1972). Mechanical diversion techniques are relatively more expensive than the techniques that utilize chemicals. Therefore, more attention and research were directed toward chemical diversion techniques during that time.

One of the polymer-based materials that was developed and used during the 1960's includes the unibeads ™ introduced by Union Oil Co. of California and patented in 1967. Unibeads are polymer-wax blends that can be used as blocking material. These beads were one of the first chemical diverters that were specifically invented for hydraulic fracturing applications. Some of the advantages of these beads include their solubility in oil and insolubility in water. Moreover, they are deformable and degradable at temperatures ranging between (100-150°F) depending on their composition. This advantage keeps the beads in a solid form while they are being pumped into the formation in the relatively low-temperature carrier fluid. In addition, since the particles are deformable under certain

temperatures, they can completely seal the fractures or opening that needs to be plugged. Furthermore, once the temperature of the particles increases to the formation temperature, they start to dissolve, making for easier downhole cleanup (Watanabe 1967).

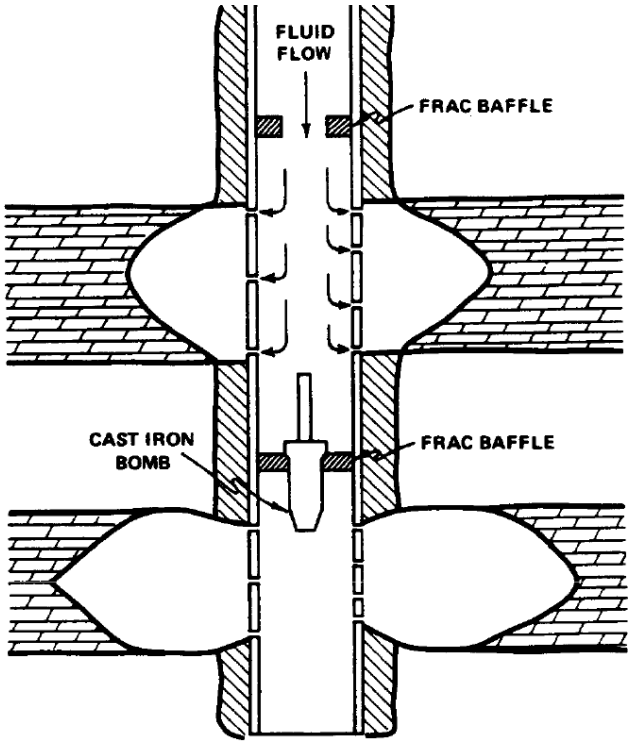

Figure 2.1 A drawing of a frac baffle (Harrison 1972). Frac baffles were invented for the use in multiple hydraulic fracturing treatments.

The time it takes for the beads to dissolve can be controlled based on the hydrocarbon-waxes and polymer material used, and their respective concentrations. In addition, hydrogenated oil can be used instead of hydrocarbon waxes, as well as a mix of the two. The preferred polymers that were introduced in the patent for the beads have a low softening temperature (130-150°F) to make sure that the beads deform and achieve a good seal. Some of the polymers that can be used include "synthetic resins such as polyethylene, polypropylene, polybutylene, polyisoprene, polyisoprene, polyisobutene, copolymers of ethylene and vinyl acetate, copolymers of ethylene and ethylacrylate, copolymers of ethylene and methylacrylate, polyvinyl chloride, and the like" (Watanabe

1967).

The use of such wax-polymer beads proved successful in acid treatments as well as hydraulic fracturing treatments. Another advantage of these beads is that they can be manufactured in different sizes. Most common sizes used are either coarse button particles, ranging from 0.125-0.250 in. diameter, or finely graded particle ranging from 8-100 mesh. Their use as a diverting agent aided in accessing additional pay zones and at relatively low cost (Harrison 1972).

Another diversion material that has been used and widely accepted since the 1960's is benzoic acid flakes. Those flakes are soluble in both oil and water and at low temperatures. In addition, their use was proved successful of diverting stimulation treatment especially for acidizing. Benzoic acid works by establishing a filter cake on the formation, allowing the treatment fluids to divert to untreated zones, where additional pay can be accessed. One of the main advantages of benzoic acid is their ability to dissolve in low-temperature reservoirs, which make for easy and fast cleanup after operation (Harrison 1972). This means that their application includes formations with lower temperatures. However, benzoic acid flakes have high solubility in water, making beads a better option for hydraulic fracturing. The only advantage of benzoic flakes over the wax-polymer beads in hydraulic fracturing applications, is their usability in low temperature formations.

In 1969, Smith et al. discussed the use of foam as a diverting agent and included field case results for acidizing applications. Some of the advantages of foam is that it could be applied in different types of completions, including open hole, perforated cased hole, and gravel-packed completions. In addition, the foam blocks inside the formation, as opposed to near-wellbore. Moreover, the foam can be applied in wide range of temperatures up to 250°F and they are soluble in both water and oil (Smith et al. 1969). The use of foam started to become popular and is still used today as a diverting agent especially in acid treatments.

Up until the 1970's the main purpose of using diverting agent was to prevent the stimulation of water-producing zones, to bypass already stimulated zones and or naturally fractured zones, or to stimulate multiple intervals to achieve multi-stage fracturing. However, newer techniques were being introduced that help achieve a more complex fracture system, by creating a barrier in the far-field, as Smith et al. (1969) discussed with the use of foam. This in turn helps to prevent leakoff and to create a more complex fracturing network. This is a little different than the techniques used previously, where chemical diversion was applied on or inside the perforation tunnels, inside the fractures, or on the formation in the near-wellbore.

One example of these methods includes a method described by Hannah in 1976. The author described a hydraulic fracturing technique that uses a "extremely viscous, non-Newtonian water gel that exhibits a yield point and follows the Bingham plastic model". The fluid is pumped with sand and the pumping stops for a period of time to allow the fracture to partially close. This creates an overpressure that causes diversion. Pumping then resumes, which can help open more fractures either vertically or laterally. This technique helps opening multiple fractures within the same stage, which helps achieve a more complex fracturing system and increase pay. This technique worked in the Mississippian Trend in Oklahoma where regional stresses were low enough, making the diversion achievable with the fluid. However, this technique was limited to areas with low regional stresses (Hannah 1976).

In 1978, Hill et al. described a technique that uses diverting agents, as well as high rates and high volumes of fracturing fluid to fracture an entire vertical length of a formation. This in turn can achieve complete fracturing coverage of the entire zone as opposed to fracturing limited number of intervals; thus, improving the productivity of thick formations that previously had low productivity, such as the Austin Chalk formation. The technique is aimed to achieve both casing and formation diversion. Hill et al. proposed that to obtain this full coverage, a use of ball sealers (casing), along with crosslinked

polymer, and high injection rates and volumes are required. This in turns create multi-stage fracturing and results in complex fracture systems. A fracture is initiated by injecting high volume of fracturing fluids at a high rate and followed by pumping crosslinked polymers to divert fluids within the fracture. Additional injection of high volumes of fracturing fluids at high injection rate is then resumed to achieve complex fracture network within the same stage. Once a stage has been fractured, ball sealers are used to plug the already fractured stage. This in turn helps to divert fracturing fluids into another stage and initiate even more complex fracture networks. This diversion method was tested in the Austin Chalk formation, with good results that improved the overall economics of these wells (Hill et al. 1978).

During the 1970's and 1980's, more fluids were being introduced, studied, and used in the field for diverting stimulation treatments. Especially since the use of fluids as diversion agents in both acidizing and fracturing applications had seen encouraging results coupled with lower costs as compared to the use of mechanical diversion practices. Some of these fluids included foams, polymers with Bingham plastic properties, self-gelling, acid-activated and water-activated, as well as visco-elastic diverters. During these times, fluids were also becoming more favorable than particulates because they were easier to place and easier to clean up downhole. Additionally, fluids and foams can be used in gravel packed completed wells, where particulates were hard and at times, impossible to pump through.

One of the new fluids that was being introduced and used included a surfactant that is soluble in hydrocarbons. The surfactant is then mixed with dry hydrocarbon and the mixture turns into a gel substance once it encounters water. This causes the material to set in water, therefore diverting the acidizing treatment to the oil-bearing zones and preventing the acid from contacting the water-bearing zones. The authors shared field tests results from 12 wells. The results proved that the use of this material is an economical diverting option for the application of acidizing treatments especially in limestone and dolomite formations (Groves et al. 1981).

High friction gel (HFG) was another fluid that was studied and applied in the field as describe by Wiley in 1981. The HFG was successfully tested in the San Andres Field to help divert acid in a carbonate reservoir. The use of the gel proved successful where multiple intervals were shown to have been treated as indicated by temperature logs. This field study showed that HFG had better vertical sweep efficiency than benzoic acid flakes and even straddle packers when diverting acid treatments (Wiley 1981).

In 1988, Erbstoesser et al. patented the use of ball sealers made from polyester polymers to seal casing perforations and achieve diversion of stimulation fluids. Although the use of degradable polymers was not new, this invention was the first to use degradable polyester polymers to make ball sealers. The type of materials proposed by Erbstoesser et al. is insoluble in wellbore fluid but degrade in fluids at high temperatures. The author further describe the material that can be utilized in making these ball sealers as being "selected from the group compromising poly(D,L-lactide), cross-linked poly(D,L-lactide), and copolymers of glycolide and D,L-lactide". Since the material is insoluble in neither water nor oil, their use can be more effective because wellbore fluids usually contain both. Moreover, these polymers degrade only at high temperatures and with time, which means the ball sealers can perform and plug the perforation during the entire duration of the stimulation treatment. When the ball sealers degrade, they become smaller molecules, called oligomers. The oligomers in turn can become partially soluble in oil or water allowing them to easily flow back to surface and commence production. The degradation of the material can start in temperatures ranging between 45–200°C. The degradation process can take between one to seven days. The well can be shut off after the treatment to allow the formation to return to its original temperature. However, the author recommends the injection of steam or other hot liquids if speeding up the degradation process is necessary. When they tested the different types of degradable diverters, they found that PLA and crosslinked PLA are some of the best options to use in this method (Erbstoesser et al. 1988).

During the 1980's more wells were being drilled horizontally. It was soon evident that diversion was crucial for effective stimulation of the lateral for both acidizing and fracturing applications. However, all the particulate diverters that have been developed up until then were designed for vertical wells. Bell et al. (1993) was one of the first published work that discusses the application of using diverters in horizontal wells. The authors tested different diverters that were being used in the industry in vertical wells to find the ones that could perform best in horizontal wells. The study concluded that the use of wax buttons and beads were the best diverting agents to use in open hole horizontal wells. (Bell et al. 1993).

In their 1997 paper, Dingxiang et al. describe a new method called the technique of multi-fracture fracturing using diverting agent (TMFUD) and tested it in the field. In this method, up to nine thin sand interlayers within a zone can be fractured using particulate diverters. Only 2-4 sliding sleeves are used to break down the well into other stages where each one of those stages contain up to nine thin sand layers. Therefore, achieving multiple hydraulic fractures with the use of particulate chemical diverters, which is done in a consecutive order and starting with fracturing a thin sand layer followed by pumping particulate diverter to plug the created fracture. Next is preforming another fracturing treatment to fracture another layer while repeating the processes until up to nine thin layers have been fractured before having to move the string and use another sliding sleeve. This method was much more economical to use, specially that using a sliding sleeve for each thin interlayer was not physically or economically possible. 1524 oil wells and 303 water injection wells were fractured in the Daqing Field by the "multi-fracture fracturing" method. The method was successful where 50% production increases were seen as compared to conventional fracturing techniques usually used in the field. Moreover, the method was proved successful in increasing the injectivity of water injection wells (Dingxiang et al. 1997).

At the turn of the century, more chemicals were being developed and tested as diverting agents. For examples, Chang et al. developed a novel self-diverting acid (SDA)

using a visco-elastic surfactant (VES) in 2001. While utilizing this system, acidizing and diversion can be achieved using the same chemical in one step. This is accomplished as the solution develops and becomes viscous when the acid reacts to the carbonate formation. This in turn causes the diversion of additional acid to the zone of interest. The viscous gel later breaks down by either flushing a solvent, or once it contacts the produced hydrocarbons. The chemical was tested in the lab showing promising results (Chang et al. 2001). By 2003, approximately 70 wells have used this novel diverting agent. Taylor et al. discussed the application of this chemical on a new well that was not producing due to formation damage, and on a water injector well where injectivity was declining. The non-producing well IP'ed at 2350 BOPD, a rate much higher than what was expected. Meanwhile, the water injector showed 24% increase in injectivity (Taylor et al. 2003). Later, Lungwitz et al. (2004) and Zelier et al. (2006) conducted case studies using this system with promising results.

Although the use of degradable polymeric diverting methods was introduced much earlier, Glasbergen et al. (2006) introduced similar polymeric material but in the form of particulates. These particulates completely degrade under certain temperatures with time. The name given for this proposed novel diverting agent is degradable particulate diverting agent (DPDA). The DPDA is made from polymeric material, which degrade through hydrolysis with time and temperature. Some polymeric material includes "polymers such as polyanhydrides, polyesters, polyorthoethers, polylactones, polyamides, and polyurethanes are such material". These materials can be manufactured to have different properties, including rigid or pliable, varying degradation rate, different sizes and shapes, and varying degradation temperature ranging from room temperature and up to 400°F. Initially, the authors proposed this material for the use of matrix acidizing application (Glasbergen et al. 2006).

The chosen material for the study conducted by Glasbergen et al. (2006) was aliphatic polyester that is rigid. It degrades by hydrolysis, with the degradation rate between six

hours at 250°F and up to seven days at 200°F. Some of the disadvantages seen in other conventional particulates were eliminated with the use of this DPDA, making DPDA a more favorable option to use. Some of the problems and disadvantage that were eliminated include the requirement of using other chemicals to clean up the diverters after stimulation to remove them. In addition, DPDA has limited solubility at surface conditions, but degradable at bottomhole conditions, and have negligible environmental impact. Moreover, the permeability of a particulate pack can be controlled to meet the set requirement. The novel diverting agent was tested in both, the lab and the field. The authors specified that the type of the polymeric material used in this experiment is aliphatic polyester (Glasbergen et al. 2006). Aliphatic polyester are biodegradable polymers. However, the authors did not specify the actual chemical composition of the diverters used in their lab and field studies.

The introduction of biodegradable diverters, although for acidizing applications, coincided with the shale boom the utilizes horizontal drilling and multi-stage fracturing technology. Multi-stage fracturing in horizontals traditionally use mechanical methods for diversion, such as plugs and sliding sleeves, to divide the length of the horizontal section into stages. In addition, large volumes of fracturing fluid are generally used. Soon, companies started to test whether these biodegradable particulates can help maximizing the number of perforation clusters that receives the stimulation fluids especially since field data shows that usually only few perforations clusters end up receiving most of the hydraulic fracturing treatment, leaving a lot of untapped potential. This in turn can help accessing additional pay and maximizing production potential especially that the success of shale plays relies heavily on the success of the hydraulic fracturing treatment.

Some of the applications in shale include fracturing (Daniel et al. 2007) and refracturing (Allison et al. 2011). Meanwhile Arnold and Fragachan (2014) completely replaced using mechanical diversion methods and used the biodegradable particulate diverters for the entire horizontal well. These studies and others are discussed in detail in

the field studies section. In 2012, McNiel et al. introduced another technique for far-field diversion to dilate the natural fractures and achieve a more complex fracturing systems in unconventional reservoirs. This was done by using coiled-tubing fracturing with downhole mixing method (CTFDM). Far field diversion with the CTFDM method was applied to overcome stress anisotropy, further opening natural fractures, creating complex fracture system, and maximizing the contact area with the reservoir, which in turn increases productivity. The technique includes monitoring the pressure during the fracturing treatment and making required changes based on observations made in real time to make sure a complex fracture system is achieved (McNiel et al. 2012).

Soon, the slow degradation rate of biodegradable diverters started to become an issue in many applications. The degradation rate took longer than desired, postponing the process of flowback and production. In 2013, Reddy and Cortez proposed a solution for the prolonged degradation of polymeric diverting material. They conducted laboratory experiments for activator development to understand how to control and speed the degradation process for these degradable materials (Reddy and Cortez 2013).

2.2 Laboratory Experiments Done on Degradable Diverters

Based on the literature review performed, diverting particulates' performance is based on the ability of the different particles to achieve a filter cake, or a permeability pack that is low enough to cause resistance and divert the injected stimulation treatment to the zone of interest. However, further studies on the wax beads revealed an advantage of their use over other diverting particulates. Gallus and Pye studied the mechanical behavior of polymer-wax blends in the lab in 1969. They found that wax-polymer beads' most notable advantage is their ability to deform above the congealing temperature. This in turn makes their ability to cause better resistance increase, resulting in better diversion performance (Gallus and Pye 1969).

Gallus and Pye found that the ability to reduce fluid loss through the wax-polymer diverters was much better than that of rock salts or naphthalene. This is due to the ability

of the wax-polymers to form a very low permeability seal that was developed by the deformation of the particles under differential pressure above the congealing temperature. The results of this comparison can be seen in Figure 2.2. However, one limitation of the wax-polymer is that it needed to be mixed in oil to work, or in water if they are used with surfactants (Gallus and Pye 1969).

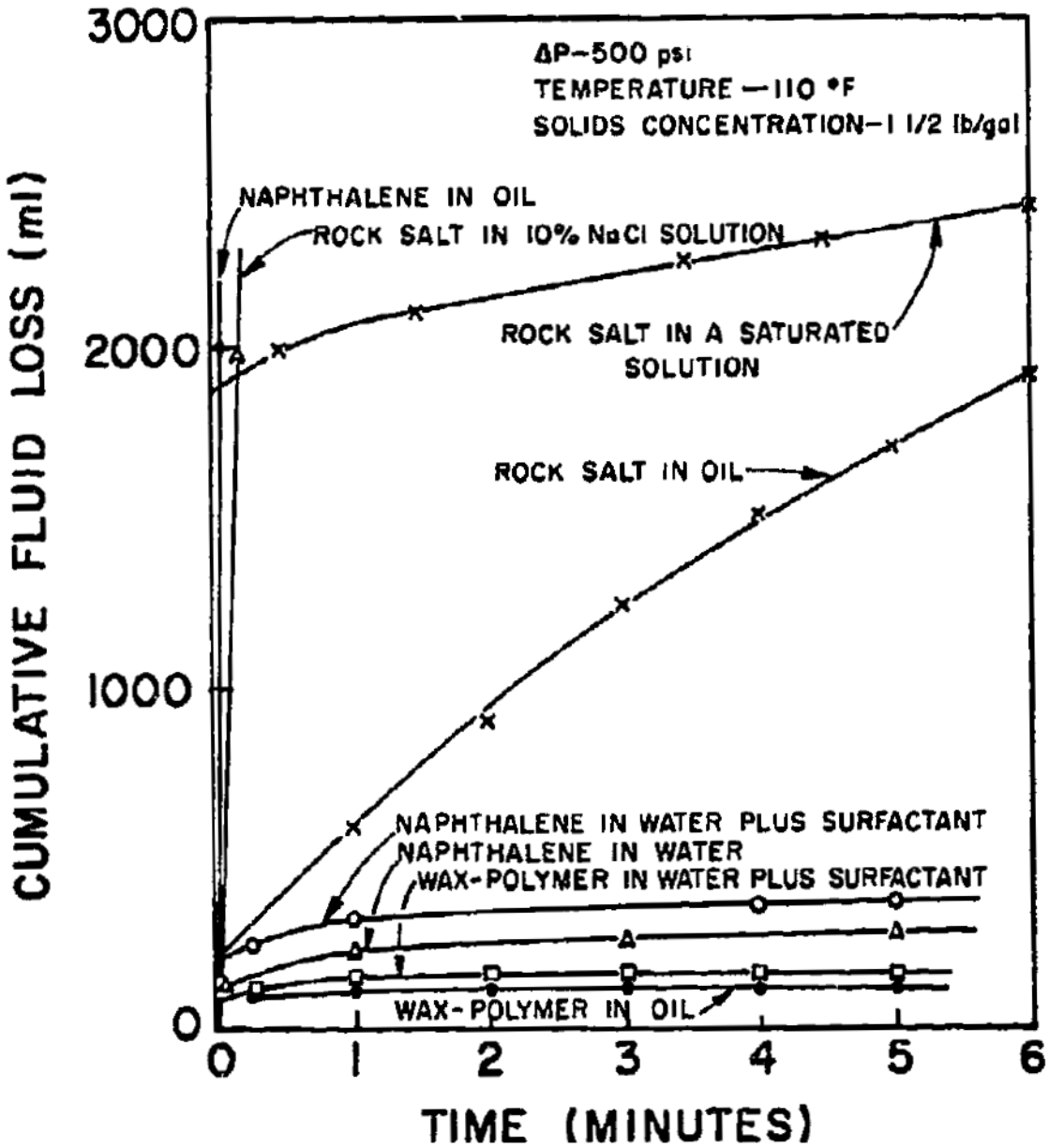

Figure 2.2 A graph comparing the results of the sealing capabilities of rock salt, naphthalene and wax-polymers. Looking at the cumulative fluid loss, the wax-polymer diverters in oil had the best plugging performance (Gallus and Pye 1969).

In addition, Gallus and Pye studied the changes in mechanical properties of the wax-polymer beads as a function of temperature. They found that the hardness and the impact strength of the wax-polymer particulates change with temperature as seen in Figure 2.3. The impact strength of the particulates gets substantially higher between 90-100°F and is at its highest at the beginning of the transition zone between breaking and bending. However, once in the transition zone between breaking and bending, the strength continues to decrease. While on the other side, the Brinell Hardness values continually decrease as temperature increases before stabilizing (Gallus and Pye 1969).

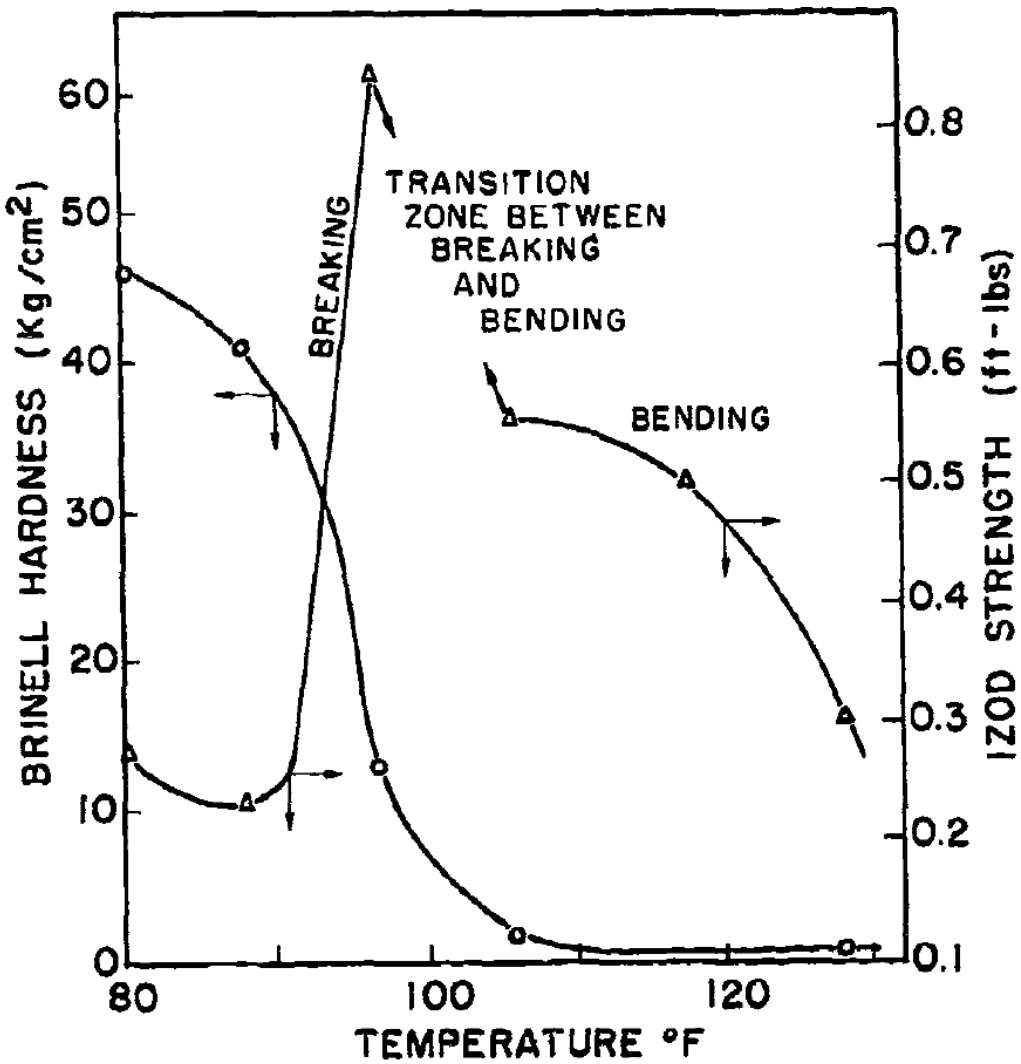

Figure 2.3 A graph showing the results for the changes of Brinell Hardness and Izod Strength of the wax-polymers with temperature (Gallus and Pye 1969).

Laboratory tests were done on degradable diverters and the results were published in the study conducted by Glasbergen et al. (2006) who introduced the degradable diverters in particulate form. The authors tested the degradation rate of the DPDA in seawater at 250°F in a high-pressure cell. The height of the diverter pack with time was recorded as the particulates degrade. This degradation test was done with and without pressure. The authors found that the pressure had minimum influence on the degradation rate. The relative height of the particles was decreasing slowly at first going from 100% to approximately 80% in eight hours. However, after 8 hours, the relative height started to drop dramatically and went from approximately 80% to zero in only 3.5 hours. The degradation rate test results can be seen in Figure 2.4 (Glasbergen et al. 2006).

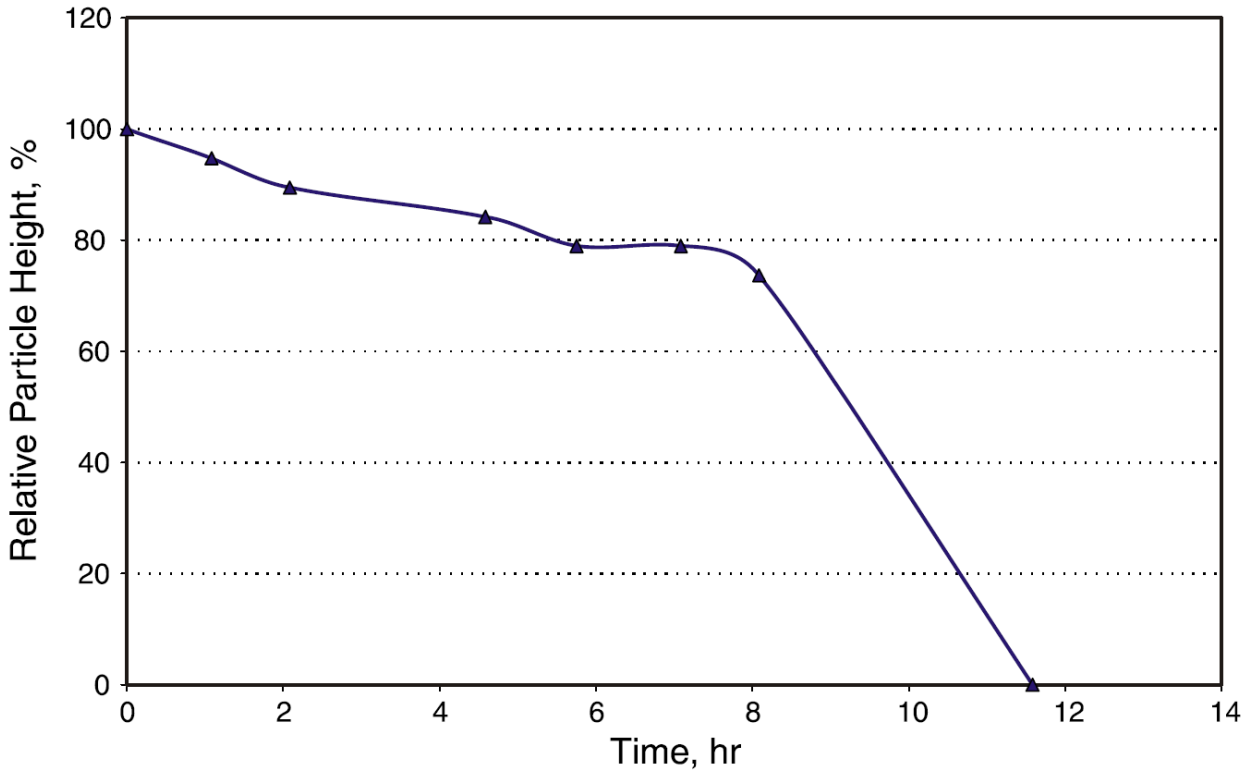

Figure 2.4 A graph showing the degradation rate of the degradable particulate diverters in seawater at 250°F. The degradation rate was measured as the change of the particle's high with time at high temperature (Glasbergen et al. 2006).

Another part of the experiment conducted by Glasbergen et al. included testing the permeability of the diverter pack. Permeability was determined without applying any pressure to the diverter pack, and while applying differential pressure in incremental values. They found that differential pressure has a significant impact on permeability. The initial permeability of the diverter pack was 2,700 mD with no differential pressure and decreased to 1,000 mD after applying 1,150 psi differential pressure. The results of the permeability tests can be seen in Figure 2.5 (Glasbergen et al. 2006).

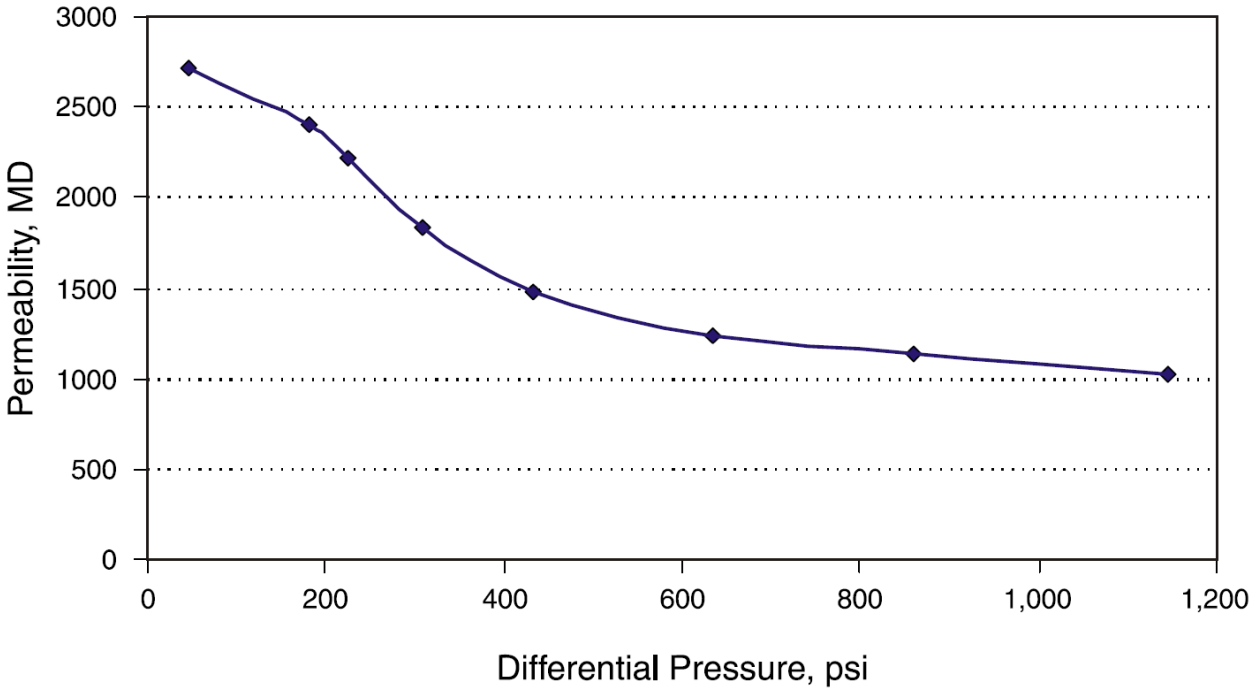

Figure 2.5 A graph showing the change of permeability of the diverter pack with differential pressure. Differential pressure have an impact on the pack permeability (Glasbergen et al. 2006).

In 2014, Reddy and Cortez studied degradable diverters extensively in the lab to understand the degradation process and how it can be accelerated. Some of their most notable conclusions included that the degradation rate can be different if the polymers used are amorphous versus semi-crystalline. For example, they found that amorphous aliphatic polyesters degrade faster than semi-crystalline ones. Moreover, water was effective

for degrading amorphous but not semi-crystalline aliphatic polyesters where water ends up causing the semi-crystalline polymers to swell. (Reddy and Cortez 2013).

In 2015 Okura et al. published a study done using polyglycolic acid (PGA) but in the form of degradable ball sealers. They tested PGA with different additives in the lab to formulate degradable tools with desired properties. Their aim was to form a mixture of PGA and additives that will result in ball sealers that will be suitable to use with low temperature reservoirs. The issue they were aiming to solve is that PGA frac balls can shatter while using them in reservoirs with low temperatures. Therefore, they were successful at formulating a mixture that improved the impact strength of the balls to prevent them from shattering at such conditions (Okura et al. 2015).

The reason that the authors used PGA as opposed to other aliphatic polyesters is their advantage that they degrade faster than other polyesters such as PLA and polyethylene. The stated that the reason that PGA diverters degrade faster is "because of the large numbers of hydrolysable ester groups per unit volume". The results of how PGA degrade with temperature and time can be seen in Figure 2.6 (Okura et al. 2015).

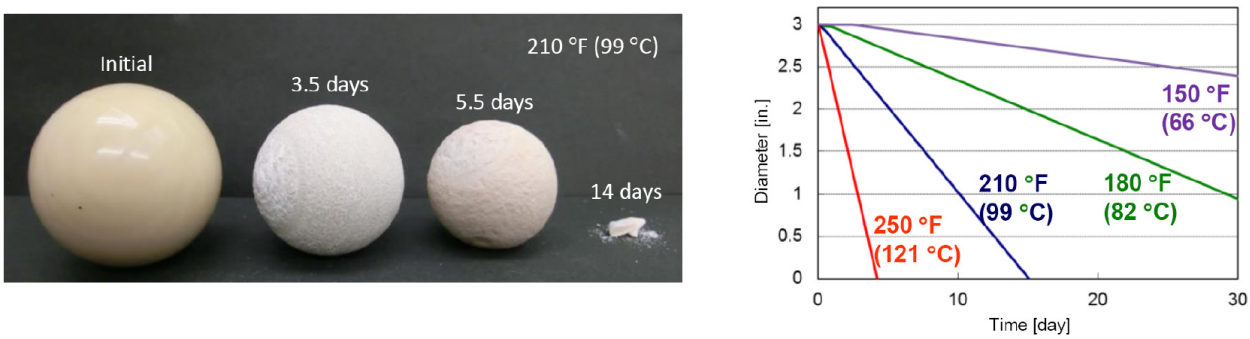

Figure 2.6 The effect of temperature on degradation rate of PGA and the decrease of the diameter of the PGA frac balls with time (Okura et al. 2015).

Additional tests conducted by Okura et al. include how the impact strength changes with temperature as seen in Figure 2.7. The authors also compared the compressive strength of PGA to other polymers (Figure 2.8). As seen in Figure 2.8, PGA has a higher compressive strength than other polymers including PLA. Based on their results, the

authors found that core-shell impact modifiers, including poly(butyl acrylate) core with methyl methacrylate copolymer or methyl methacrylate homopolymer shells, as well as butadiene-styrene core with methyl methacrylate copolymer shell, helps to toughen the PGA to prevent the ball sealers from shattering at low temperatures (Okura et al. 2015).

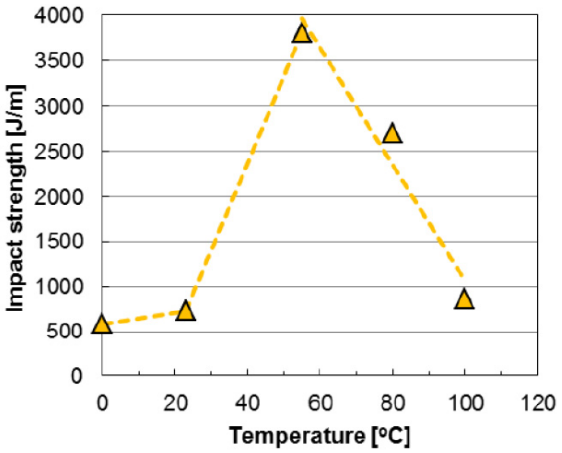

Figure 2.7 Test results showing the change of the impact strength of PGA with temperature (Okura et al. 2015).

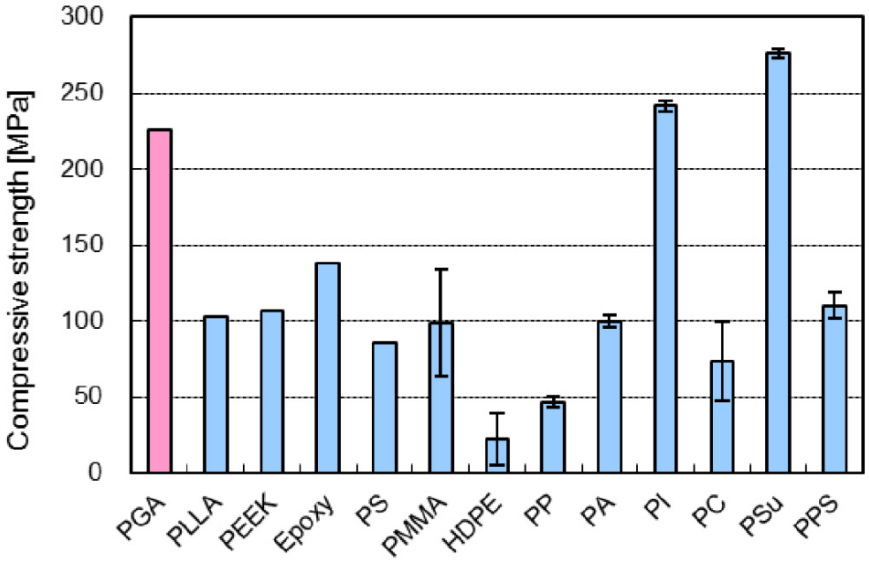

Figure 2.8 A graph comparing the compressive strength of PGA to other ball sealer materials including poly-L-lactic acid (PLLA), polyetheretherketone (PEEK), epoxy resin (Epoxy), polystyrene (PS), poly(methyl methacrylate) (PMMA), high-density polyethylene (HDPE), polycarbonate (PC), polysulfone (PSu), and poly(phenylene sulfide) (PPS) (Okura et al. 2015).

In 2016, Gomaa et al. conducted lab experiments to study and understand the effect of particulates' different parameters have on their performance. This understanding can be used to optimize the design of particulate diverters. Parameters that were studied included the particulate chemistry, size, and shape, as well as the effect of the carrier fluids. The authors accomplished this by conducting bridge tests and pack permeability tests to help find the optimum particle size distribution that is necessary to decrease the particulate pack permeability to achieve diversion. These tests were conducted with a 1,000 psi differential pressure and used different slotted discs to simulate different fracture sizes with the fracture width ranging between 0.2-0.08 in. and perforation diameter of 0.2 in. and 0.4 in. In addition, they conducted dynamic dissolution tests to study the effect of different fluids, temperatures, and particulate size on the degradation or dissolution rate of the particulates (Gomaa et al. 2016a).

Gomaa et al. found that for larger fractures, with 0.2 in. width or higher, which are more common for near wellbore applications, they require coarse particulate size to bridge the fractures. In addition, for the larger fractures, they do require a tri-modal particulate distribution. To achieve division, it is required to have coarse material bridge the fracture, and medium and fine particulates to further reduce the pack permeability. The authors also found that smaller size fractures that range between 0.04-0.08 in. width, which is a typical range of fracture width for far-field applications, do not require diverters with large particle size. However, very tight particle pack permeability is needed, and a bi-modal size distribution is optimum to achieve diversion in these smaller fractures. In addition, to lower the pack permeability, the concentration of the finer materials needs to be higher than the concentration of the medium size material (Gomaa et al. 2016a).

Later, Gomaa et al. published additional conclusions based on the continuation of their experimental work. As far as their dynamic dissolution experiments, they found out that smaller diverting particles degrades faster than larger particles. They also found that the diverters degraded more slowly in slickwater fluid as compared to DI water. Moreover,

using KCl caused lower degradation rate due to the higher salinity. In addition, the diverters dissolved more slowly in HCl as compared to DI and KCl solutions. They also found that dissolution rate increases with increasing temperature. As far as the optimum particle size, they found that to bridge a fracture, the ratio of fracture width to particle size of 2.4 is required (Gomaa et al. 2016b).

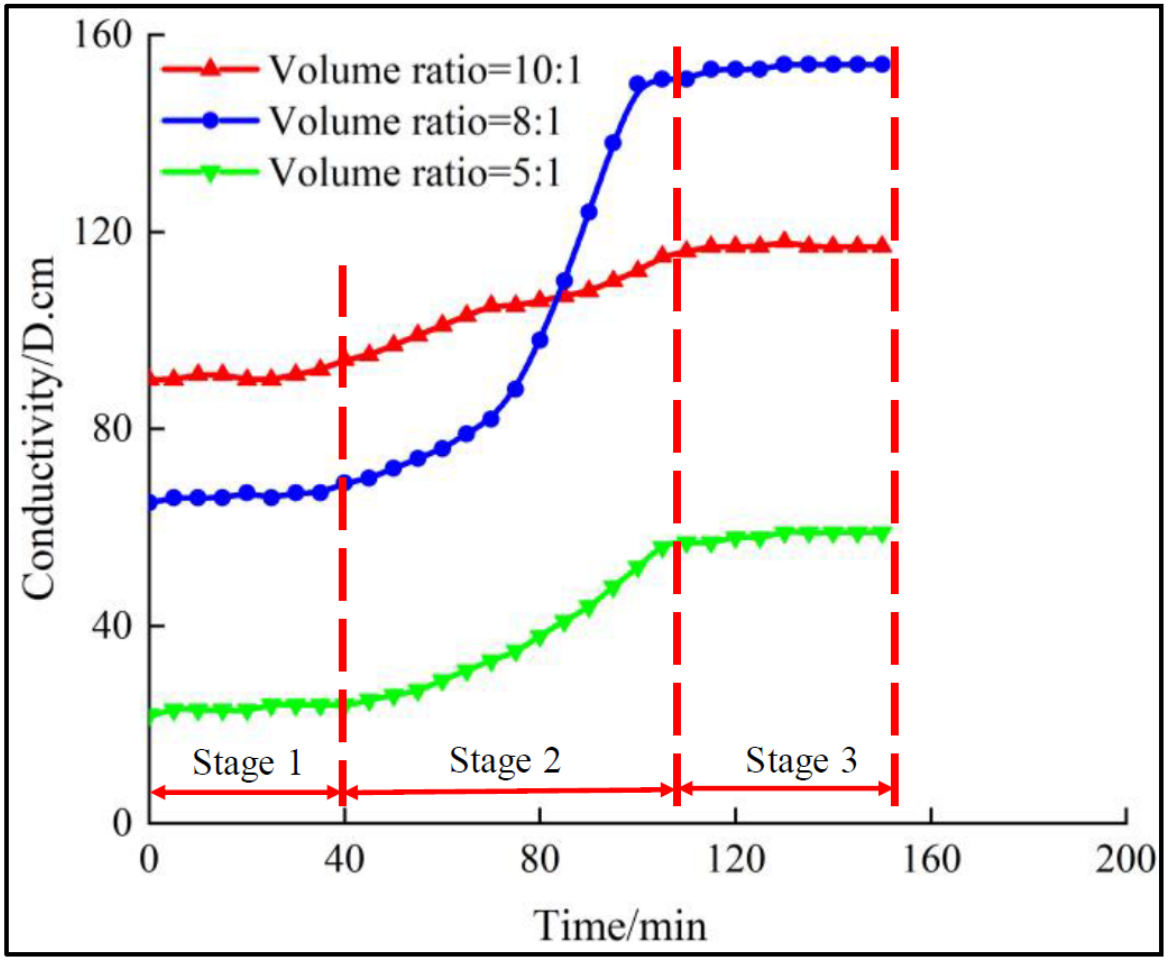

Figure 2.9 Test results of the conductivity testing showing that the volume ratio of proppants to diverters of 8:1 produced the most favorable conductivity results for far-field diversion applications (Zhang et al. 2019).

Another laboratory study on biodegradable particulate diverters included a study done by Zhang et al. (2019). Their lab experiments included conductivity analysis of biodegradable diverters mixed with proppants to study their effectiveness for far-field

diversion application. Few degradable particulates were investigated for hydrolysis, and they found that a copolymer made of lactic acid and glycolic acid was the best to use for conducting their conductivity analysis. Different volume of proppants-to-diverters ratios were selected, including 10:1, 8:1 and 5:1. The study was conducted in three stages, where stage one included testing at room temperature, and stages two and three were conducted at 90°C. Based on Figure 2.9, the results show that the 8:1 volume ratio of proppant-to-diverters produced the most favorable conductivity results (Zhang et al. 2019).

2.3 Field Case Studies Using Degradable Diverters

In 1993, Bell discussed the application of using diverters in horizontal wells in the Austin chalk formation for hydraulic fracturing applications. Since longer horizontals were being drilled up to 6000 ft, the use of a diverter was crucial specially in open hole completions and for slick water fracturing applications. Bell analyzed a total of 63 wells in Brazos and Burleson Counties. Graded salts, benzoic acid, naphthalene, and wax buttons and beads were used as diverting agents. Bell later concluded that the use of wax buttons and beads were the best diverting agents to use in open hole horizontal wells. Reasons for this included "Product availability, solubility in hydrocarbons, cost and the lower concentrations required to achieve diversion" (Bell et al. 1993).

In the 2006 Glasbergen et al. technical paper discussed earlier, the authors conducted a trial in the field to test the new DPDA diverters. They used 1.5 ft^3 bulk volume of DPDA in the perforations of estimated volume of 0.2 ft^3 in a two 5-bbls of KCl water. This calculation was based on what is common for gravel packing placement in perforation. Usually, much more gravel is needed than what is calculated in high perm sandstones. When comparing baseline injectivity profile, to the injectivity profile after diversion, as well as the changes seen on the temperature log, it was concluded that DPDA was successful and that a more uniform injection was the result. This was different than what was seen in the baseline injection where the fluid seemed to go predominately to one lower zone. The authors then waited for a day to restore the bottomhole static condition and test if the

diverters were degrading. Based on the change of the injection profile, they concluded that those particulates did degrade (Glasbergen et al. 2006).

In 2007, Daniel et al. were one of the first to publish literature to discuss the use of biodegradable diverters in fracturing horizontal shale wells. Results from a horizontal well drilled in the Barnett shale formation utilized degradable fibers for diversion. In addition, they used real time seismic monitoring to determine the placement of the diverters. The authors concluded that utilizing seismic monitoring to engineer the completions and the use of fiber diverters in real time has helped them reduce the number of fracturing stages while still successfully stimulating the reservoir (Daniels et al. 2009).

Other applications of the degradable fibers include studies done in 2008 by Solares et al. and Al-Ismail et al. Both studies applied the degradable fiber-diverting agent but for acid stimulation in multi-layered deep gas wells in Saudi Arabia. Both studies concluded in a successful field application based on pressure response during stimulation treatment as well as from the production logging data that showed uniform production from multiple zones (Solares et al. 2008) and (Al-Ismail et al. 2008).

In 2009, Dashti et al. published their work for combining a chemical diverter that is a viscoelastic surfactant base with degradable fibers. This was done to prevent leakoff and the loss of the acid treatment into the natural fractures in a Jurassic carbonate reservoir in North Kuwait Jurassic fields. The reservoir where this was applied included high pressures of 11,000 psi, and high temperatures of 275°F. They concluded that the combination of both fluid and degradable fibers achieved better results than the use of one method or the other (Dashti et al. 2009).

Based on a paper written by Allison et al. in 2011, 30 wells were successful refractured using biodegradable diverters. Moreover, the authors provided data on two wells that were successfully refractured using those biodegradable particulates. The provided data included one vertical well and one horizontal well with a 1700 ft lateral section. Both wells experienced a substantial increase in production following the refracturing treatment

(Allison et al. 2011).

Another interesting field case study was presented by Arnold and Fragachan in 2014. The authors discussed how they applied biodegradable diverters to hydraulically fracture two horizontal wells in the Marcellus shale in Pennsylvania. The mechanical bridge plug and perf method, the normal method used in this field, were completely replaced by the utilization of biodegradable particulates to fracture all stages. One well consisted of 28 different zones, while the other consisted of 18 zones. Each zone from each well had a total of 54 perforation sets per zone. They used wireline to perforate a zone, followed by fracturing that stage, then dropping a diverter pill and repeating the process again until all zones were treated. The estimated pressure required to break down new perforation sets was 6500 psi. The success of their diversion attempts was determined by "a significant pressure increase and the formation showing a break or multiple breaks followed by a slight decrease in pressure." They experimented with different concentrations and amounts of diverters used in each stage to learn more about the amount and concentrations that work best. The authors did not share if this method resulted in production rates comparable to the wells that utilized mechanical diversion methods. However, the authors believed that with all the advantages and cost saving potential that is associated with using biodegradable diverters, this method can successfully replace the mechanical bridge plug that is normally used in fracturing long horizontals (Arnold and Fragachan 2014).

In 2015, Gutierrez et al. preformed a field study to assess the effectiveness of self-degradable diverters. Distributed temperature surveys (DTS) data and radioactive tracers were used to test the effectiveness of the diverters for near-wellbore diversion. Furthermore, seismic monitoring was used to test the effectiveness of the diverters for far-field diversion. In addition, production rates were compared for wells that were fractured with diverters, and wells that were not fractured with diverters. The field tests were conducted on ultra-low permeability reservoirs as well as highly fractured reservoirs. The tests conducted provided evidence for the effectiveness of degradable diverters

near-wellbore as well as far-field application, for both hydraulically fracturing treatments as well as acidizing treatments. The authors provided four cases; tight gas vertical well, a horizontal wet-gas shale well, a vertical tight oil, and a highly fractured carbonate (Gutierrez et al. 2015).

For the tight gas vertical well, three zones needed to be treated. Diverters were used twice to fracture all three zones. Pressure response was monitored along with the use of temperature survey and radioactive tracers to assess the effectiveness of the diverters. Based on the pressure response, the wellhead pressure increased by 1,000 psi following the first diverter pill and increased by 400 psi following the second diverter pill, which can indicate a successful diversion. However, based on the temperature log responses, the results showed that the middle zone received approximately 60% of the proppants while the upper and lower zones received the remaining 40%. Moreover, the radioactive tracers showed that only the upper two zones were successfully fractured, but not the third lower zone. The production rate for the treated well that utilized the degradable diverters had 50% more production than offset wells that were not treated with the particulate diverters (Gutierrez et al. 2015).

The second case study was conducted on a horizontal well in a wet-gas shale formation. A horizontal well with two offsets was drilled. Two wells were fractured conventionally, while the third was fractured using the degradable diverters. All three wells had similar petrophysical properties, which helps with comparing the wells with different stimulation treatments. All wells had 16 stages of stimulation. The well that utilized diverters pumped eight stages of the 16 total using diverters. The authors concluded that the pressure response that was noted along with the increase in the surface treating pressure after the diverters were dropped indicate that diversion was achieved. In addition, after three months of production, the well that used diverters had a higher cumulative liquid production than the other two wells (Gutierrez et al. 2015).

The third case study was done on a vertical tight oil well. There were three perforation intervals that needed to be treated with two hydraulic fracturing stages, and only a single diverter pill utilized. The first stage contained only hydraulic fracturing fluids. Meanwhile, the degradable particulates diverter pill was dropped before injecting the second hydraulic fracture stage. The hydraulic fracturing job was then completed after pumping the second and final stage. Downhole micro-seismic was used to study the effectiveness of the self-degrading diverter. After completing the first stage, it was observed that the lowest two perforation intervals received most of the fracturing fluid. However, after using the diverters and pumping the second stage, the fracturing fluids were diverted to the upper interval as observed by the micro-seismic. After using the diverters and pumping the second stage, the micro-seismic also showed that some of the fracturing events did take place in the lower two zones as well. Although the use of diverters helped fracture the upper zone, more fracturing occurred in the lower two zones as well post diversion. The well ended up producing volumes of oil that are higher than originally predicted. It is also important to note that the author mentioned that the first interval, which was not fractured initially, was the zone with highest initial permeability. The micro-seismic data results can be seen in Figure 2.10 (Gutierrez et al. 2015).

The fourth case study was conducted on a naturally fractured deviated oil well that has eight different zones. The well was stimulated using an acidizing treatment with 48 stages and four degradable diverter pills. Using DTS monitoring, the diverters were observed to have been effective in diverting acid to other areas. The production of this well preformed much better than other wells treated without diverters in the area with approximately 750 BOPD more than other wells (Gutierrez et al. 2015).

This study was a comprehensive study that showed how degradable diverters can be utilized for fracturing and acidizing treatments. Moreover, it focused on how these particulates can work in different types of reservoirs, ranging from permeable and highly fractured, to ultra-low permeability ones. They can work successfully in different types of

wells, including vertical, deviated and horizontal wells. In addition, there was also indication that diversion can happen near wellbore as well as far-field (Gutierrez et al. 2015). However, it is important to note that based on the first well case study that the pressure response was not a good indicator of successful diversion. Although an increase in wellhead pressure was observed, the radioactive tracer's response shows that one interval was not successfully fractured.

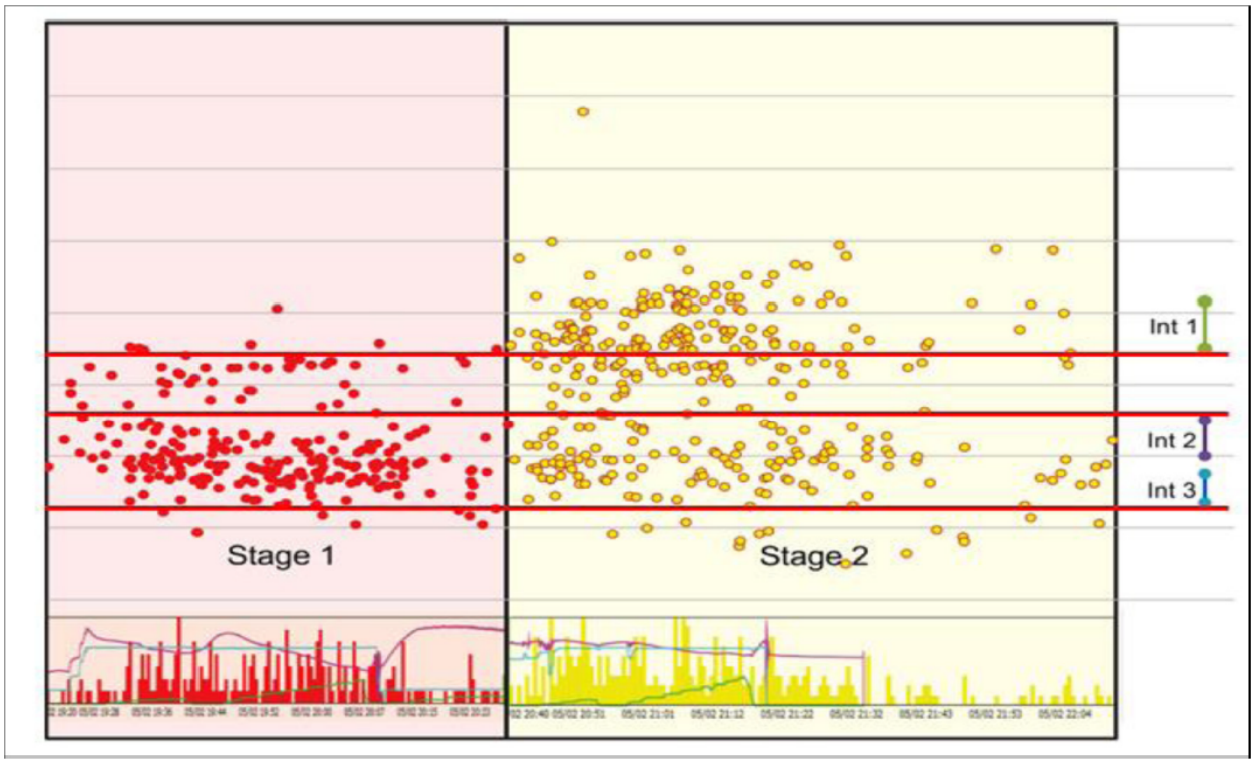

Figure 2.10 Microseismic data showing the successful fracturing of the first interval in stage two after using the particulate diverters (Gutierrez et al. 2015).

In 2017, Malik et al. used biodegradable diverters for both near-wellbore and far-field applications in acid fracturing treatments in deep high-temperature carbonate reservoir in Saudi Arabia. They used multi-modal biodegradable particulates for diversion. They were able to successfully divert multiple perforation clusters and evenly fracture the entire zone based on observed pressure response and temperature log data (Malik et al. 2017).

Another study done by Huang et al. in 2018 used the self-degradable diverters for both hydraulic fracturing and matrix acidizing applications. They conducted lab experiments and field studies for their work and analyzed the data. They concluded that "analyses suggest that the success of the diverter system application is governed by the particle characteristics (size, shape, ratio, and concentration) and diverter slurry displacement (rate, viscosity and volume of displacing fluid)". Moreover, they presented models and a workflow to help in designing for the particulate diversion treatment (Huang et al. 2018).

Another field study in 2018 is done by Senters et al. that was conducted on a total of 222 stages. Their case studies included ghost stages, as well as diverting using PLA in a plug and perf method. Ghost stages includes rate cycling with similar rate changes as if using a diverter pill, but without dropping any particulate diverters. Based on the results, the authors observed that 20 out of the 222 stages showed no diversion at all and effective diversion was less common in the 202 stages that showed diversion. Although some stages were successful at opening new perforation clusters, the total numbers of perforation clusters treated towards the end were reduced for these wells. Additional observations showed that division was more effective for wells with higher perforation clusters per stage (Senters et al. 2018).

2.4 Guidelines and Design Criteria for Particulate Diverters

In 1972, Harrison was one of the first to introduce some guidelines for the use of chemical diverters. These guidelines included determining the best diverting agent to use based on application, and the required volumes necessary to achieve diversion. Harrison recommended that five pounds of diverter agent per foot of the zone that needs to be plugged is required when using unibeads or naphthalene. Meanwhile, 10 lbs/ft for benzoic acid, a maximum of 20 lbs/ft for graded rock salt, and up to 60 lb/ft using ungraded rock salt (Harrison 1972).

Harrison recommended that for low temperature reservoirs, unibeads should be used in oil-based carrier fluid so that the unibeads can dissolve after treatment. However, if

diversion is needed in perforations, then 1.5–2 lbs of graded unibeads or naphthalene is required per perforation. In addition, the recommended concentration of particulate diverters in the carrier fluid is different based on the different application. Harrison recommended a concentration of 1 ppg if using the limited entry technique for one perforation and 2 ppg for multiple perforations, and 2 ppg for open hole completions (Harrison 1972).

In 1984 Hill and Galloway presented one of the first theoretical models aimed to understand diverting agent behavior. They used finely grained oil-soluble resins in an experimental laboratory. Then they attempted to model the behavior of the fluid flow when using oil-soluble resins. This was done by analyzing the pressure drop versus diverter volume injected in a core plug. Darcy's law was used for fluid flow prior to injecting the diverters, and the equation was modified based on the pressure changes observed in the laboratory for the results after injecting the diverters. Their conclusions included that "fluid placement simulations of diverting agent behavior show that continuously adding diverting agent to treating fluids equalizes flow to all zones. Slugs of diverting agent preceding treating fluids can lead to a highly skewed distribution of injected fluid. This effect is most pronounced for the first sequence of diverting agent injected" (Hill and Galloway 1984).

Later, in 1987 Doerler and Prouvost also worked on modeling flow behavior using oil-soluble resins as diverting agents. First, they measured the flow resistance caused by the filter cake of the diverters in a laboratory experiment. Then, they developed a numerical model to predict flow distribution from diversion. The results of their work can be used to design the volume of diverting material required, as well as the pumping schedule to use based on the diverter and the reservoir properties. Their work can be used for utilizing diverters in matrix acidizing applications (Doerler and Prouvost 1987).

In 1989 Nitter and Davis provided a theoretical model based on an experimental study done with benzoic acid diverters. Their computer model predicts that "too small batches

of diverter slurry can have adverse results". They found that using benzoic acid is especially advantageous because their solubility in water will result in different particle size distribution, thus reduced permeability, before the particulates reach the perforations. Moreover, due to their high solubility, continuous pumping of benzoic acid is required to maintain that low permeability of the diverter pack (Nitter and Davis 1989).

Other guidelines were developed for fluids as diverting agents, including a study done by Thompson and Gdanski in 1993 for the use of foam as a diverting agent for acidizing treatments. Meanwhile, in 1997, Lietard provided guidelines for viscous diverter slugs for open-hole horizontal. Menzies et al. modeled the placement of gel as a diverting agent for horizontal wells in 1999 (Thompson and Gdanski 1993) (Lietard 1997) and (Menzies et al. 1999).

Glasbergen et al., who introduced the biodegradable particulate diverters in 2006, also discussed what makes particulate diverters effective. They discussed that the three main particulates sizes, very coarse, coarse, and fine particulate, can be used for different applications. The very coarse, usually 40/60 or 20/40 mesh size can be used to bridge over perforation tunnels. Meanwhile, the coarse-size particulates, usually a 100-mesh particle size can be used in the perforation tunnel to lower the permeability of the diverter pack within the very coarse particles. Finally, the fine particles, usually 325-mesh size or lower, usually have a very low permeability, and can be used to form a filter cake on the formation face (Glasbergen et al. 2006).

In their 2015 field study, Gutierrez et al. also discussed how particulate diverters function in a general manner. The particulate should generate enough flow resistance to achieve diversion. Like Glasbergen and others, they also discussed that very coarse material, 40-60 to 20-40 mesh, is usually used to bridge over perforation tunnels while coarse material that have average particle size distribution of 100 mesh is used to pack the perforation tunnels. Furthermore, fine particulates, which have an average size distribution of 325 mesh, is used to form a filter cake on the formation. Therefore, the design for

selection the particulate's size distribution, should generate a permeability that will allow for enough flow resistance to achieve diversion (Gutierrez et al. 2015).

Gutierrez et al. also discussed how the self-degradable diverters are usually pumped. Usually, diverting agents are pumped with the flush stage right before pumping the pad of the following stage. The authors also discussed how the bottomhole temperature plays a huge rule on the degradation rate of the particulates. If the bottomhole temperature is relatively low, this can cause a longer time of degradation, and in turn, constrain the production. A rule of thumb of how much diverter is needed depends on the volume of the perforation. The volume of the perforation tunnel in ft^3 needs to be multiplied by 54.4 lbm/ft^3 to determine the mass of diverters required to plug a perforation tunnel. Current recommendations are to start with one lbm per perforation at concentrations of 0.5-1.0 ppg to divert over perforations for acid treatments. Moreover, higher concentrations usually plug faster than lower concentrations. The concentration criteria are usually dependent on the objective of the treatment as well as the parameters of the well (Gutierrez et al. 2015).

One of the first comprehensive studies aimed at providing practical guidelines for designing degradable particulates diversion treatments was provide by Van Domelen in 2017. The author described that to deliver the appropriate flow resistance for effective diversion, the particle size distribution is a very important criteria to consider. The smaller the size of the particles, the higher the size distribution is, and the lower the permeability of the pack. Coarse particles are usually used to bridge on perforations, open fractures, and large vugs. Meanwhile medium-sized particles are used to plug inside perforations or to bridge on proppant-filled fractures. Fine particles are used to either bridge on the larger particles to reduce permeability, or to seal the pore-throats. In addition, very fine particles can be used to further reduce the pack permeability or to bridge on the formation for far-field applications. Figure 2.11 provides an illustration of how particulate diverters can bridge over proppant-filled fracture to achieve diversion (Van Domelen 2017).

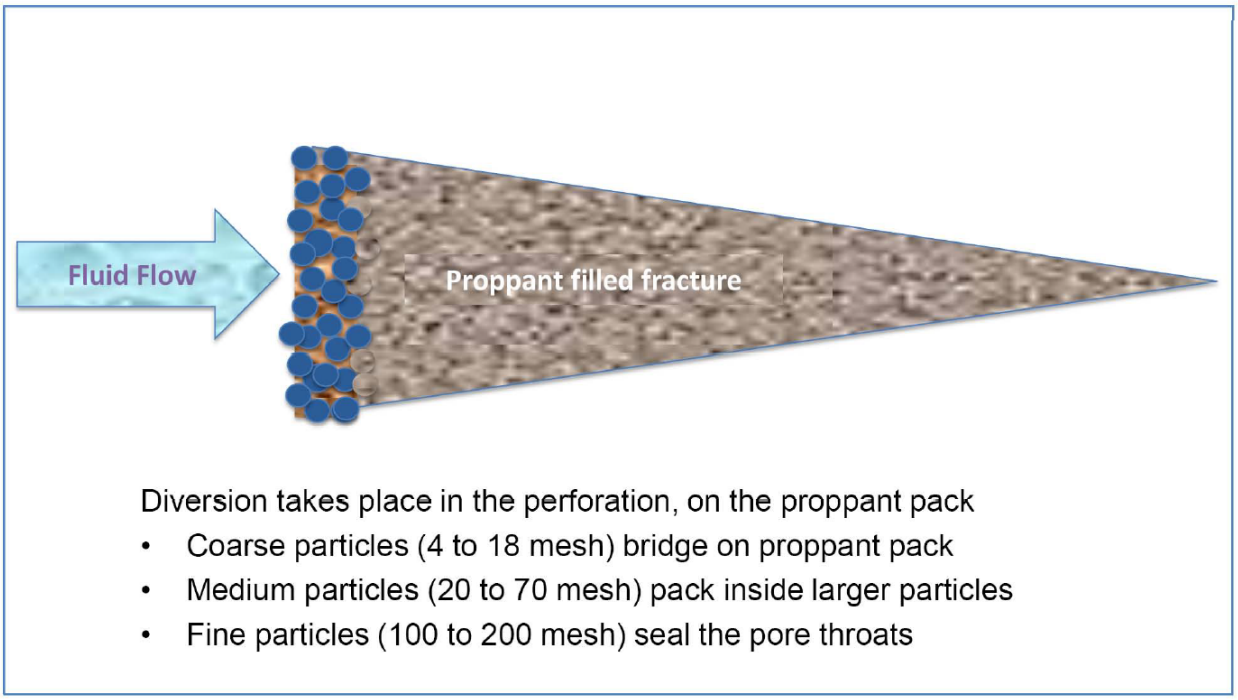

Figure 2.11 An illustration of how particulate diverters can bridge over a proppant-filled fracture to achieve diversion (Van Domelen 2017).

Van Domelen (2017) also provided a summary of current industry guidelines on how much conventional particulates are usually used and at what concentrations. She stated that conventional particulate diverters are usually pumped at low concentrations ranging from 0.5-1 ppg per perforation for cased hole completions, and up to 5-10 ppg for open hole or vuggy formations. Moreover, 0.25-2 lbs of particulates are usually used in perforations, and 1-5 lbs per ft^2 in open hole completions. Figure 2.12 shows a summary of concentrations and amounts usually used for conventional particles diverters in different field applications (Van Domelen 2017).

In addition to providing a summary of the guidelines used in the industry for conventional diverters, the author developed and proposed new guidelines to be used for PLA particulates. The guidelines proposed are summarized in the following steps:

1. *Choosing the most appropriate base material.*
2. *Choosing the correct particle size distribution*

3. *Determine the amount of PLA required per stage or perforation*
4. *Monitor injection well; and*
5. *Monitoring the offset wells* (Van Domelen 2017).

Type	Applications	On Perforations	In Perforations (lbs per perforation)	Open Hole Formations (lbs per ft^2)
Rock salt	HCI and non-HF Acid Treatments	16 lbs @ 1 Ib/gal	0.5 to 2	5
Benzoic Acid	Gas, Oil, Injection Wells	9 lbs @ 0.5 Ib/gal	0.25 to 1	2.5
Naphthalene	Oil Wells Only	8 lbs @ 0.5 Ib/gal	0.25 to 1	2.5
Wax beads	Oil Wells Only	n/a*	0.25 to 0.5	1.0 to 2.0
Oil soluble resin	Oil Wells Only	n/a*	0.25 to 0.5	1.0 to 3.0
Foam	Preferably in higher permeability gas wells	n/a*	60 to 80 Quality	60 to 80 Quality
Ball Seallers	Sinkers - Vertical Wells	200% excess	n/a	n/a
	Neutral density or floaters - Vertical wells	50% excess	n/a	n/a
	Mixed density - Horizontal wells	no excess	n/a	n/a

Figure 2.12 Summary of current industry guidelines for different conventional particulate diverters (Van Domelen 2017).

The material chosen should be based on the material's solubility in and compatibility with treatment fluids and reservoir fluids. Meanwhile, choosing the correct particle size distribution can be based on guidelines already established and used in the industry. These guidelines include gravel packing recommendations developed by Saucier (1974) and the selection of the smallest particles required to seal the pore throat of large particles, developed by Abrams (1977). The author recommended to choose the amount of material to use and then to choose the appropriate concentration required to deliver the pill, and finally, to select the appropriate injection rate. Moreover, the author offered a guideline on how much PLA diverters to use based on what pumping companies are recommending and based on data mining conducted by the author on Frac Focus (fracfocus.org) data. Frac Focus data includes the amounts and types of chemicals used in stimulation operations for wells. The recommendation is to start between 0.8-1 lbs per perforation on earlier stages

and work up to 5 lbs per perforation for cemented laterals and up to 10 lbs per perforation for uncemented laterals. The last few steps include monitoring pressure response to determine diversion effectiveness. Although pressure monitoring is not the most accurate method to use, it is one of the most cost-effective methods that can be done in real time (Van Domelen 2017).

In 2017, Safari et al. conducted a 3D numerical study, and a coupled computational fluid dynamic and discrete element model. The study aimed at understanding the jamming and plugging mechanism of degradable particulate diverters for carbonate acidizing applications. The premise is that jammed structures (made by the coarse particulates) can effectively plug when they are filled with finer particulates. One of their conclusions included "the plugging will be efficient for the jammed structure on the mouth of opening and not for jammed structure inside of the opening. In other words, the small particles cannot plug the jammed structure inside the perforation/wormhole efficiently" (Safari et al. 2017).

Huang et al. provided an experimental and numerical study for degradable diverters in 2018 for the use in unconventional fracturing, and carbonate acidizing applications. Their work aimed at understanding the plugging and jamming mechanism of particulates. A 3D fracturing simulator and a computation fluid dynamic/ discrete element method were used to model the particulate transport and diversion behavior. The results from their experimental work and numerical study suggests that the size, shape, ratio, and concentrations of the diverters, as well as the rate, viscosity and volume of displacing fluids have a major role in determining the success of diversion. Moreover, they included an engineering workflow to design for an efficient degradable diverting treatment as seen in Figure 2.13. The workflow includes the use of multiple analytical models to ensure "a stable jamming ad sealing structures at the mouth of the active flow channels that needs to be plugged", and the use of numerical techniques to provide operation guidelines (Huang et al. 2018).

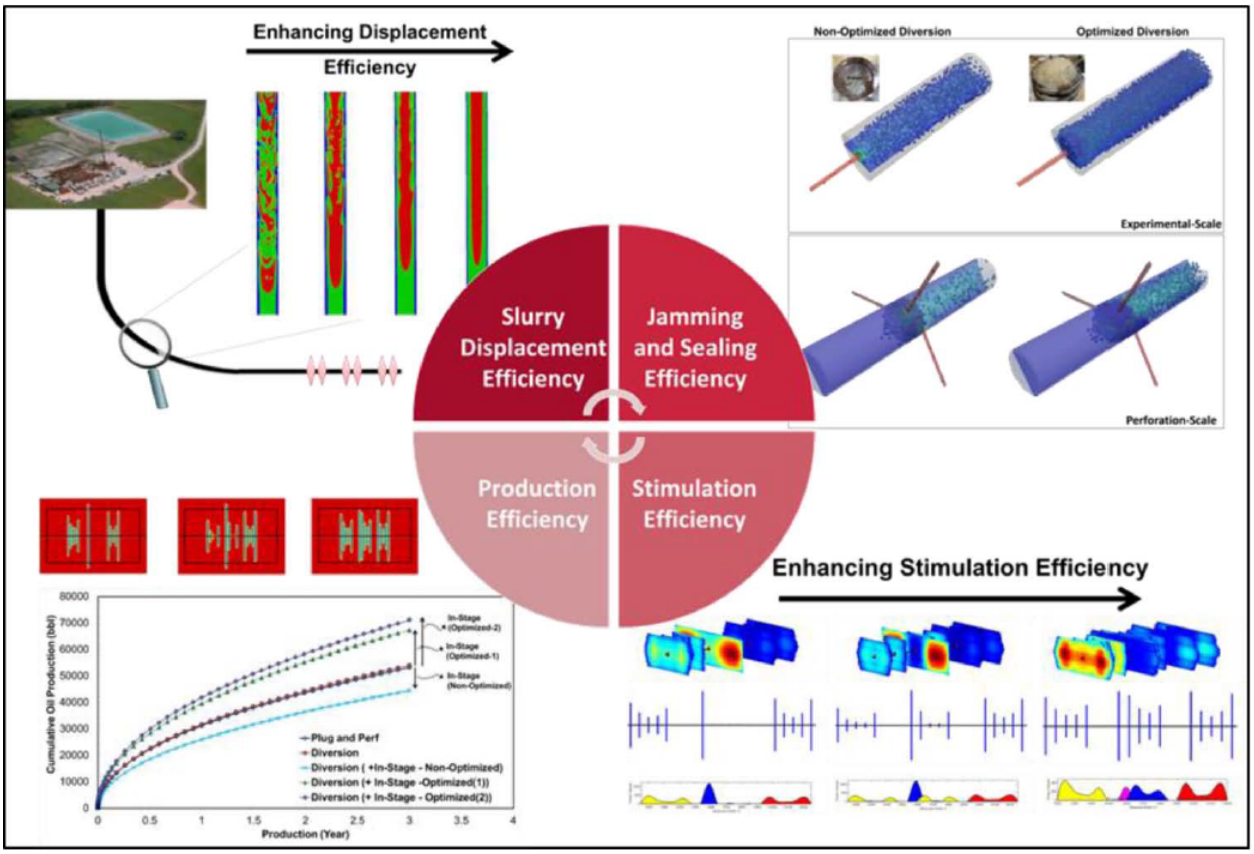

Figure 2.13 Proposed engineering workflow used for efficient and effective degradable particulate diversion design (Huang et al. 2019).

CHAPTER 3
METHODS AND EQUIPMENT

Laboratory experiments were conducted for this research on polylactide resins (PLA) particulate diverters. To achieve the objective of this research of understanding what parameters affect the plugging performance of biodegradable particulate diverters, an automated permeability plugging apparatus (APPA) was used. A total of 56 experimental tests were done including seven repeatability tests.

The laboratory experiment tests the effect of different variables and testing conditions on plugging performance. These variables and conditions include temperature, differential pressure, heating duration, pressurization duration, and the size and shape of the area that is plugged. Additionally, different PLA particulates with different sizes, shapes, and volumes were tested. The APPA equipment used in this work is usually used to test lost circulation material.

3.1 Material: Biodegradable Particulate Diverters

The particulate diverters used in this experimental work are commercial products provided by a supplier. They are biodegradable, which means they degrade by hydrolysis. Thus, when placed in water, they degrade with time and temperature and change from a solid phase to a clear liquid phase. Three types of diverters were used for this experiment. The three types of diverters are similar in composition but have differences in characteristics.

One of the similarities that all three diverters have in common is that they are made from more than 98% by weight polylactide. They have a specific gravity of 1.24 and a relative density of 1.25. In addition, the glass transition temperature of the particulates, which is the temperature when the particulates start to transition from solid to liquid, is

55°C (131°F). The melting temperature of all three diverters is 180°C (356°F) (DiverterPlus 2018a, 2018b, 2018c).

The used particulate diverters are made to bridge and plug off perforation tunnels as well as near wellbore fractures. The recommendation for using these particulates for a stimulation treatment, is 0.25–1 ppg concentrations and 5-20 bpm pump rate. The recommendation is to start with 0.5 lbs of diverters per perforation for cemented wellbores and go up as high as eight lbs per perforation for other types of completions. The particulates can be mixed with water, brine, slickwater, or gelled fluids as the base fluid (DiverterPlus 2018d, 2018e, 2018f).

Some of the differences between the three particulate diverters include the shape of the diverters, the degradation rate based on hydrolysis reports, and the recommended bottomhole temperature. The three diverters used are the DIV+1306, DIV+1135, and DIV+1359. A description of these properties for all three diverters is as follows.

The DIV+1306 particulates are made up of 6-mesh coarse beads with an opaque appearance and translucent color as shown in Figure 3.1. The suggested bottomhole temperature where these diverters can be applied is between 140-225°F. Based on the provided hydrolysis reports, after heating the diverters to 190°F for 72 hours, only 5.02% by weight of diverters should remain. This is considered a fast degradation rate, which allows for the well to start producing within three days. At a lower temperature of 160°F, 99.25% by weight of diverters remain after being heated for 72 hours. This shows that the higher the temperature is above the glass transition temperature, the faster and more complete the degradation. However, when looking at the hydrolysis data at lower temperatures, 99.59% of the diverters remain after being heated to 140°F for 72 hours. In addition, it takes approximately 288 hours for the diverters to lose 51.37% of their weight at 140°F. Approximately 99.5% by weight of this coarse diverters remained after being heated to 120°F for 72 hours[1]. This shows that if the bottomhole temperature is within 10°F of the

[1]Personal communication with N. Koster. 2021.

glass transition temperature of the diverters used, the degradation rates can be extremely slow, and it could take weeks before the well can start production from any plugged areas.

Figure 3.1 Bead particulate diverters, DIV+1306 (DiverterPlus 2018e).

The second type of particulates used in this work is the DIV+1135. These particulates are coarse in size and have a flake shape with an opaque appearance and translucent color (Figure 3.2). Unlike the DIV +1306 beads, these flakes are suggested to be used for reservoirs with a little higher bottomhole temperatures ranging from 160-225°F. Based on the hydrolysis report, after heating these flakes to 190°F, 67.48% by weight of diverters remained after 72 hours. Meanwhile, 99.9% by weight of the diverters remained after being heated for 72 hours to 160°F. At 120°F, which is below the glass transition temperature, 99.25% by weight of the diverters remained after being heated for 720 hours[2]. The data shows that flakes degrade at a much slower rate than the beads even though both diverters are composed of more than 98% PLA.

The third diverter analyzed is the DIV+1359 type. This diverter is a blend made of a mixture containing coarse flakes and fine powder (Figure 3.3). The blend is a solid mixture of white and translucent color particulates, where the powder is white while the flake is translucent. Like the previously discussed DIV +1306 beads, this blend is also suggested to

[2]Personal communication with N. Koster. 2021.

be used for reservoirs with a bottomhole temperature ranging between 140–225°F. However, the hydrolysis report for this blend differs from the other two diverters. After heating this blend for 72 hours to 190°F, only 19.57% by weight of diverters remain. Meanwhile, at a 120°F, 99.65% by weight of the diverters remain after being heated for 72 hours[3]. Based on the hydrolysis data, the blend diverters degrade at a slower rate than the coarse beads and at a faster rate than the flakes.

Figure 3.2 Flake particulate diverters, DIV+1135 (DiverterPlus 2018d).

Figure 3.3 Blend particulate diverters, DIV+1359 (DiverterPlus 2018f).

[3]Personal communication with N. Koster. 2021.

3.2 Equipment: Automated Permeability Plugging Apparatus

An Automated Permeability Plugging Apparatus (APPA) is used to preform permeability plugging tests under difference testing conditions. The APPA apparatus that is used in this experimental work is a Model 389AP made by Fann Instrument Company. This APPA model is a high pressure, high temperature instrument ideally designed for predicting how a drilling fluid and loss circulation material can form a permeable filter cake to seal off depleted or under-pressured intervals (Fann Instrument Company 2013). To achieve the objectives of this research, this equipment was used to test the sealing performance of biodegradable particulate diverters with different characteristics, and under different testing conditions. The different testing conditions that were investigated include various differential pressures, various amounts of diverter that correspond to different concentrations, various temperatures, various heating duration, and three different slotted discs to simulate a large fracture, a small fracture and a perforation.

The APPA 389AP model is capable of preforming tests up to 500°F temperature and 750 psig differential pressure. Stainless steel discs with different slotted geometries are used to simulate different size fractures and different size perforations. The equipment can be operated through a software that automatically records the change of differential pressure with time during the experiment (Fann Instrument Company 2013). The collected pressure data is used to assess the plugging performance of particulates for this experimental work.

The APPA equipment consists of an APPA pressure cell, a backpressure system, a heating system, a hydraulic oil pumping system, a variety of slotted or ceramic filter discs, an LCD screen, keypad for manual control, and an emergency stop button. The equipment can be operated manually through the keypad on the equipment, or it can be controlled through the software. The manual control that can be used through a keypad can be used to set different testing functions including heating and pressurizing the sample. An image of the equipment with the different components is shown in Figure 3.4.

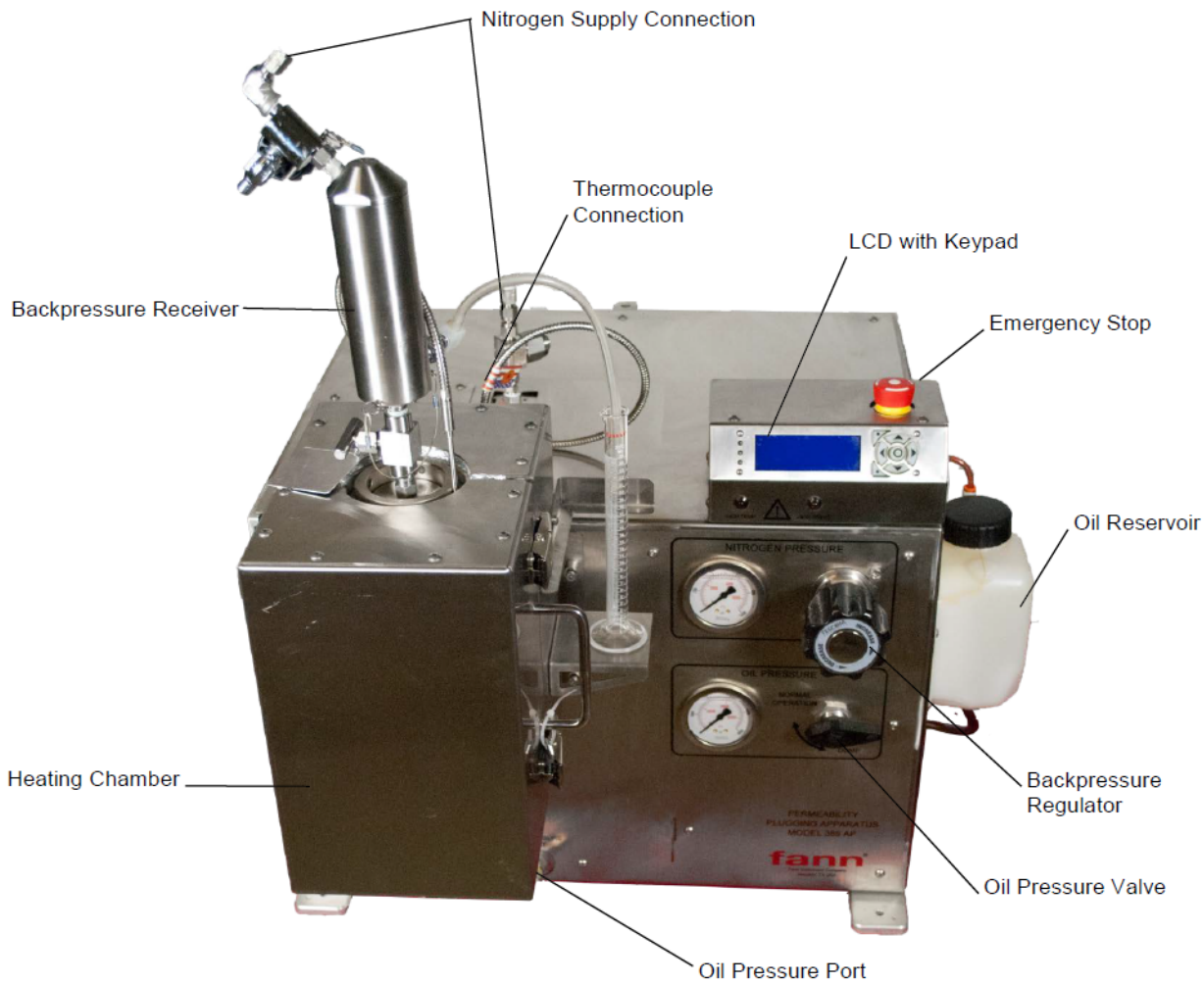

Figure 3.4 Automated permeability plugging apparatus (Fann Instrument Company 2013).

3.2.1 Slotted Discs

The equipment can test either ceramic discs that come in several pore sizes to simulate formations with different porosities and permeabilities, or stainless-steel slotted discs to simulate fractures and perforations. For this laboratory experimental work, the stainless-steel slotted discs were utilized. The first disc used was a tapered disc with a width opening range of 0.04-0.10 in. This tapered disc is used to represent a small fracture that has 0.04 in. width and 1.7 in. length as seen in Figure 3.5. The second slotted disc used is a two-radial arms disc where the two arms representing two fractures with each

having 0.12 in. width and 0.313 in. length as seen in Figure 3.6. The third slotted disc used was manufactured to have a 0.4 in. circular hole to represent a perforation as seen in Figure 3.7.

Figure 3.5 Tapered slotted disc representing a small fracture with 0.04-0.10 in. width and 1.7 in. length.

Figure 3.6 Two-radial arms slotted disc representing a large fracture with 0.12 in. width and 0.313 in. length.

Figure 3.7 Slotted disc representing a perforation with 0.4 in. diameter.

3.2.2 The Hydraulic Oil System

The hydraulic oil system is used to pump hydraulic oil into the APPA cell to pressurize the system. This system consists of a hydraulic oil reservoir, a pressure port hose, a pressure valve, a hydraulic oil pump, and an air pump that is connected to the air supply. The hydraulic oil pump is used to move the hydraulic oil from the reservoir, though the oil pressure port hose and into the APPA cell through the APPA cell's quick disconnect coupling socket (Fann Instrument Company 2013). The hydraulic oil level inside the oil reservoir is used as an indicator to track the location of the floating piston inside the APPA cell.

3.2.3 APPA Cell

Another part of the APPA equipment is the APPA cell that is a pressure vessel. The APPA cell is where the testing fluids are loaded. A schematic of the APPA cell with its different components can be seen in Figure 3.8. The different components of the APPA cell include the cell body, a quick disconnect coupling socket, a floating piston, a bottom cap, a top cap, and a back pressure nipple. The cell body of the APPA (as seen in Figure 3.9) is where the testing fluids are placed within the APPA cell. In addition, the different slotted

or filter discs are placed at the top part within the APPA cell, right below the top cap. The backpressure nipple is used to connect the APPA cell to the lost circulation material (LCM) evaluation receiver (Fann Instrument Company 2013).

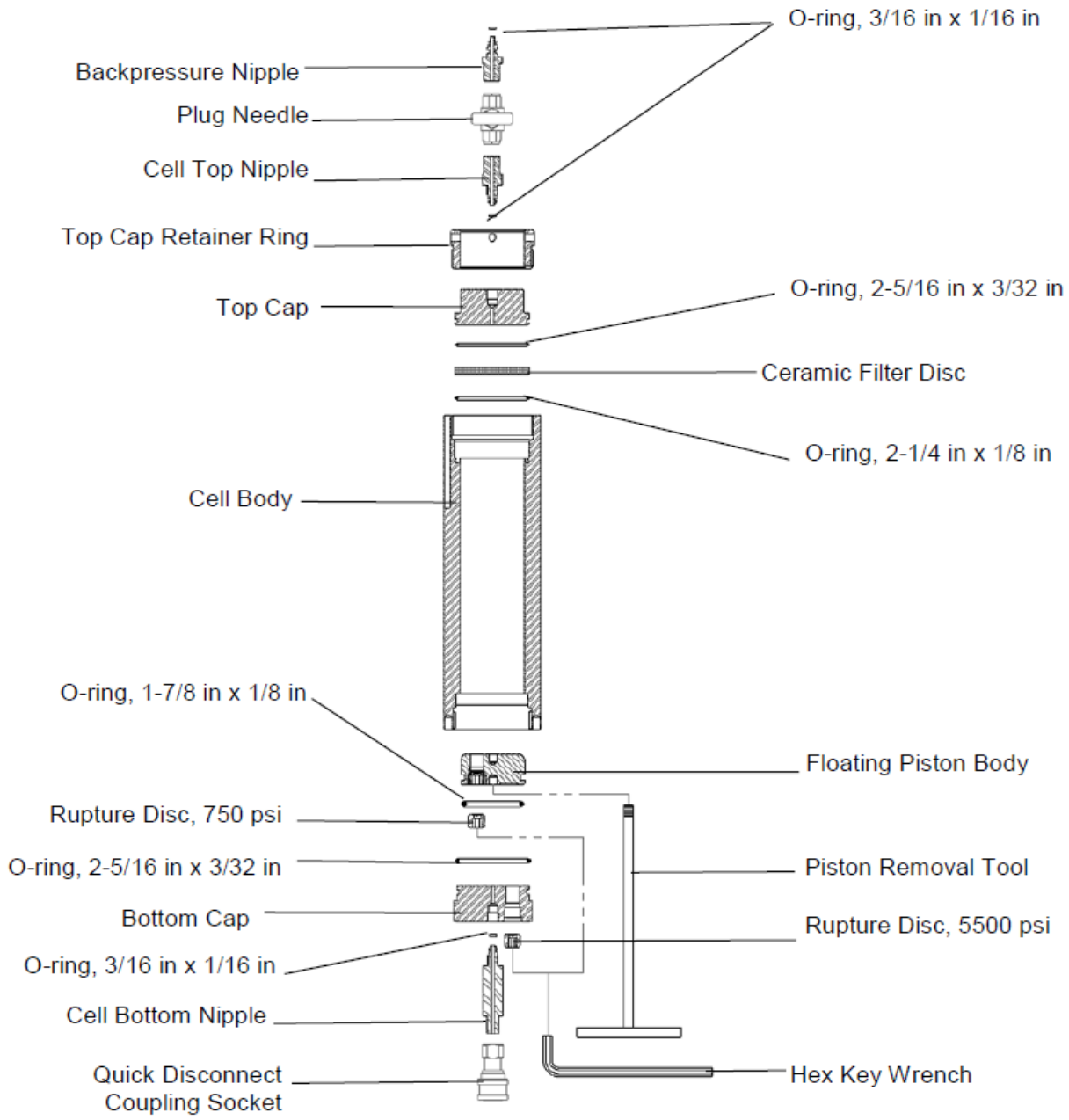

Figure 3.8 A schematic of the APPA cell (Fann Instrument Company 2013).

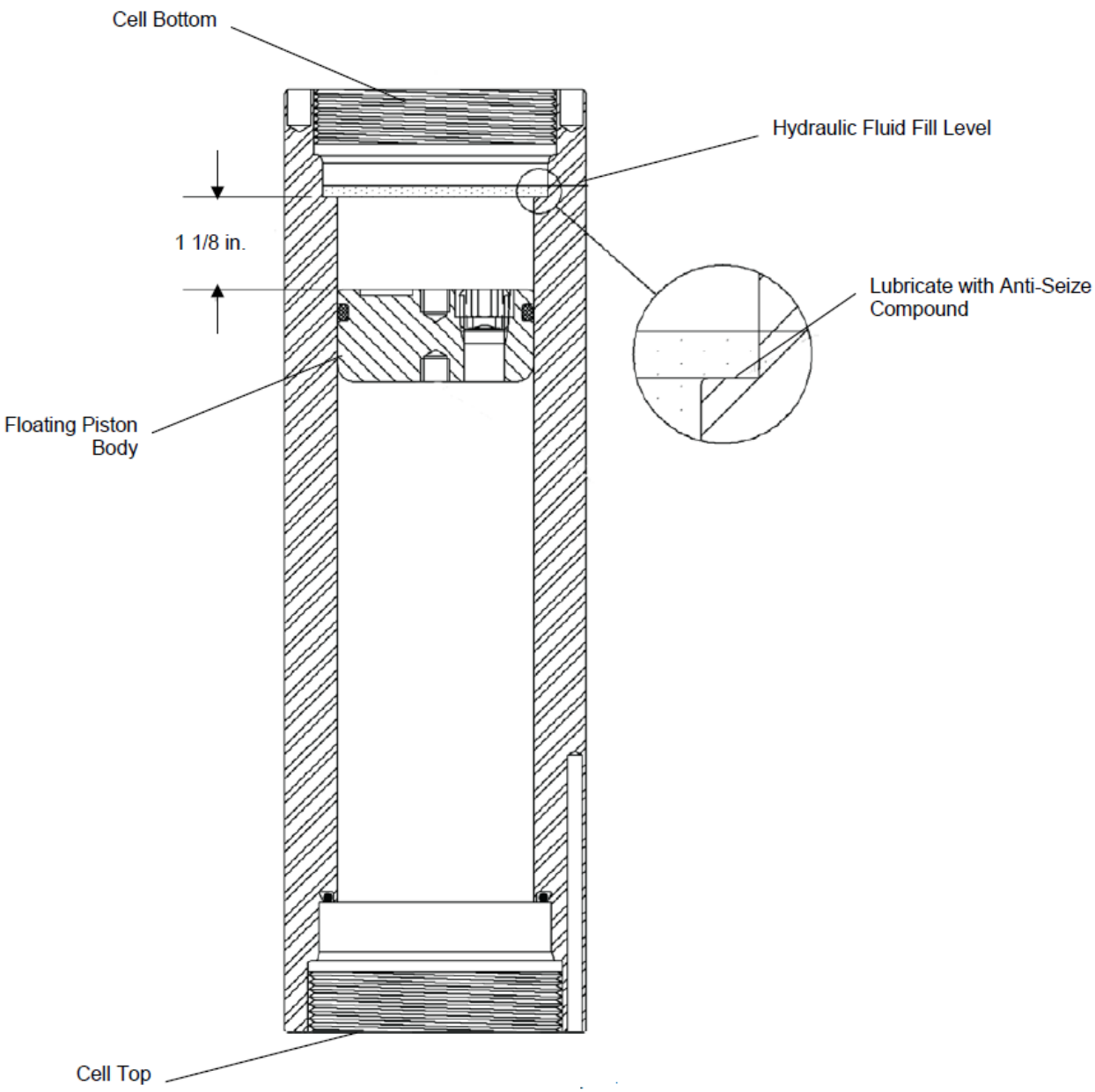

Figure 3.9 A schematic of the APPA cell Body (Fann Instrument Company 2013).

The floating piston is installed inside the APPA cell just above the bottom cap. The hydraulic oil from the hydraulic oil pumping system enters the APPA cell through the quick disconnect coupling socket. Once the hydraulic oil enters the APPA cell, it starts to fill the space between the bottom cap and the floating piston. As more hydraulic oil gets

pumped into the cell, the floating piston starts to move upward. As the floating piston gets pushed up by the hydraulic oil, it starts to move the testing material upward and toward the slotted disc. The testing fluid sample can then either plug the slotted disc and achieve the desired differential pressure or move past the disc and unable to build pressure. Testing fluid samples that make it past the disc will either go through the collection valve or they can be temporarily stored within the LCM receiver. Once a plug has been established, the pressure should stabilize. However, if pressure decreases during a test, this indicates that the formed plug was not effective.

The location of the floating piston was continuously monitored during testing to prevent damage to the equipment. This was done through monitoring the level of the hydraulic oil inside the oil reservoir. If the hydraulic oil gets below a certain level in the oil reservoir, this will indicate that the piston made it to the top of the APPA cell, and the particulates were not able to form an impermeable plug.

3.2.4 Heating System

One part of the system that was utilized during this research is the heating system, which consists of a heating chamber, built-in resistance temperature detectors (RTD), and a thermocouple connection with an RTD probe. The heating chamber is located at the front part of the equipment as shown in (Figure 3.4). Once the testing sample have been loaded into the APPA cell, the cell can then be placed on a stand inside the heating chamber. This is done by closing the heating chamber and locking the latches into place. The temperature on the heating chamber can heat the APPA cell up to 500°F. To use the heating feature and obtain a continuous record of the temperature, the RTD probe is inserted inside a dedicated hole within the APPA cell (Fann Instrument Company 2013).

It is important to note that the heating chamber has a safety feature to prevent over-pressurizing the system. Due to the rapid expansion that results from heating the hydraulic oil that gets pumped into the APPA cell, the pump can automatically release the hydraulic oil and decrease the pressure for safety measures (Fann Instrument Company

2013). This can be seen as a rapid pressure loss once the pressure gets above a certain threshold. This information is used later in the data analysis of this work to distinguish between pressure loss due to ineffective plugging performance from the automatic pressure release due to this safety feature.

3.2.5 Lost Circulation Material Evaluation Receiver

The lost circulation material (LCM) evaluation receiver connects to the top of the APPA cell. A schematic of the LCM receiver as it is connected to the APPA cell can be seen in Figure 3.10. This LCM receiver is rated to a maximum pressure of 750 psi. During testing, when the sample fluids make it past the slotted discs, they enter the LCM receiver. A filtrate drain valve, which is located on the side of the LCM receiver, is used to drain any filtrate that make it past the slotted disc. The filtrate can then be collected into a graduated cylinder. Filtrate loss measurements can be used to quantitatively determine the plugging effectiveness of the tested material (Fann Instrument Company 2016).

As discussed above in the APPA cell section, the testing fluid samples get pushed up toward the slotted discs. It was observed that most of the water carrier fluid that was used with the particulate samples were getting pumped quickly. Meanwhile, the majority of the particulates were settling and leaving only a small volume of the mixed water inside the APPA cell. As a result, the fluid loss versus time was not a good indicator for testing the effectiveness of the particulate diverters. It was determined that the pressure versus time data is a more accurate indicator of the effectiveness of the particulate's plugging performance. Therefore, the recorded pressure versus time data were used in the discussion and analysis chapter for this study. The LCM receiver was used to collect and drain the pumped water, as well as collect any particulates that made it past the slotted disc.

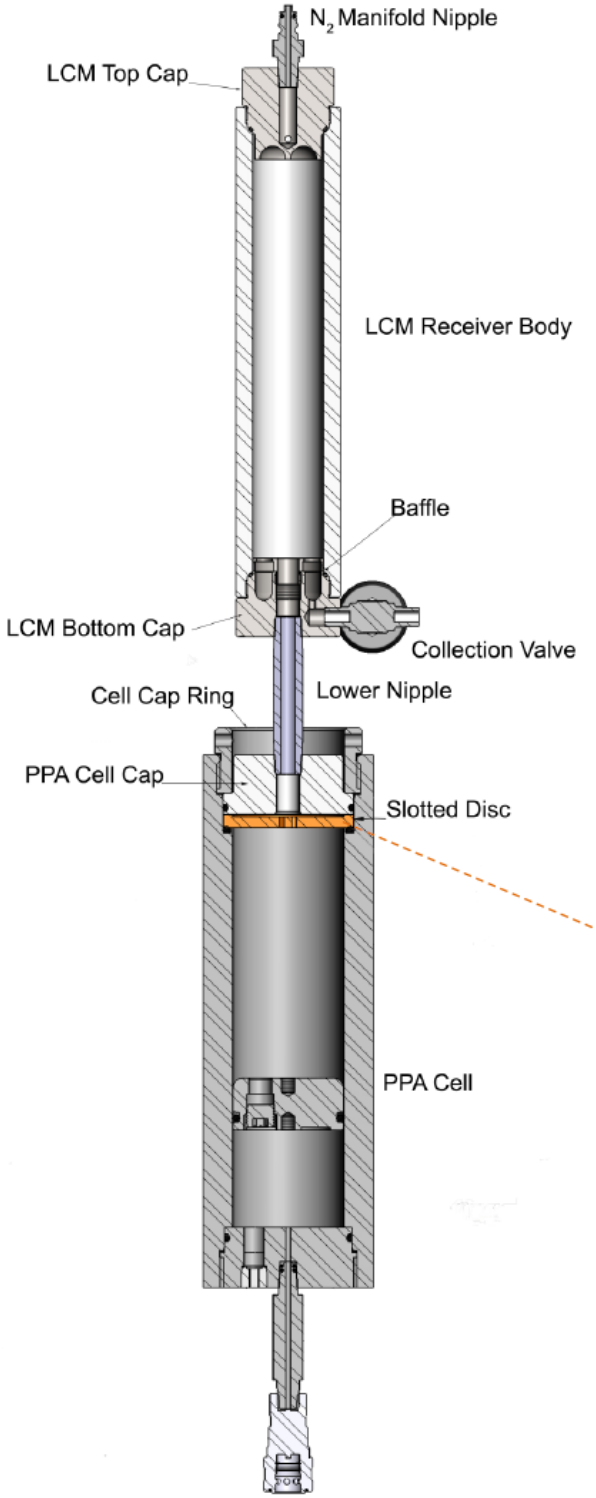

Figure 3.10 A schematic of the LCM evaluation receiver connected to the APPA cell (Fann Instrument Company 2016).

3.3 Testing Variables

A total of 56 tests were conducted using the APPA equipment including seven repeatability tests to verify the repeatability of the method used. Among the preformed tests, there are seven different variables used. Those variables are the three different slotted discs used, the three different types of diverters used, the testing temperature, the applied differential pressure, the heating duration, the pressurization duration, and the mass of diverters used.

During the beginning stages of the experimental work, the smaller 0.04-0.1 in. tapered disc was used. These tests were conducted using a high range of differential pressure (0-500 psi), and a high range of temperatures (70-225°F). These tests were conducted to determine whether the temperature and pressure influenced the plugging performance. In addition, the results obtained from these tests were used to determine the baseline parameters to use for conducting additional tests. Since it was noted early that temperature had a substantial effect on plugging performance, three tests were conducted to determine how long the diverters need to be heated for to form an impermeable plug. Those tests included heating the samples for 10 minutes, 30 minutes, and 60 minutes.

The baseline parameters that were used for most of the experiments included heating the samples for 60 minutes to 150°F, which is above the diverter's glass transition temperature. Additionally, the samples were pressurized in the APPA cell to 50 psi for 10 minutes. The tests that were performed using these baseline criteria were run using two of the slotted discs, while varying the mass of diverters used. In turn, the data collected is used to determine the minimum amount of diverters required to plug a large fracture and a perforation. The range of diverter's mass used in baseline tests is 4.5–72 g, which corresponds to a concentration ranging from 0.25-4 ppg.

A few additional tests were conducted at room temperature (approximately 70°F) in order to use the data for comparison against the amount of diverters required to plug at the higher 150°F. Furthermore, to determine if flowback is possible within one day, a few

tests were conducted to test the plugging performance of the diverters after heating the samples to 200°F for 24 hours. Some long-term tests were also conducted. These long-term tests were performed on samples that were pressurized to 200 psi while holding that pressure for 4 hours. These results were used to determine if the formed plugs can withstand 200 psi differential pressure, which is a pressure that is within a typical range during hydraulic fracturing treatment, for a period of four hours, a typical duration of how long the diverters are needed to perform during a stimulation job.

A few observations were made during the experimental work, and pictures were taken to document those observations. Table 3.1 provides a summary of the tests that were conducted, and the corresponding testing variables used.

Table 3.1 Testing Matrix.

Slotted Disc	Diverters	Diverter Mass (g)	Temperature (°F)	Differential Pressure (psi)	Heating Duration (Hours)
0.04-0.1 in. Tapered	Blend	18	70-100	0-500	During Test
0.04-0.1 in. Tapered	Blend	18	100-150	0-500	During Test
0.04-0.1 in. Tapered	Blend	18	150-200	0-500	During Test
0.04-0.1 in. Tapered	Blend	18	200-230	0-500	During Test
0.04-0.1 in. Tapered	Flake	18	70	0-500	0
0.04-0.1 in. Tapered	Flake	18	70-100	0-500	During Test
0.04-0.1 in. Tapered	Flake	18	130	0-50	During Test
0.04-0.1 in. Tapered	Flake	18	150	0-500	During Test
0.04-0.1 in. Tapered	Flake	18	200	0-500	During Test
0.04-0.1 in. Tapered	Flake	18	225	0-500	During Test
0.12 in. Fracture	Bead	18	70	50	0
0.12 in. Fracture	Bead	18	150	50	1/6
0.12 in. Fracture	Bead	18	150	50	1/2
0.12 in. Fracture	Bead	18	150	50	1
0.12 in. Fracture	Bead	18	150	50/one hour	1
0.12 in. Fracture	Bead	18	150	50	1
0.12 in. Fracture	Bead	18	150	50	1
0.12 in. Fracture	Bead	18	70	50	0
0.12 in. Fracture	Bead	9	150	50	1
0.12 in. Fracture	Bead	4.5	150	50	1
0.12 in. Fracture	Blend	18	150	50	1
0.12 in. Fracture	Blend	9	150	50	1

Table 3.1 Continued.

Slotted Disc	Diverters	Diverter Mass (g)	Temperature (°F)	Differential Pressure (psi)	Heating Duration (Hours)
0.12 in. Fracture	Blend	4.5	150	50	1
0.12 in. Fracture	Flake	18	150	50	1
0.12 in. Fracture	Flake	9	150	50	1
0.12 in. Fracture	Flake	4.5	150	50	1
0.12 in. Fracture	Bead	36	70	50	0
0.12 in. Fracture	Bead	36	70	50	0
0.12 in. Fracture	Bead	36	70	50	0
0.12 in. Fracture	Blend	18	70	50	0
0.12 in. Fracture	Flake	18	70	50	0
0.4 in. Perforation	Flake	36	150	50	1
0.4 in. Perforation	Flake	54	150	50	1
0.4 in. Perforation	Flake	72	150	50	1
0.4 in. Perforation	Blend	18	150	50	1
0.4 in. Perforation	Blend	36	150	50	1
0.4 in. Perforation	Blend	36	150	50	1
0.4 in. Perforation	Blend	54	150	50	1
0.4 in. Perforation	Blend	72	150	50	1
0.4 in. Perforation	Bead	18	150	50	1
0.4 in. Perforation	Bead	36	150	50	1
0.4 in. Perforation	Bead	54	150	50	1
0.4 in. Perforation	Bead	36	70	50	0
0.4 in. Perforation	Bead	54	70	50	0
0.4 in. Perforation	Bead	72	70	50	0
0.4 in. Perforation	Bead	144	70	50	0
0.4 in. Perforation	Blend	72	150	200/ 4-hour	1
0.4 in. Perforation	Bead	72	150	200/ 4-hour	1
0.4 in. Perforation	Blend	36	150	200/ 4-hour	1
0.4 in. Perforation	Blend	18	150	200/ 4-hour	1
0.12 in. Fracture	Blend	9	200	50	24
0.12 in. Fracture	Blend	36	200	50	24
0.12 in. Fracture	Flake	9	200	50	24
0.12 in. Fracture	Bead	9	200	50	24
0.12 in. Fracture	Bead	36	200	50	24
0.12 in. Fracture	Bead	36	200	50	24

3.4 Methodology

The selected diverters were mixed with 150 ml of tap water from Golden, Colorado. The mass of diverters used ranged from 4.5–144 g, which corresponds to a concentration ranging from 0.25-8 ppg. The testing sample was then loaded into the APPA cell and the LCM receiver was connected to the APPA cell. The RTD probe was then inserted into its designated place inside APPA cell to utilize the heating capabilities of the equipment. The heating chamber was then closed around the APPA cell, and the latches were locked.

To commence the experiment, the desired temperature was set manually on the equipment using the keypad. Once the desired temperature was set, the sample was left inside the heating chamber for 60 minutes to allow the diverters to heat and transition. The software was then used to set the desired pressure buildup profile and allow for the pressure data to be collected and recorded automatically.

To determine the length of time for the particulates to plug the slotted discs, the equipment was set to pump the hydraulic oil as fast as possible to reach the desired differential pressure. If the desired differential pressured was achieved, the equipment was programmed to continue holding that pressure for 10 minutes for the baseline tests. If the desired differential pressure was not achieved before the floating pressure piston made it to the top of the APPA cell (as indicated by the hydraulic oil level in the reservoir) the testing was terminated. This meant that the particulates did not form an effective plug under the selected conditions.

The collected pressure data were then broken down into three categories and interpreted in the following manner:

1. Pressure was not sustained before the piston made it to the top of the APPA cell. The particulate diverters were not able to form an effective plug under the selected testing variables and the results are labeled “no plug/failed test”.

2. Pressure was sustained during some parts of test, but excessive pressure loss was seen, and the piston eventually made it to the top of the APPA cell. Although a plug was formed or was in the process of forming, it was not an effective plug. These results are labeled “ineffective plug/failed test”.

3. Pressure was sustained throughout the length of the test. The results are labeled “effective plug/successful test”.

CHAPTER 4

RESULTS

At the start of the experimental work, 10 APPA tests were conducted on the 0.04-0.1 in. width tapered slotted disc. This disc was chosen because it has the smallest size opening to simulate a thin fracture. This smaller size opening disc can then allow for multiple trial and error tests to find out what would be the appropriate amounts of diverters and water samples to use for the subsequent experiments. The trial-and-error tests were also used to figure out how to pressurize and heat the samples in a safe and constructive manner. This step was crucial especially since the APPA equipment is generally used for loss circulation material that blends well with drilling mud, as opposed to the PLA particulates, which do not mix well with water.

Once the trial-and-error tests were conducted, and an idea was formed regarding proper amounts to use and proper heating and pressurization procedures, ten tests were done on the tapered discs to get an idea of the range of the different pressures and temperatures to use for other tests. In addition, these tests were used to preliminary assess whether pressure and temperature influence the behavior of the biodegradable diverters. In total, 56 different APPA tests were conducted, including seven tests done to confirm the repeatability of the results.

4.1 Tapered Disc Initial Tests

For the experiments conducted on the 0.04-0.1 in. tapered disc, 18 g of diverter samples were mixed in 150 ml of water corresponding to 1 ppg concentration. Pressure was incrementally increased from 0-500 psi while the diverter samples were heated during the tests to different temperature ranges. Either blend or flake diverters were used for the initial 10 tests.

To interpret the data, the solid blue line on the following graphs represents the actual pressure reading from the pressure transducer, while the dashed blue line is the pressure that was set on the APPA equipment. In addition, the red line represents the temperature of the samples inside the APPA cell. Initially, as the pressure piston floats up, it pushes the sample upward as well. During this time, some pressure losses are expected (represented by the decrease in pressure seen in the blue solid line). These pressure losses continue until the diverters start arriving at the slotted disc. However, after the diverters arrive at the slotted disc, the pressure should start to stabilize if the diverters successfully plug.

The first test was conducted using 18 g (1 ppg) blend diverter that was heated from room temperature (70°F) to 100°F. Looking at Figure 4.1, the transducer pressure was fluctuating initially as the particulates were making their way upward toward the slotted disc. The first spike in pressure around 0.5 minutes indicates that the particulates started to arrive at the slotted disc. It can also be seen that there are no significant pressure losses above 50 psi. The pressure started to stabilize and continued to stay stable from 50 psi and up to 500 psi, indicating a plug was formed.

The second test done on the tapered disc included heating 18 g (1 ppg) blend diverters from 100-150°F. The glass transition temperature for the blend diverter is 131°F. This means that this test was conducted while the particulates are transitioning from solid state to liquid state. Looking at Figure 4.2, the transducer pressure was fluctuating initially as the particulates were making their way upward toward the slotted disc. The pressure then started to stabilize around 50 psi. This fluctuation in pressure below 50 psi is like what was seen in Figure 4.1. However, as the particulates started to heat and transition from solid to liquid, some minor pressure losses can be seen above 300 psi at approximately 8 minutes into testing. However, despite the pressure fluctuation occurring from 8-10 minutes, the diverters were able to hold a pressure above the set pressure on the equipment, indicating that the particulate diverters were successful at plugging the slotted disc.

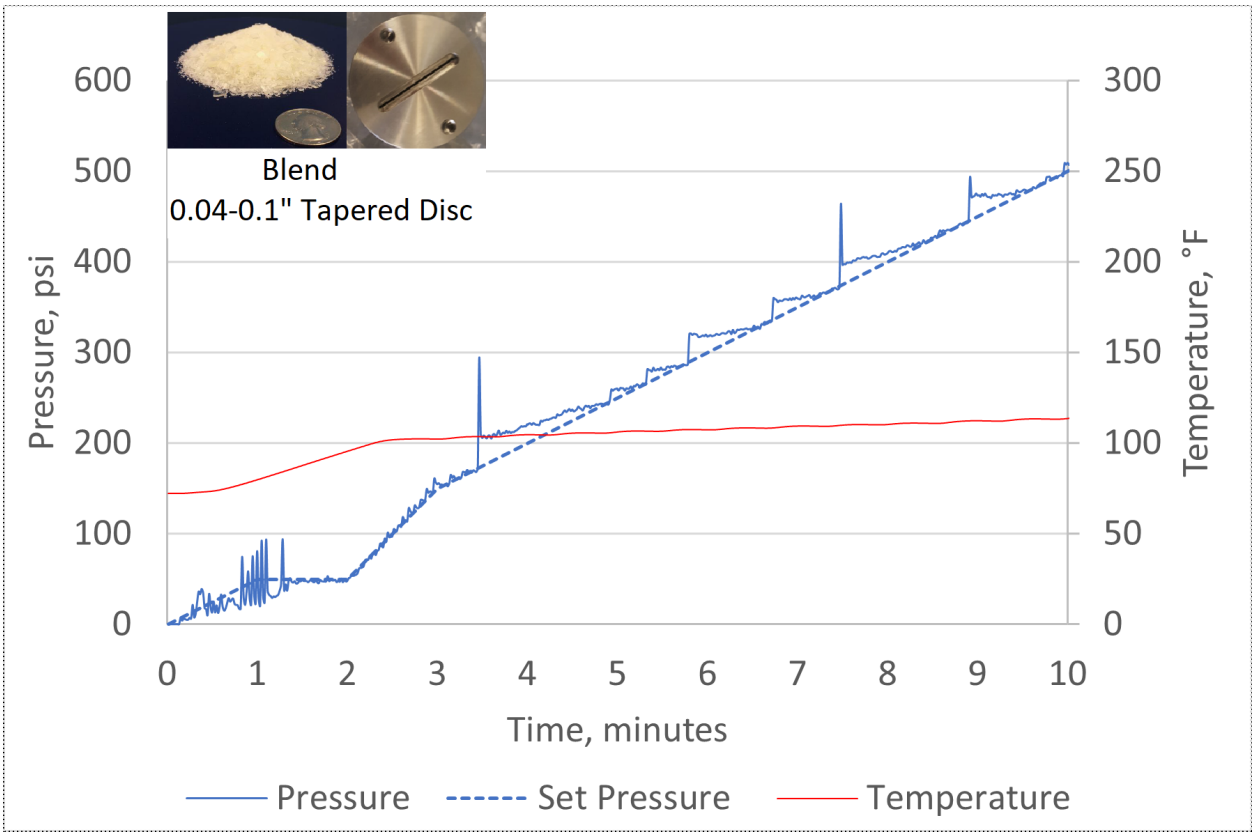

Figure 4.1 APPA results for 18 g of the blend diverter mixed with 150 ml water (1 ppg) tested using the 0.04-0.1 in. tapered slotted disc while heating the sample from 70–100°F. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line is the temperature of the APPA cell. The pressure started to stabilize above 50 psi, approximately one minute and a half into testing. As the pressure continued to increase from 50-500 psi, no pressure losses are seen, and the pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc.

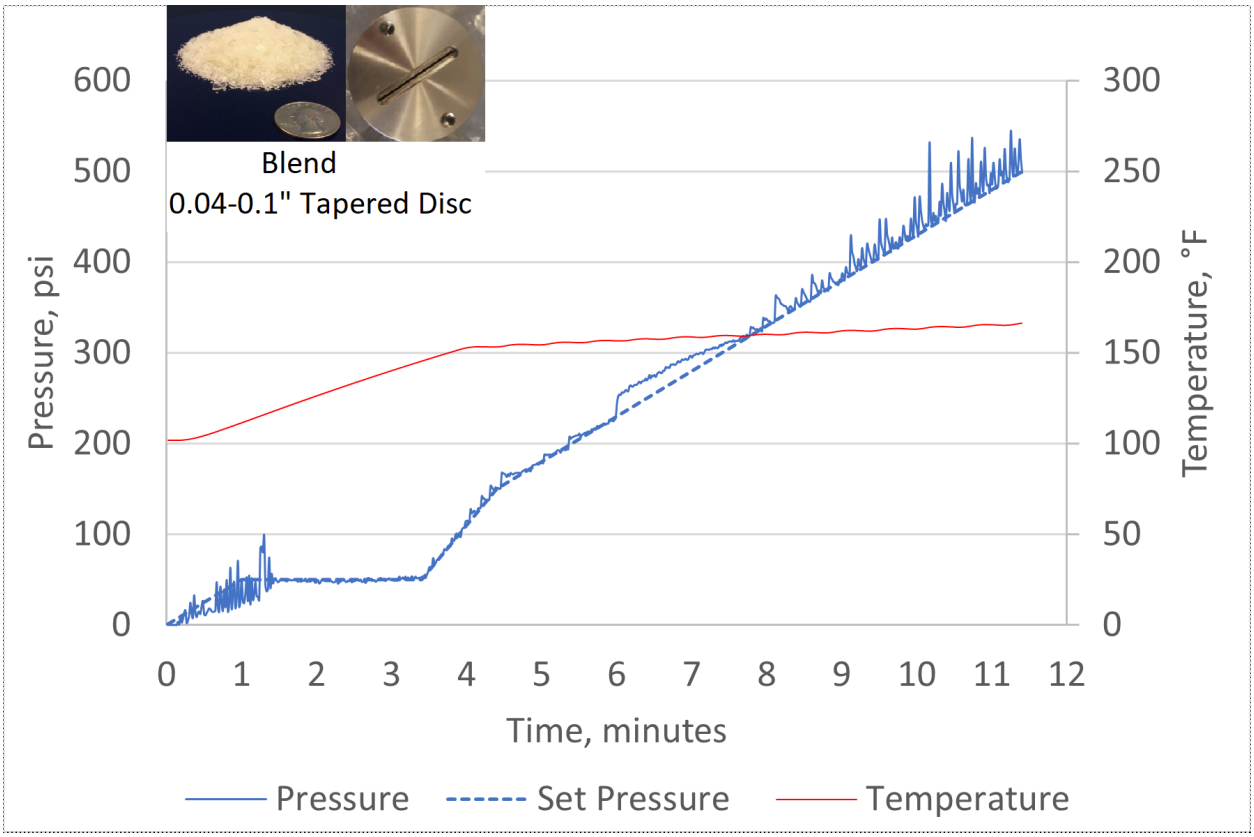

Figure 4.2 APPA results for 18 g of blend diverter mixed with 150 ml water (1) ppg tested using the 0.04-0.1 in. tapered slotted disc while heating the sample from 100–150°F. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the temperature of the APPA cell. The pressure started to stabilize above 50 psi, approximately 1.5 minutes into testing. As the pressure continued to increase from 50-300 psi, no pressure losses are seen. As the particulates were heating up and transitioning from solid to liquid (above 131°F glass transition temperature), some minor pressure fluctuations are seen approximately 8 minutes into testing. However, the pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc.

The third test done on the tapered disc included heating 18 g (1 ppg) of blend diverter from 150-200°F. The sample was heated to 150°F prior to commencing the test to allow the diverters to transition above the 131°F glass transition temperature. Looking at Figure 4.3 the transducer pressure was fluctuating initially as the particulates were making their way upward toward the slotted disc. The pressure then started to stabilize around 50 psi. However, once the pressure stabilized above 50 psi, no pressure losses are seen. The

differential pressure reading remained higher than the set pressure on the equipment, indicating that the diverters were successful at plugging the disc for the remainder of the testing up to 500 psi. In addition, after 5 minutes of testing, no pressure spikes are seen on the pressure graph, indicating that the equipment was not pumping any additional hydraulic oil to move the piston and increase the pressure. This is probably due to the thermal expansion of the fluid inside the APPA cell.

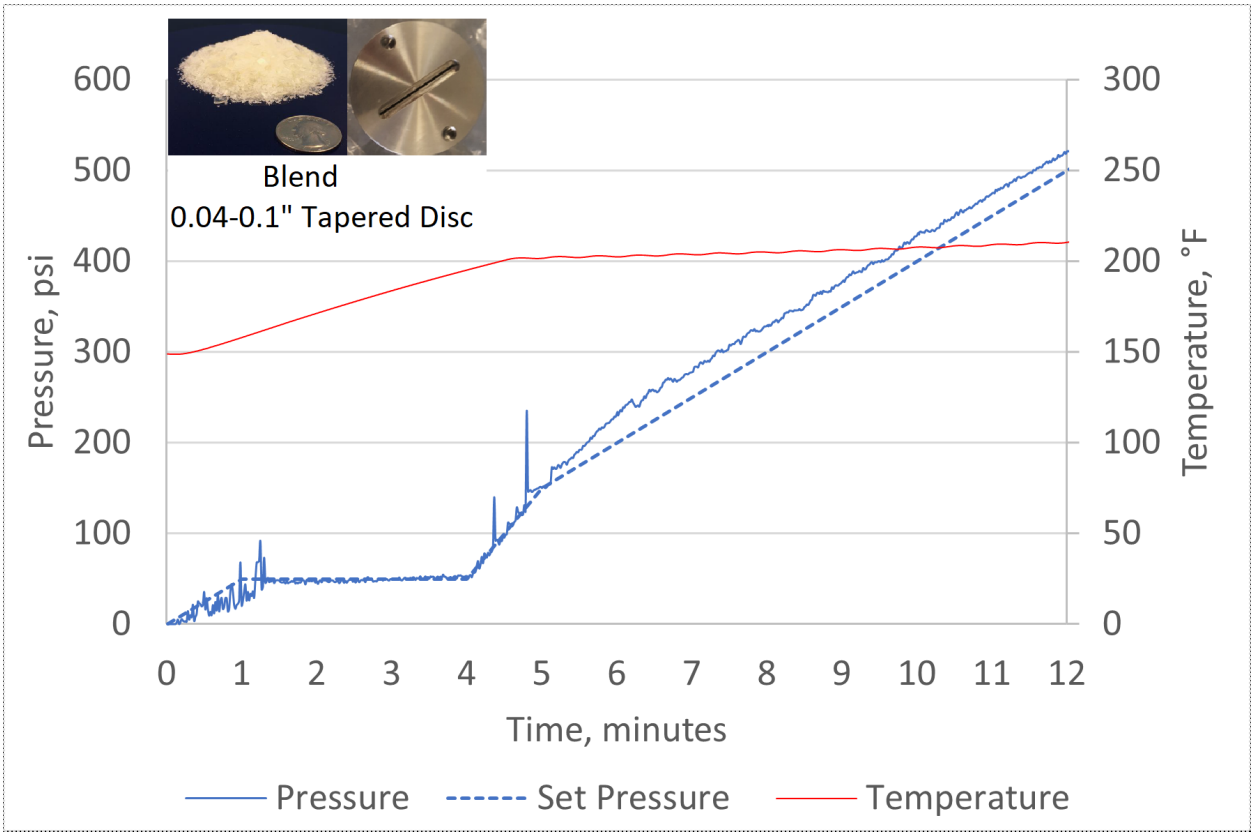

Figure 4.3 APPA results for 18 g of the blend diverters (1 ppg) tested using the 0.04-0.1 in. tapered slotted disc while heating the sample from 150-200°F. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the differential pressure achieved, and the solid red line represents the temperature of the APPA cell. The pressure started to stabilize above 50 psi, approximately 1.5 minutes into testing. As the pressure continued to increase from 50-500 psi, no pressure losses are seen. The pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc. In addition, no pressure spikes are seen after five minutes into testing, which indicates that the pressure kept building up without the need of the equipment to pump additional hydraulic oil to pressurize the cell. This is most likely due to the thermal expansion of the fluids inside the APPA cell.

The fourth test done on the tapered disc included heating 18 g (1 ppg) of blend diverters from 200-230°F. Looking at Figure 4.4, the transducer pressure was fluctuating initially as the particulates were making their way upward toward the slotted disc and before the pressure started to stabilize around 50 psi. This fluctuation in pressure below 50 psi is like what was seen in Figure 4.1, Figure 4.2, and Figure 4.3.

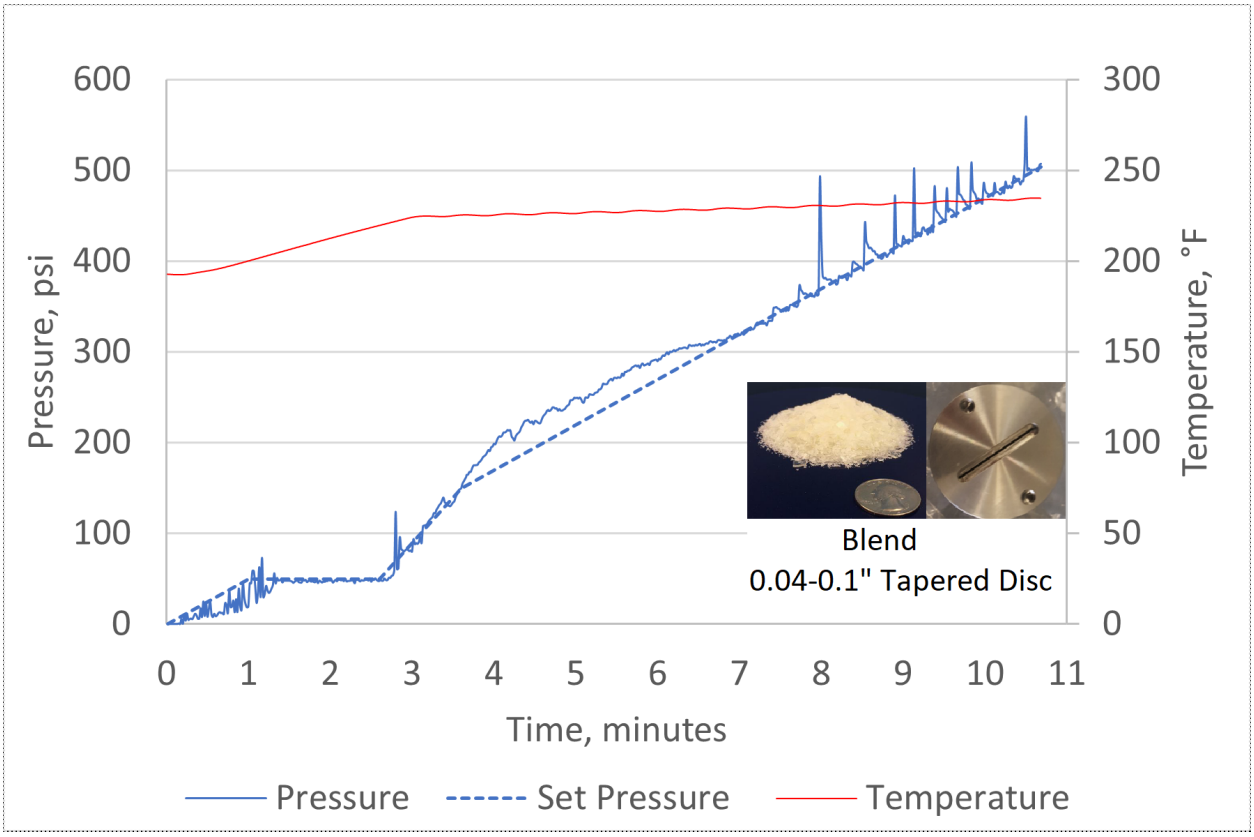

Figure 4.4 APPA results for 18 g of the blend diverter in water (1 ppg) tested using the 0.04-0.1 in. tapered slotted disc while heating the sample from 200-230°F. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the differential pressure achieved, and the solid red line represents the temperature of the APPA cell. The pressure started to stabilize above 50 psi, approximately after 1.5 minutes into testing. As the pressure continued to increase from 50-350 psi, no pressure losses are seen until 7.5 minutes into testing. In addition, no pressure spikes can be seen from 3.5–7.5 minutes. This indicates that the pressure kept building up without the need of the equipment to pump additional hydraulic oil to pressurize the cell. However, some pressure losses can be seen from 7.5 minutes till the end of the test. However, the pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc.

Once the pressure stabilized above 50 psi, no pressure losses are seen until 7.5 minutes into testing. In addition, no pressure spikes are seen on the pressure graph from 3.5–7.5 minutes. This means that the equipment was not pumping any additional hydraulic oil to move the piston and increase the pressure. However, after 7.5 minutes into testing, a few pressure losses were seen for the remainder of the test. These pressure losses, specially at higher pressure ranges, could indicate more severe transitioning of the diverters from solid to liquid state and thus decreasing their hardness and strength. Moreover, the differential pressure reading remained higher than the set pressure on the equipment, indicating that the diverters were successful at plugging the disc for the remainder of the testing to 500 psi.

The next five tests shown below are also done using the tapered disc but conducted using the flake diverters. For each test, 18 g of diverter was used in 150 ml of water, which is equivalent to 1 ppg. The flake diverters were heated at different temperature ranges while incrementally increasing the pressure from 0-500 psi. These tests can be seen in Figure 4.5, Figure 4.6, Figure 4.7, Figure 4.8 and Figure 4.9.

Figure 4.5 shows the results for the test done on the tapered disc while utilizing 18 g of flake diverters mixed in 150 ml of water (1 ppg) and conducted at room temperature without heating the sample. The pressure was increased incrementally from 0-500 psi. Looking at Figure 4.5, the pressure was fluctuating through-out the entire length of the test. Pressure losses were more frequent and more severe for pressures below 250 psi and up until 10 minutes into testing. However, for pressures above 250 psi starting at 10 minutes into testing and till the end of the test, the pressure losses became minimal. However, the differential pressure reading remained higher than the set pressure on the equipment above 250 psi, indicating that the diverters were successful at plugging the disc for the remainder of the testing from 250-500 psi.

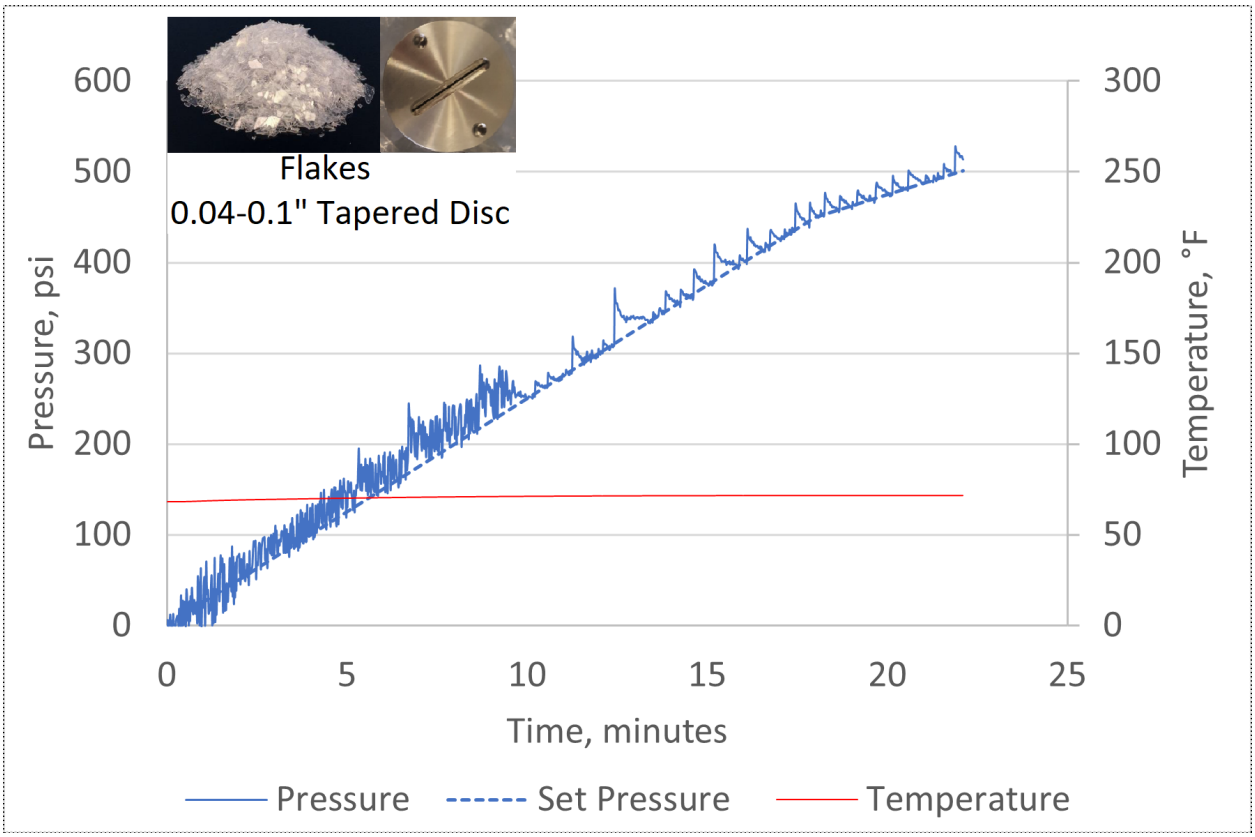

Figure 4.5 APPA results for 18 g of the flake diverter mixed with 150 ml water (1 ppg) tested using the 0.04-0.1 in. tapered slotted disc at room temperature (70°F). The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the differential pressure achieved, and the solid red line represents the temperature of the APPA cell. Pressure losses can be seen through-out the duration of the test but less frequent at pressures higher than 250 psi. For pressures from 150-500 psi, the pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc at higher pressures.

Figure 4.6 shows the test done on the tapered disc while utilizing 18 g (1 ppg) flake diverters. The sample was heated to 100°F while conducting the test. Meanwhile, the pressure was increased incrementally from 0-500 psi. Like most tests done on the tapered disc, the pressure was fluctuating initially as the particulates were making their way upward toward the slotted disc and the pressure started to stabilize around 50 psi. Although the flake particulates were heated to a temperature below the glass transition temperature, only minor pressure losses can be seen above 200 psi as opposed to the test

done at room temperature. Moreover, the differential pressure reading remained higher than the set pressure on the equipment, indicating that the diverters were successful at plugging the disc for the remainder of the test to 500 psi.

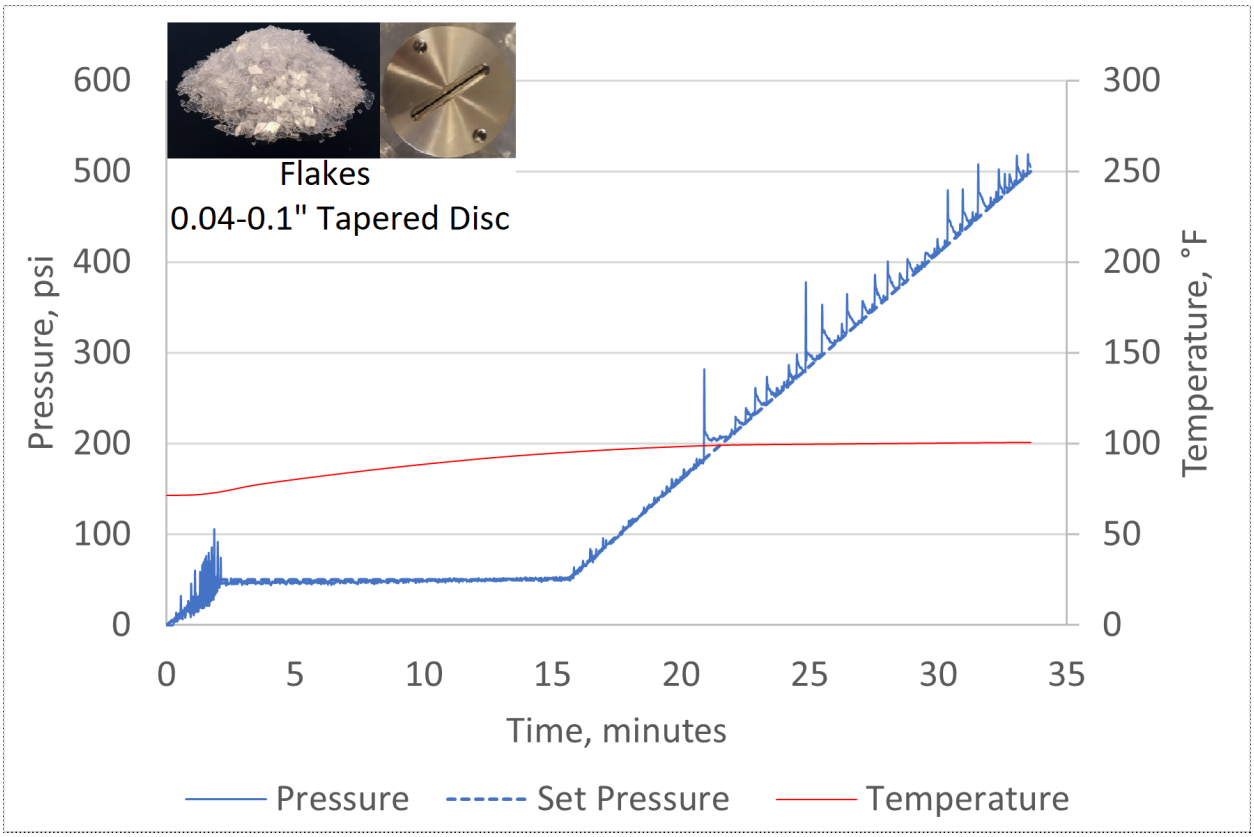

Figure 4.6 APPA results for 18 g of the flake diverter tested using the 0.04-0.1 in. tapered slotted disc and heated from 70-100°F during testing. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the temperature of the APPA cell. The pressure started to stabilize above 50 psi, approximately two minutes into testing. As the pressure continued to increase from 50-200 psi, no pressure losses are seen but minor pressure losses are visible above 200 psi. The pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc.

Figure 4.7 shows the test done on the tapered disc while utilizing 18 g (1 ppg) flake diverters. The sample was heated to 150°F prior to commencing the test to allow the diverters to transition above the 131°F glass transition temperature. Looking at Figure 4.7, the transducer pressure was fluctuating initially as the particulates were making their way

upward toward the slotted disc and the pressure started to stabilize around 50 psi.

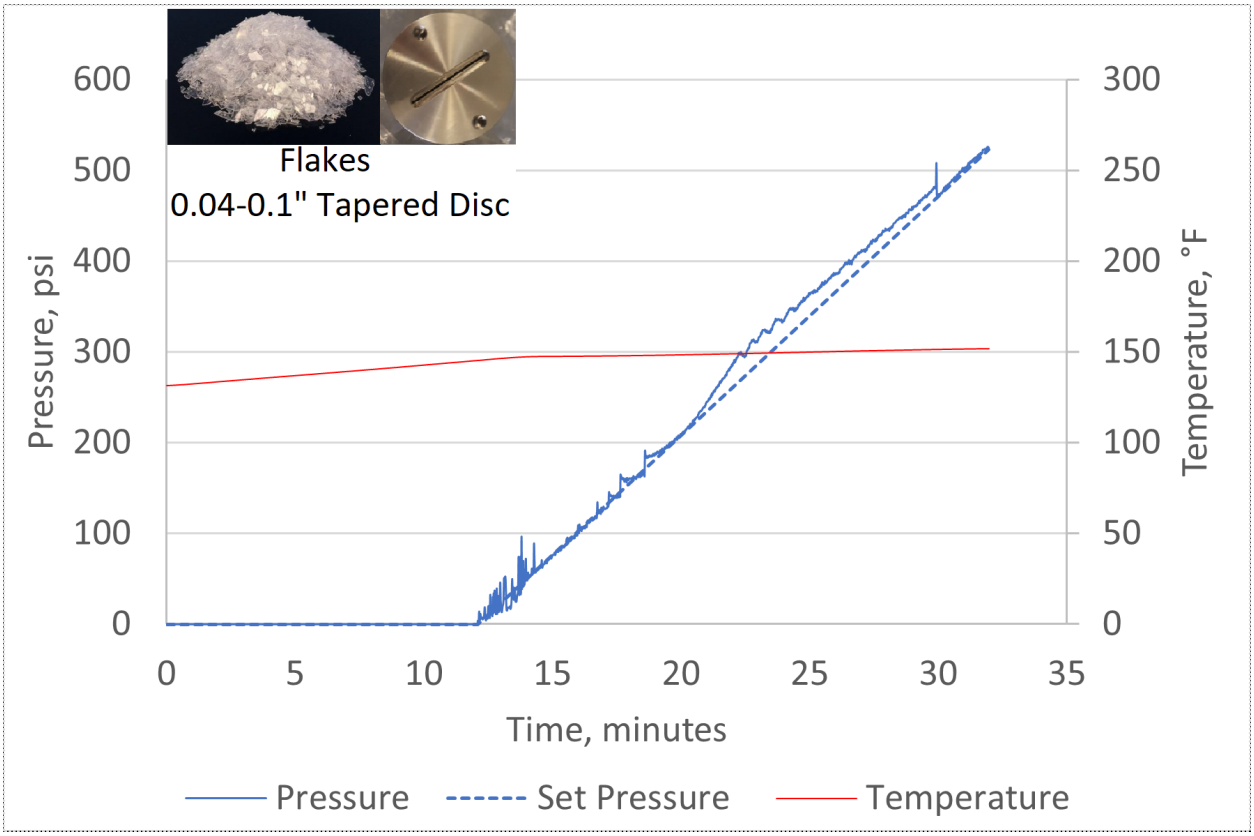

Figure 4.7 APPA results for 18 g of the flake diverter sample in 150 ml water (1 ppg) tested using the 0.04-0.1 in. tapered slotted disc and heated to 150°F. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The pressure started to stabilize above 50 psi. As the pressure continued to increase from 50-500 psi, no pressure losses are seen. The pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc. No pressure spikes are seen above 200 psi, indicating that the pressure kept building up without the need of the equipment to pump additional hydraulic oil to pressurize the cell. This is likely due to the thermal expansion of the fluid inside the APPA cell.

However, once the pressure stabilized above 50 psi, no pressure losses are seen. The differential pressure reading remained higher than the set pressure on the equipment, indicating that the diverters were successful at plugging the slotted disc for the remainder of the test up to 500 psi. In addition, no pressure spikes are seen on the pressure graph

above 200 psi, which means that the equipment was not pumping any additional hydraulic oil to move the piston and increase the pressure. This is most likely due to the thermal expansion of the fluid inside the APPA cell.

The graphs in Figure 4.8 and Figure 4.9 show the tests done on the tapered disc while utilizing 18 g (1 ppg) flake diverters. The samples were heated to 200°F and 225°F, respectively, prior to commencing the tests to allow the diverters to transition above the 131°F glass transition temperature. Looking at Figure 4.8 and Figure 4.9, the pressure was fluctuating initially as the particulates were making their way upward toward the slotted disc, before stabilizing around 50 psi. However, once the pressure stabilized above the 50 psi, no pressure losses are seen. The differential pressure reading remained higher than the set pressure on the equipment, indicating that the diverters were successful at plugging the disc for the remainder of the testing to 500 psi. In addition, no pressure spikes are seen on the pressure graph above 100 psi, which means that the equipment was not pumping any additional hydraulic oil to move the piston and increase the pressure. This is probably due to the thermal expansion of the fluid inside the APPA cell.

To summarize the tests done on the tapered disc, it is evident that temperature and pressure influence the plugging performance of the diverters. The flake particulates seem to have better plugging performance at temperatures higher than their glass transition temperature. In addition, all the test samples seem to stabilize at pressures above 50 psi. However, few minor pressure losses were seen above 200 psi in some tests. Therefore, to study and understand these effects further, additional tests are conducted using baseline testing while changing one variable at a time. Baseline variables include increasing the pressure inside the APPA cell to 50 psi as fast as the equipment allows and heating the diverters to 150°F, which is a temperature above the glass transition temperature. Having these baseline variables helps in comparing the performance of the different types of diverters. Additionally, other tests are conducted at higher pressures and different temperatures to understand the effect of pressure and temperature on the diverters'

plugging performance.

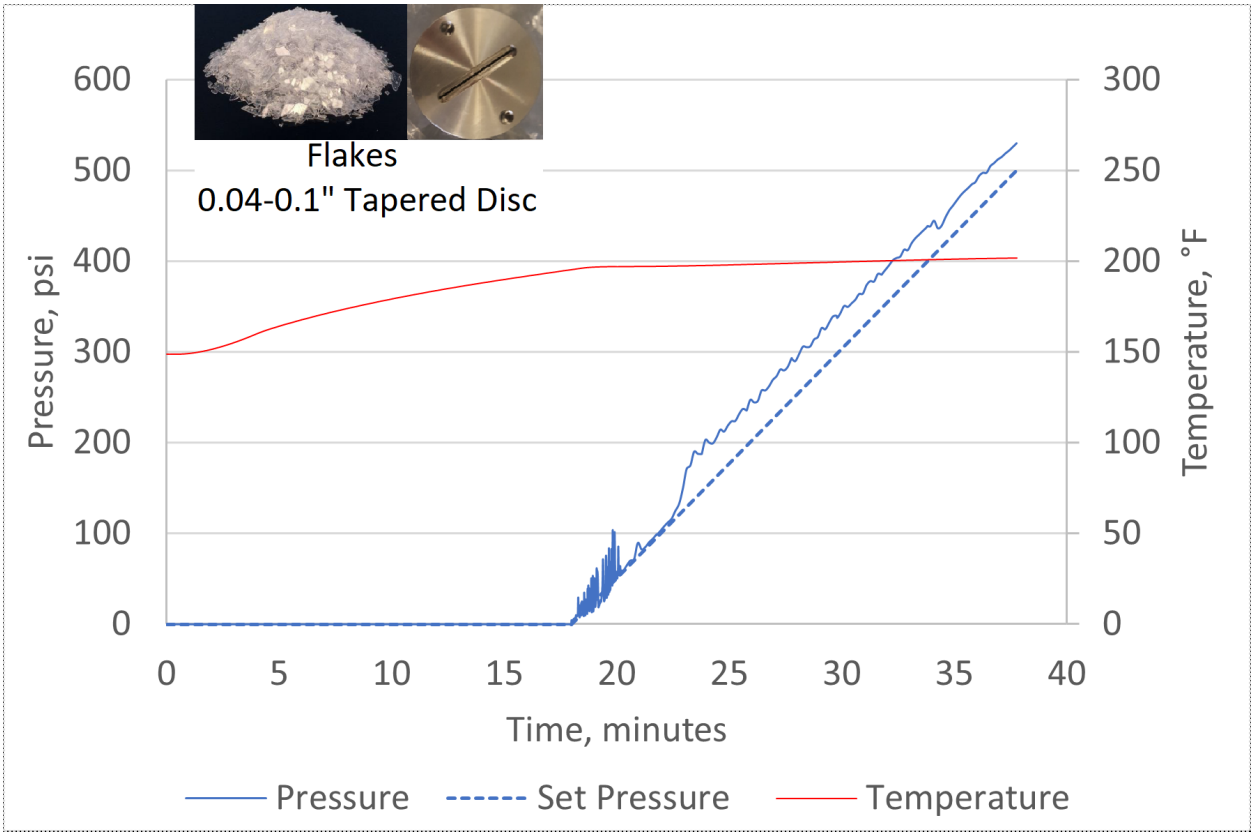

Figure 4.8 APPA results for 18 g of the flake diverter mixed with 150 ml water (1 ppg) tested using the 0.04-0.1 in. tapered slotted disc and heated to 200°F. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The pressure started to stabilize above 50 psi. As the pressure continued to increase from 50-500 psi, no pressure losses are seen. The pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc. In addition, no pressure spikes are seen above 100 psi, indicating that the pressure kept building up without the need of the equipment to pump additional hydraulic oil to pressurize the cell, likely due to the thermal expansion of the fluids inside the APPA cell.

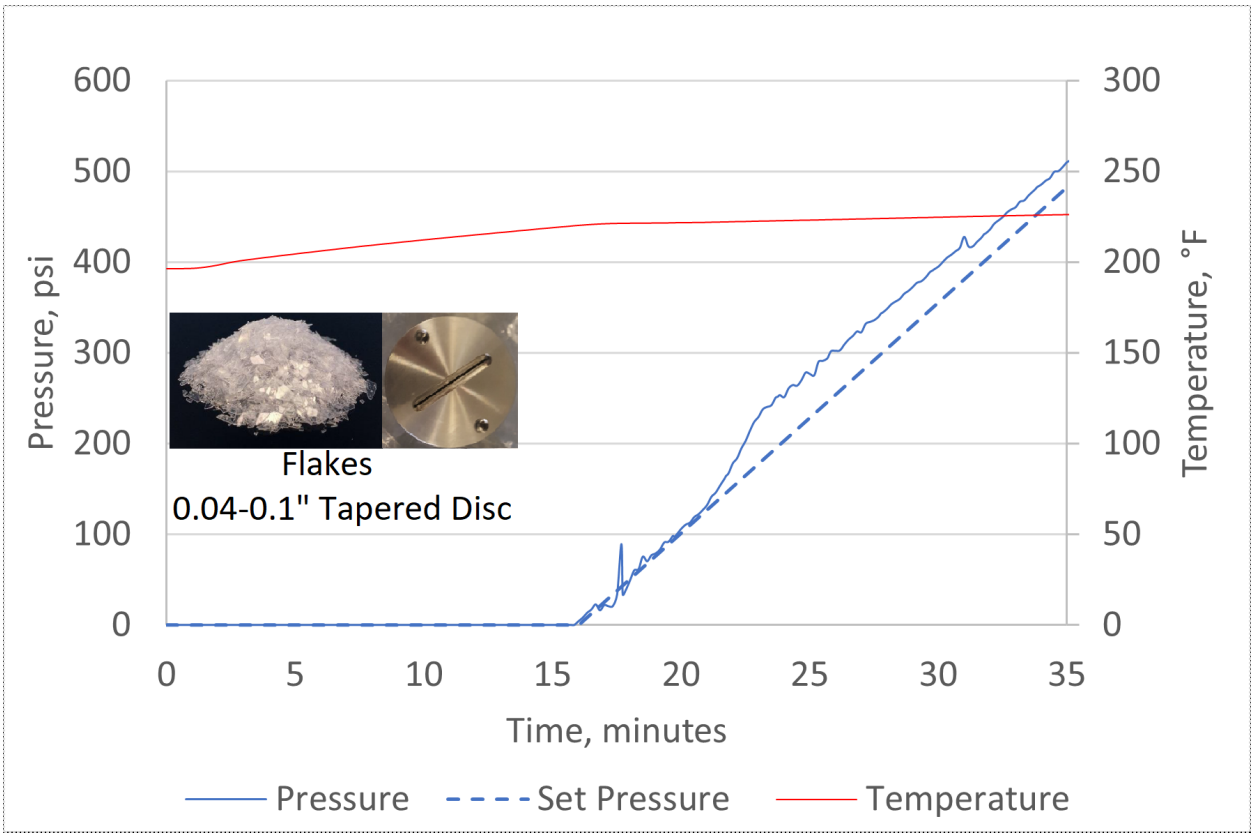

Figure 4.9 APPA results for 18 g of the flake diverter with 150 ml water (1 ppg) tested using the 0.04-0.1 in. tapered slotted disc and heated to 225°F. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The pressure started to stabilize above 50 psi. As the pressure continued to increase from 50-500 psi, no pressure losses are seen. The pressure continued to hold above the set pressure on the equipment, indicating that the particulates were successful at plugging the slotted disc. Additionally, no pressure spikes are seen above 200 psi, which indicates that the pressure kept building up without the need of the equipment to pump additional hydraulic oil to pressurize the cell.

4.2 The Effect of Temperature and Heating Duration

To understand the effect of temperature on the PLA diverters, a few tests were conducted using the beads to plug the 0.12 in. two-radial arms slotted disc under 50 psi differential pressure. Four tests were done using samples consisting of 18 g of beads mixed in 150 ml water, which corresponds to 1 ppg concentration. These tests were done at room temperature (70°F), heated to 150°F for 10 minutes, heated to 150°F for 30 minutes, and

heated to 150°F for 60 minutes, respectively.

Looking at Figure 4.10 for the unheated 18 g bead diverter sample, the pressure fluctuated throughout the test. The constant pressure losses indicate that the diverters were not successful at plugging the 0.12 in. two-radial arms slotted disc. The test was terminated as the floating piston made it to the top of the APPA cell.

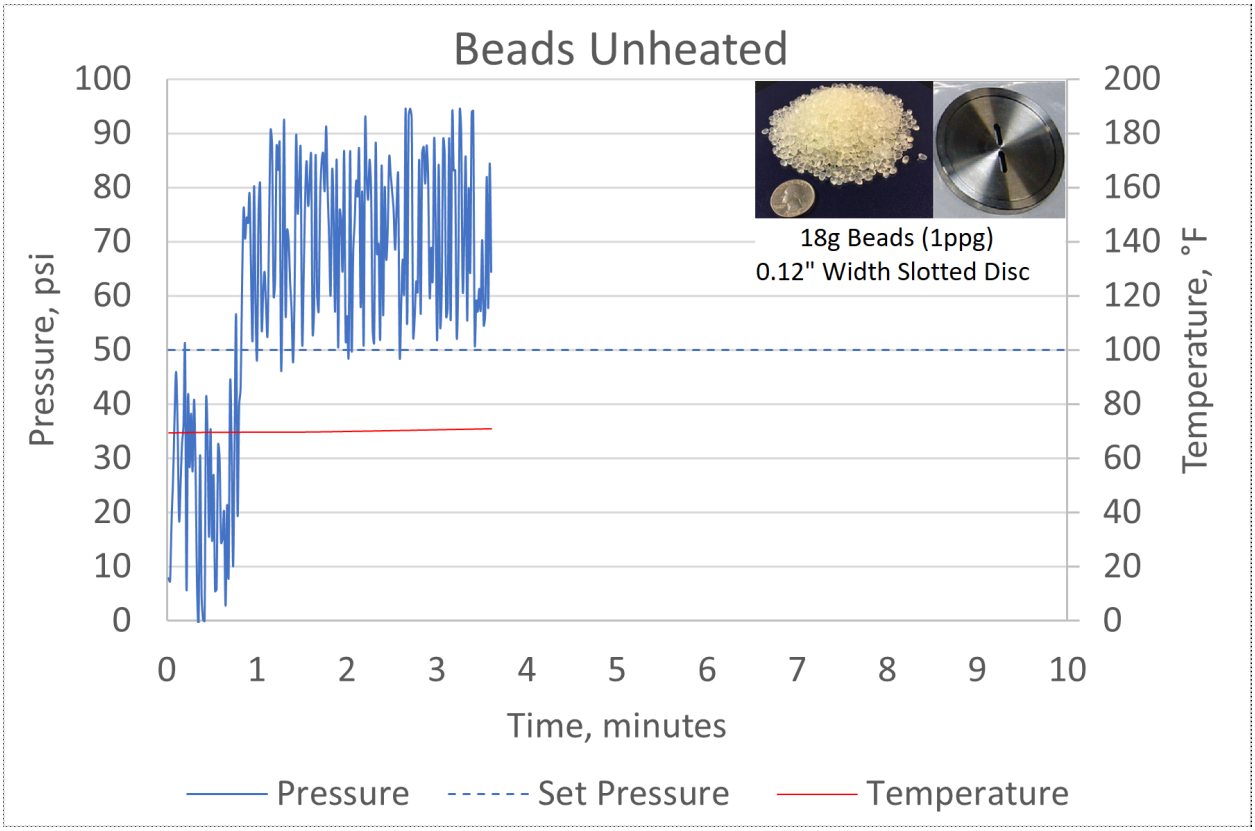

Figure 4.10 APPA results for unheated 18 g of bead diverters mixed with 150 ml water (1 ppg) tested using the 0.12 in. two-radial arms slotted disc representing a fracture with 0.12 in. width. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure reading, and the solid red line represents the temperature inside the APPA cell. The pressure is fluctuating throughout the test, and the diverters were not able to plug the slotted disc, indicating a failed test.

Next, another sample of 18 g of bead diverters mixed with 150 ml of water (1 ppg) was used. However, this sample was heated to 150°F for 10 minutes while keeping all other testing variables the same as Figure 4.10. Once the diverters started arriving at the 0.12 in.

width slotted disc, a plug was achieved immediately as seen at the 1-minute mark in Figure 4.11. The achieved differential pressure was sustained for approximately 2 minutes. However, at the 3-minutes mark, the pressure started declining again until it reached below the 50-psi pressure that was set on the equipment.

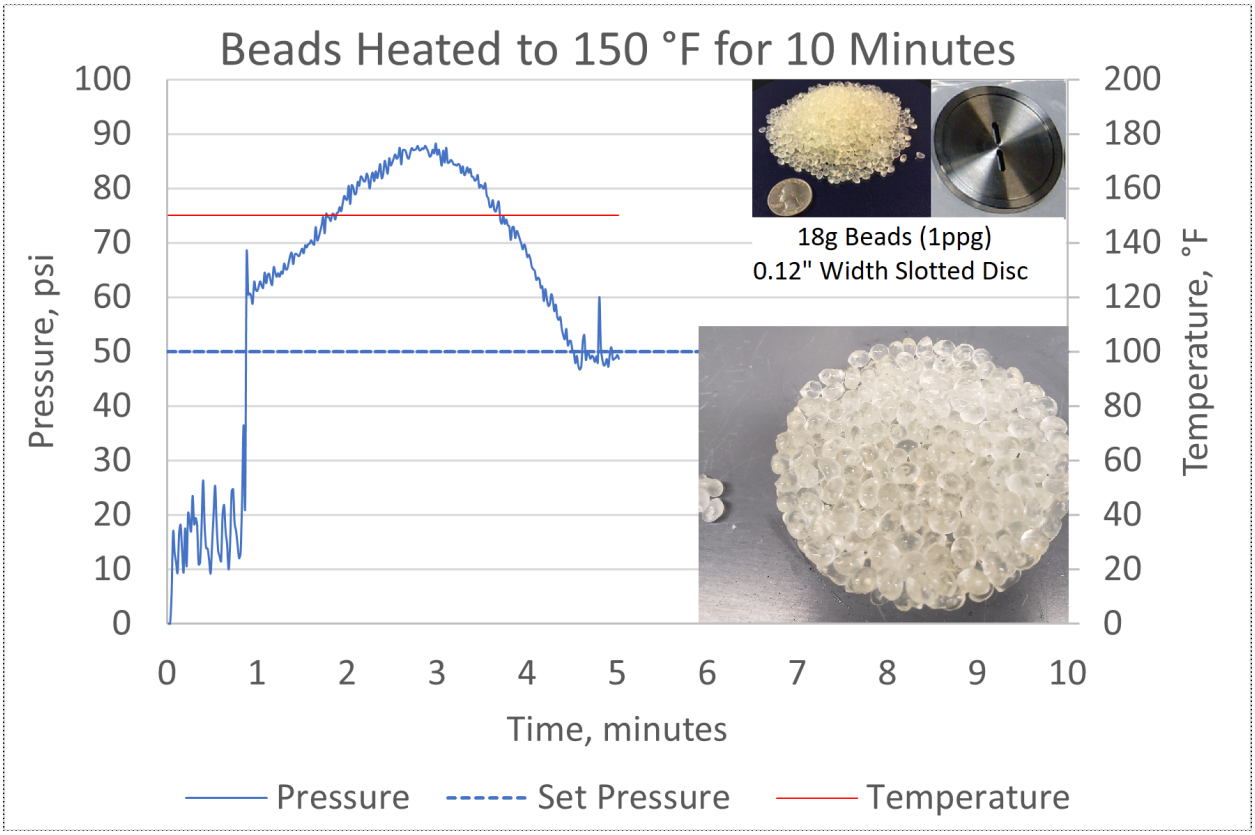

Figure 4.11 APPA results for 18 g of the bead diverters mixed with 150 ml water (1 ppg) tested using the 0.12 in. two-radial arms disc that simulate a fracture. The sample was heated to 150°F for 10 minutes prior to commencing testing. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the temperature inside the APPA cell. Once the diverters reached the slotted disc, they were able to plug it immediately and a differential pressure above 50 psi was achieved. However, the pressure started to decline at 3 minutes and fell below the 50-psi set pressure around 5 minutes. The image taken of the diverter after the test was conducted shows that some of the particulates started to bond together to form a plug. However, some loose particulates as well as open pore space between the particulates can be seen in the lower right picture.

Looking at the image of the diverters taken after conducting the test (lower right corner in Figure 4.11), it is evident that the particulates started to bond together.

However, 10 minutes was not enough for all the particulates to bond together and form one solid plug. Open pore space between the particulates can be seen in Figure 4.11 indicating a permeable plug.

For the following test, another sample of 18 g beads mixed with 150 ml water (1 ppg) was used. This sample was heated to 150°F for 30 minutes prior to commencing the testing while keeping all other testing variables the same as the tests in Figure 4.10 and Figure 4.11. The results of this test is seen in Figure 4.12.

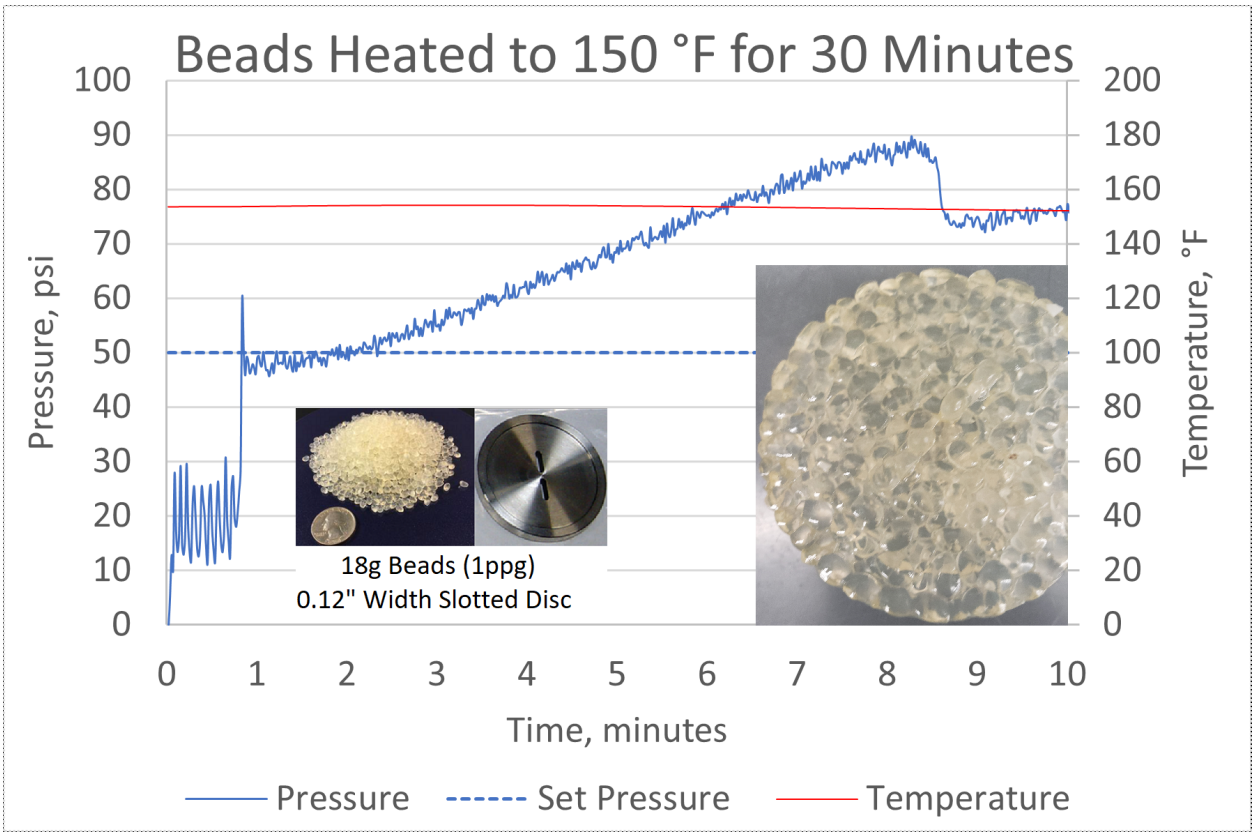

Figure 4.12 APPA results for 18 g of the bead diverters mixed with 150 ml water (1 ppg) tested using the 0.12 in. two-radial arms disc and heated to 150°F for 30 minutes. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The pressure started to stabilize and reached a pressure above the desired 50-psi differential pressure for the remainder of the 10-minute experiment. This pressure response shows that the particulates were successful at plugging the slotted disc. The image of the diverters taken after the test was complete shows that the particulates did bond together forming one solid impermeable plug (picture in lower right).

Once the diverters started to arrive at the 0.12 in. width slotted disc, the pressure started to stabilize and reached a pressure above the desired 50-psi differential pressure for the remainder of the 10-minute experiment as seen in Figure 4.12. The pressure response shows that the particulates were successful at plugging the slotted disc. It is important to note that the pressure decline seen around 8.5 minutes is due to the safety mechanism of the equipment as discussed in Chapter 3. The safety mechanism was triggered due to the rapid increase in pressure caused by the thermal expansion of the fluids inside the APPA cell.

Looking at the image of the diverters taken after conducting the test (lower right corner in Figure 4.12), it is evident that the particulates did bond together to form one solid plug. The formed plug appears to be impermeable and no open space between the particulates were observed. Additionally, the formed plug was pliable during the test that it took the shape of the APPA cell and the slotted disc it plugged under the 50-psi pressure.

Another test was conducted using the same method and baseline variables for the tests in Figure 4.10, Figure 4.11, and Figure 4.12, while heating the beads to the 150°F for 60 minutes (Figure 4.13). The pressure response seen during this experiment is similar to the response of the test conducted in Figure 4.12. The particulates were able to plug the 0.12 in. width slotted disc for 10 minutes. In addition, the image of the diverters taken after conducting the test shows that a solid impermeable plug was formed as seen in the lower right of Figure 4.13.

To find out if the formed plug from the heated bead diverters can withstand the 50-psi pressure for a longer duration of time, the test was conducted as seen in Figure 4.14. The testing parameters were the same as the parameters used in Figure 4.13 where 18 g of beads were placed in 150 ml of water (1 ppg) and heated to 150°F inside the APPA cell for 60 minutes. The APPA cell was then pressurized to 50 psi while holding that pressure for 1 hour.

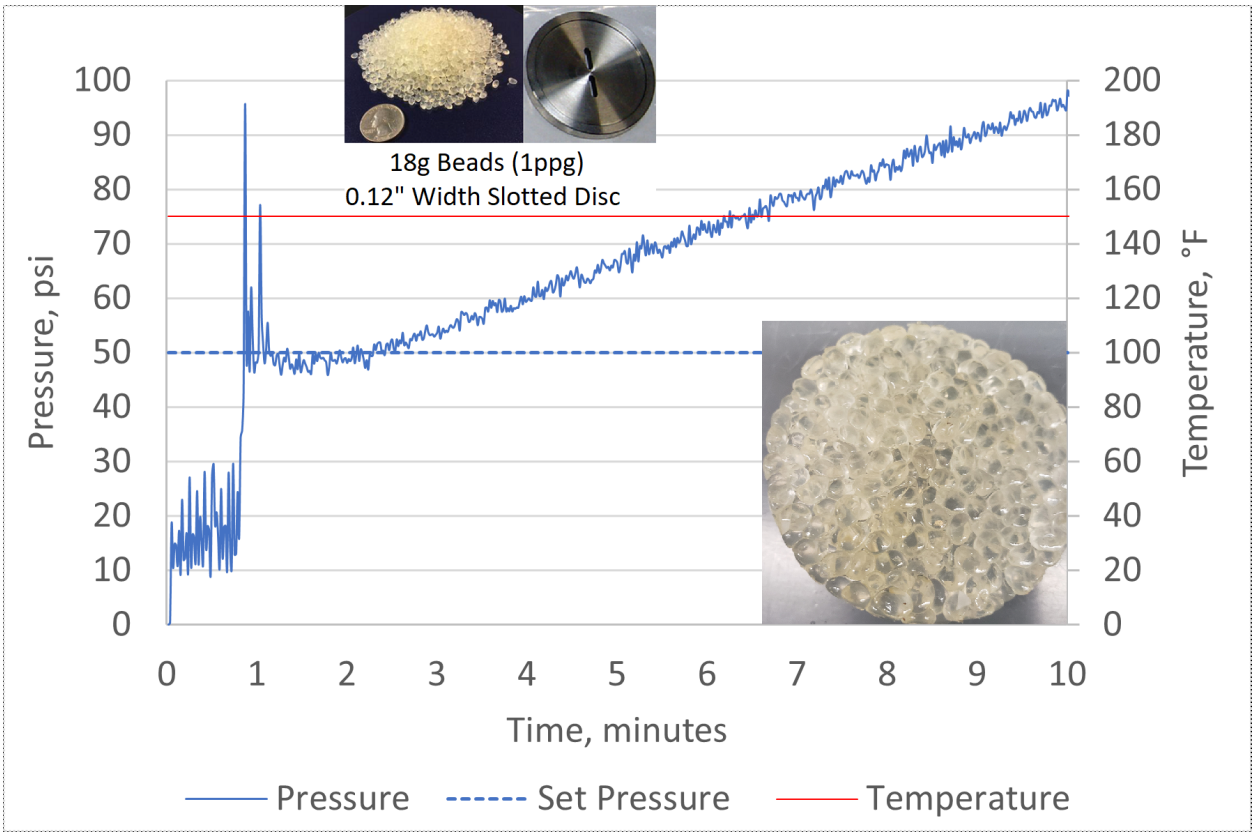

Figure 4.13 APPA results for 18 g of the bead diverters tested using the 0.12 in. two-radial arms slotted disc representing two 0.12 in. width fractures. The sample was heated to 150°F for 60 minutes. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The pressure started to stabilize and reached a pressure above the desired 50-psi differential pressure for the remainder of the 10-minute experiment. This pressure response shows that the particulates were successful at plugging the slotted disc. In addition, the image (lower right) of the particulates after the test was completed shows that the particulates did bond together forming an impermeable plug.

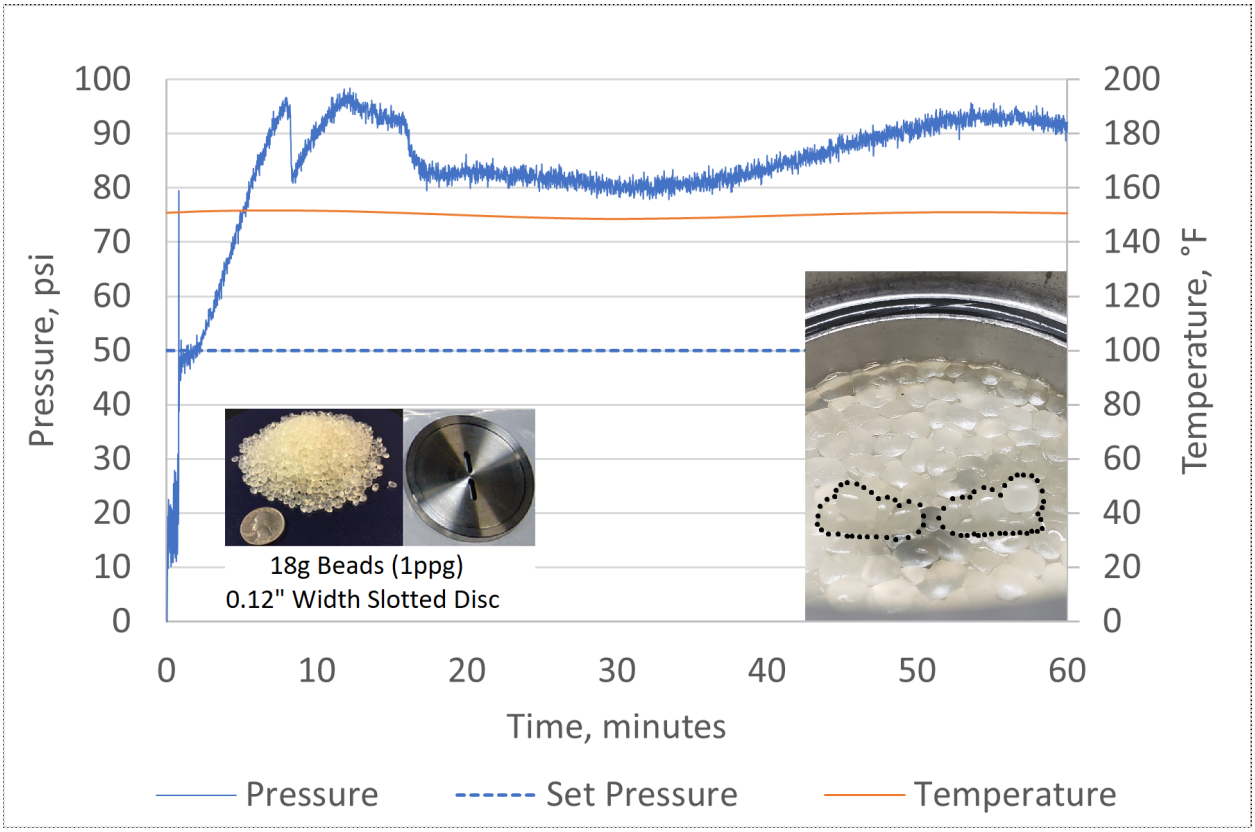

Figure 4.14 APPA results for 18 g of the bead diverters mixed with 150 ml water (1 ppg) tested using the 0.12 in. width slotted disc representing two 0.12 in. width fractures. The sample was heated to 150°F for 60 minutes while pressurizing the cell to 50 psi for 1 hour. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line is the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. This pressure response shows that the particulates were successful at plugging the slotted disc. The image of the particulates after the test was completed (lower right) shows that the particulates did bond together forming an impermeable plug. Additionally, some particulates appear to have been squeezed into the slotted disc (as outlined) taking the shape of the two 0.12 in. openings of the slotted disc.

Looking at Figure 4.14, it can be seen that the plug was able to hold the 50-psi differential pressure set on the equipment for the entire 1-hour testing period. The pressure response indicates that the particulate diverters were successful at plugging the 0.12 in. width fracture disc. Looking at the picture of the sample after the test was done, the particulates did bond together forming a solid impermeable plug. Additionally, a few bead particulates were squeezed inside the 0.12 in. disc taking the shape of the opening of the slotted disc.

To summarize the effect of temperature on the plugging performance of PLA diverters, it is evident that the diverters start to deform, and the particulates start to bond together to form an impermeable plug at temperatures above the glass transition temperature. It takes as little as 10 minutes for the bead diverters to start transitioning from a glassy-solid to a rubbery state, causing the particulates to start bonding together under differential pressure. Comparing the same mass of diverters below and above the glass transition, the unheated sample that was left at room temperature (below the glass transition temperature) was not able to plug the 0.12 in. slotted disc, while the heated diverters were successful at plugging.

4.3 Minimum Amount of Diverter Required to Plug 0.12 in. Fracture at 150°F

Since it was determined that PLA particulate diverters can perform better at temperatures above the glass transition temperature, a few tests were conducted to determine the minimum amount of diverter required to plug the 0.12 in. width two-radial arms slotted disc. This two-radial arms disc is used to simulate two large 0.12 in. width fractures. These tests can in turn help determine the minimum mass of diverters required to plug a fracture at temperatures above the diverters' glass transition temperature. The conducted tests include heating each of the three types of diverters to 150°F for 60 minutes and holding a 50-psi differential pressure for 10 minutes. The tests were initially conducted using samples containing 18 g of diverter mixed with 150 ml of water corresponding to 1 ppg concentration. If the diverters were able to pass the test and withstand the 50-psi

differential pressure, a lower mass of diverters (mixed with 150 ml water) was then tested. This resulted in conducting additional tests using 9 g (0.5 ppg) and 4.5 g (0.25 ppg) of each type of diverters.

A graph that contains the three tests done using different mass of bead diverters can be seen in Figure 4.15. All three samples (18 g, 9 g, and 4.5 g) were heated to 150°F for 60 minutes prior to pressurizing the APPA cell. The pressure results show that all three bead samples passed the test, including using only 4.5 g of diverters mixed in 150 ml of water (0.25 ppg).

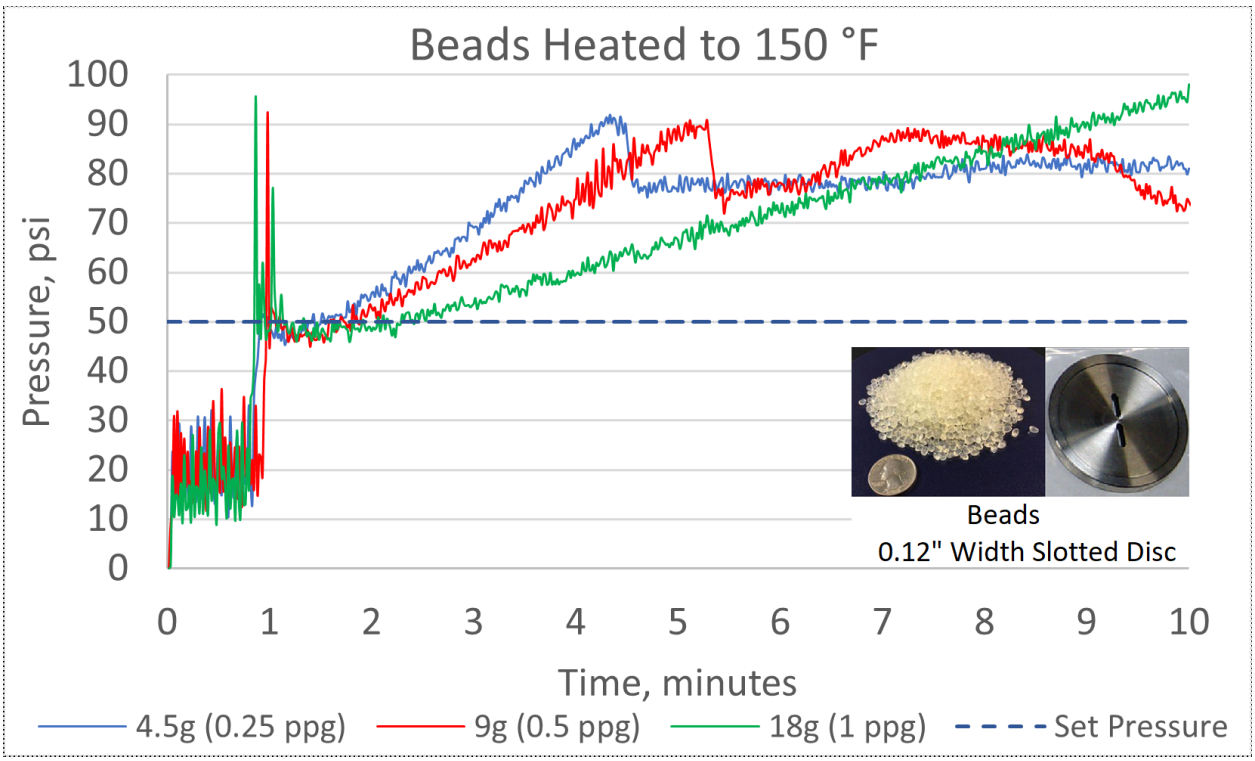

Figure 4.15 APPA results for the three tests conducted using the bead diverters heated to 150°F for 60 minutes. The dashed blue line represents the 50-psi differential pressure that was set on the equipment, while the solid blue, red, and green lines represent the actual pressure achieved using 4.5 g, 9 g, and 18 g of bead diverters, respectively. All three samples were able to sustain the 50-psi pressure for the 10-minute testing period. These pressure responses indicate that only 4.5 g of beads is needed to plug the 0.12 in. width slotted disc.

Next, the blend diverters were tested using the same criteria. Three samples with different mass of blend diverters were heated to 150°F for 60 minutes prior to pressurizing the APPA cell to 50 psi. A graph that contains the three tests done using 18 g, 9 g, and 4.5 g, of the blend diverters corresponding to different concentrations (1 ppg, 0.5 g, and 0.25 g, respectively) can be seen in Figure 4.16.

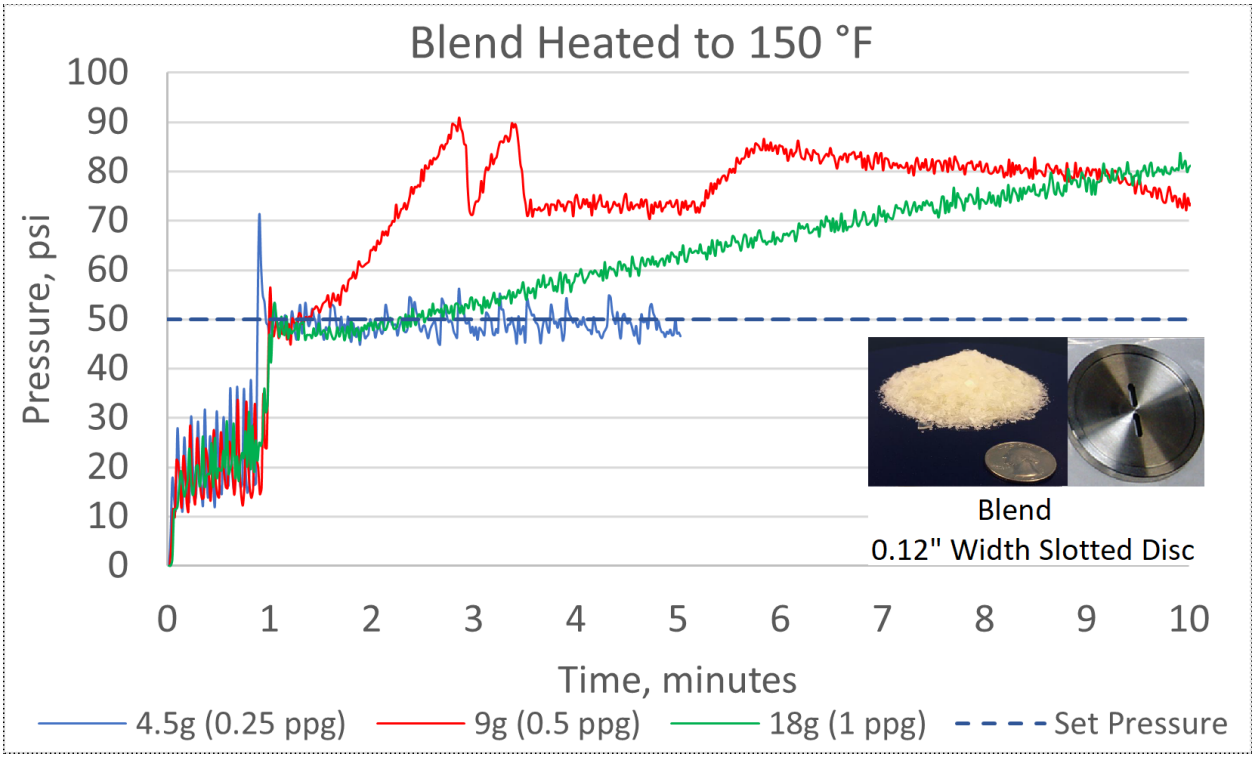

Figure 4.16 APPA results for three tests conducted using the blend diverter heated to 150°F for 60 minutes. The dashed blue line represents the 50-psi differential pressure that was set on the equipment, while the solid blue, red, and green lines represent the actual pressure achieved using 4.5 g, 9 g, and 18 g of the blend diverter, respectively. The 18 g and 9 g samples were able to plug the 0.12 in. width slotted disc. However, the sample that contained only 4.5 g of blend was not able to sustain the 50 psi-differential pressure, and thus, failed to plug the slotted disc.

The samples that contained 18 g (1 ppg) and 9 g (0.5 ppg) of blend diverters were able to sustain the 50-psi differential pressure. However, looking at the blue solid line that represents the pressure data for the sample with only 4.5 g of blend, continuous pressure losses can be seen. Additionally, the pressure kept dropping below the 50-psi differential

pressure that was set on the equipment. The floating piston made it to the top of the APPA cell and the testing had to be terminated since the 4.5 g of the blend was not enough to plug the 0.12 in. width slotted disc.

Next, the flake diverters were tested using the same criteria utilized for testing the bead and the blend. Three samples with different mass of flake diverters were heated to 150°F for 60 minutes prior to pressurizing the APPA cell to 50 psi. A graph that contains the three tests done using the flake particulate diverters at different concentrations can be seen in Figure 4.17.

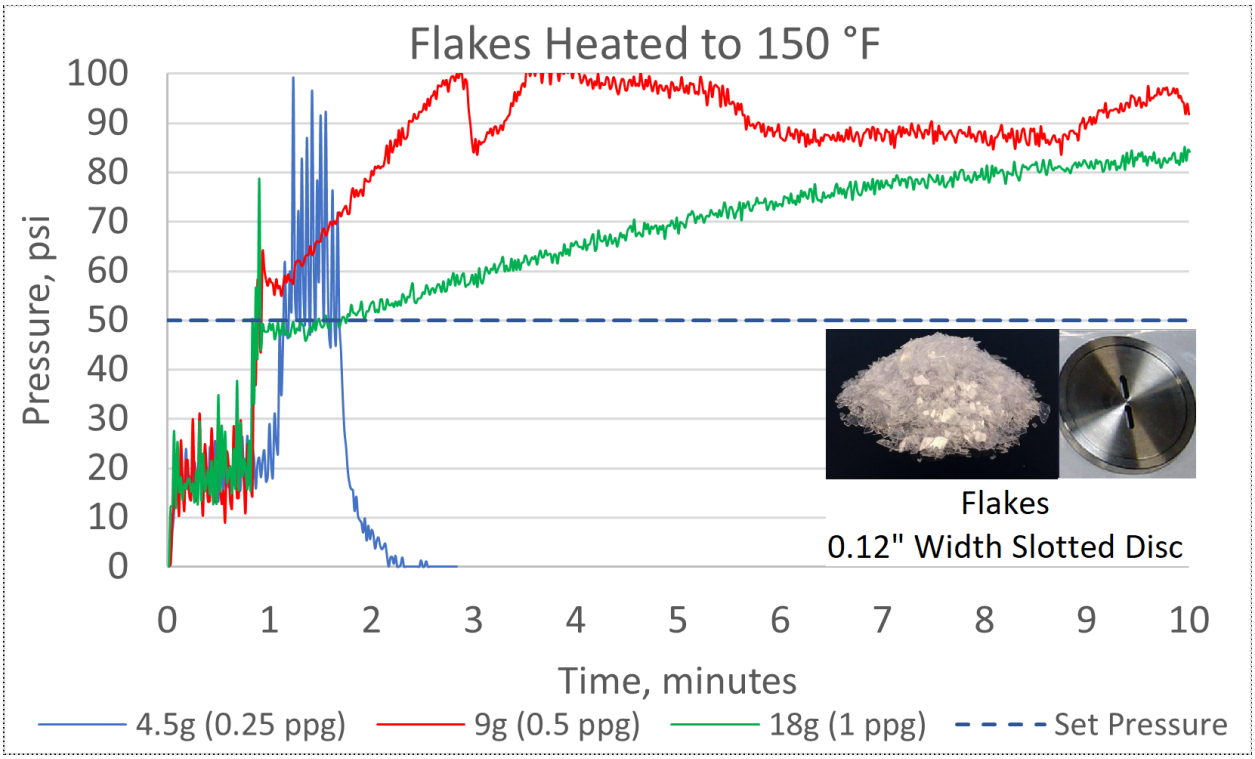

Figure 4.17 APPA results for three tests conducted using the flake diverter heated to 150°F for 60 minutes. The dashed blue line represents the 50-psi differential pressure that was set on the equipment, while the solid blue, red, and green lines represent the actual pressure achieved using 4.5 g, 9 g, and 18 g of the flake diverter, respectively. The 18 g and 9 g samples were able to plug the 0.12 in. width slotted disc. However, the sample that contained only 4.5 g of the flake diverter was not able to sustain the 50 psi-differential pressure, and thus, failed to plug the slotted disc.

The samples that contained 18 g (1 ppg) and 9 g (0.5 ppg) of flake diverters were able to sustain the 50-psi differential pressure. However, looking at the blue solid like that represents the pressure data using only 4.5 g of flake diverters shows an unstable pressure response. The pressure losses seen confirm that 4.5 g of the flake particulates is not enough to plug the 0.12 in. slotted disc. The floating piston made it to the top of the APPA cell within 2.5 minutes into the experiment and the test was terminated.

It was found that the beads, once heated to a temperature above the glass transition of the diverters, required the least amount to plug the 0.12 in. slotted disc. Only 4.5 g (0.25 ppg) of beads was needed to plug the 0.12 in. width slotted disc. Meanwhile, double that amount (9 g) was needed to plug the same 0.12 in. width fracture slotted disc using the blend or the flake diverters that were heated in the same manner.

4.4 Minimum Amount of Diverter Required to Plug a 0.4 in. Diameter Perforation at 150°F

Similar tests that were conducted in the previous section were done while utilizing the 0.4 in. perforation slotted disc. These tests were conducted to find the minimum amounts of diverters required to plug a 0.4 in. perforation if the diverters are heated above their glass transition temperature to 150°F. Different amounts of diverters were used, including 18 g, 36 g, 54 g, and 74 g mixed with 150 ml water, corresponding to 1 ppg, 2 ppg, 3 ppg, and 4 ppg concentrations, respectively. These tests were done using the blend, bead, and flake diverters.

Figure 4.18 shows the results for the tests done on four blend samples containing different mass of diverters. Once heated to 150°F for 60 minutes, all four blend samples were able to plug the 0.4 in. perforation slotted disc. Meanwhile, three tests were conducted using 54 g, 36 g, and 18 g of the bead diverter, corresponding to 3 ppg, 2 ppg, and 1 ppg, respectively. Like the blend, all three samples containing the different amounts of the bead diverter were able to plug the 0.4 in. perforation slotted disc as seen in Figure 4.19.

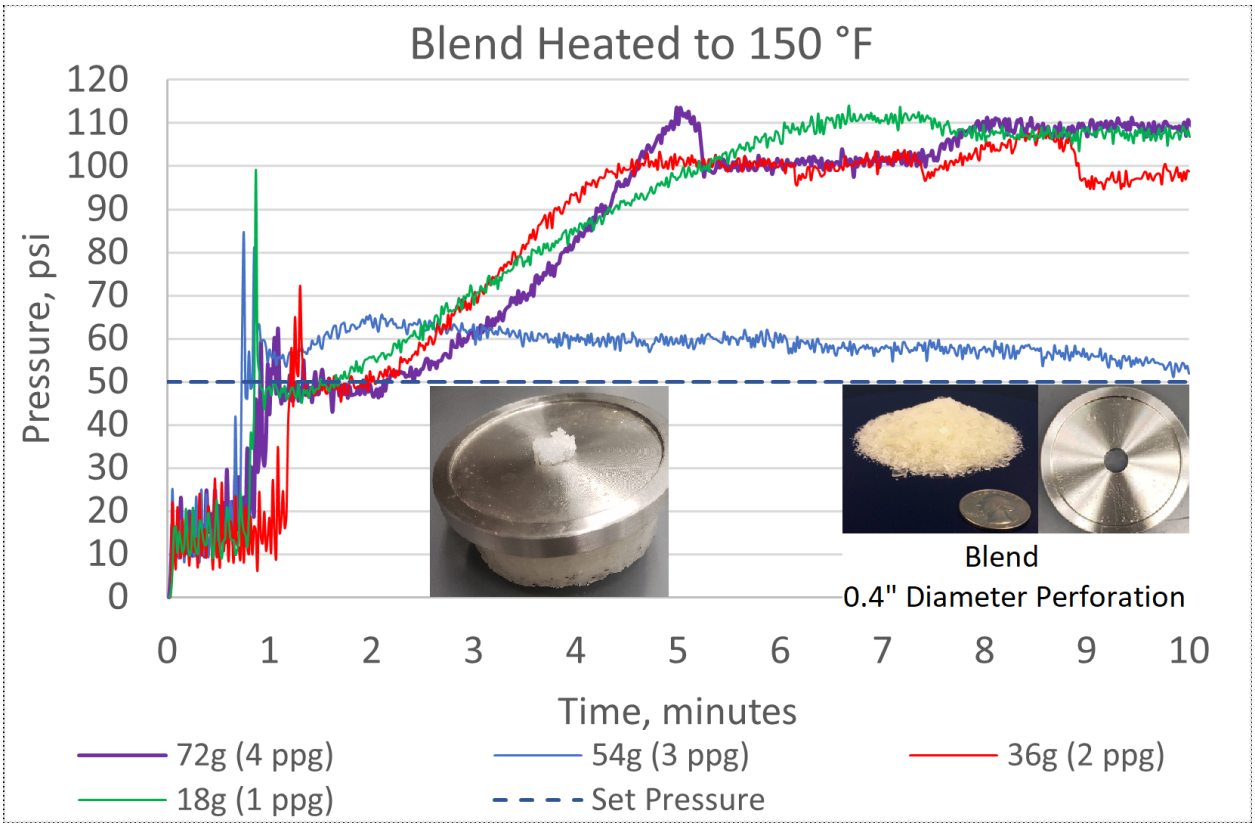

Figure 4.18 APPA results for four tests conducted using the blend diverter heated to 150°F for 60 minutes. The dashed blue line represents the 50-psi differential pressure that was set on the APPA equipment, while the solid purple, blue, red, and green lines represent the actual pressure achieved using the four blend samples containing 72 g, 54 g, 36 g and 18 g of blend diverter, respectively. All four samples with different amounts of the blend diverter were able to plug the 0.4 in. diameter perforation.

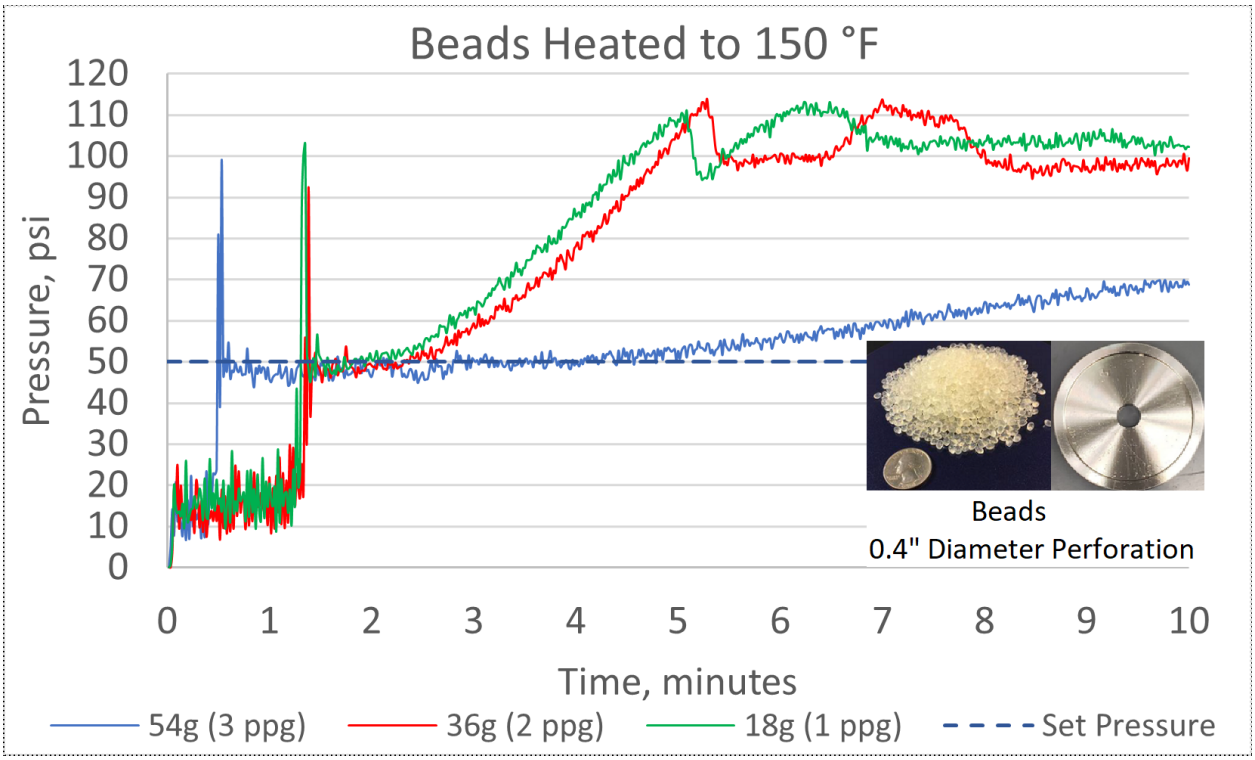

Figure 4.19 APPA results for three tests conducted using the bead diverter heated to 150°F for 60 minutes. The dashed blue line represents the 50-psi differential pressure that was set on the equipment, while the solid blue, red, and green lines represent the actual pressure achieved using 54 g, 36 g and 18 g of the bead diverter, respectively. All three samples with different amounts of bead diverter were able to plug the 0.4 in. diameter perforation.

Tests conducted using the flake particulates can be seen in Figure 4.20. Using 36 g (2 ppg) of diverter, the flakes seemed to plug the 0.4 in. perforation initially. However, 5 minutes into testing, the pressure of the APPA cell started to decrease below the 50-psi set pressure. This indicates that there was a leak that caused the pressure to decline. However, after that initial leak, the pressure started to increase again, and it remained above the 50-psi for the remainder of the test.

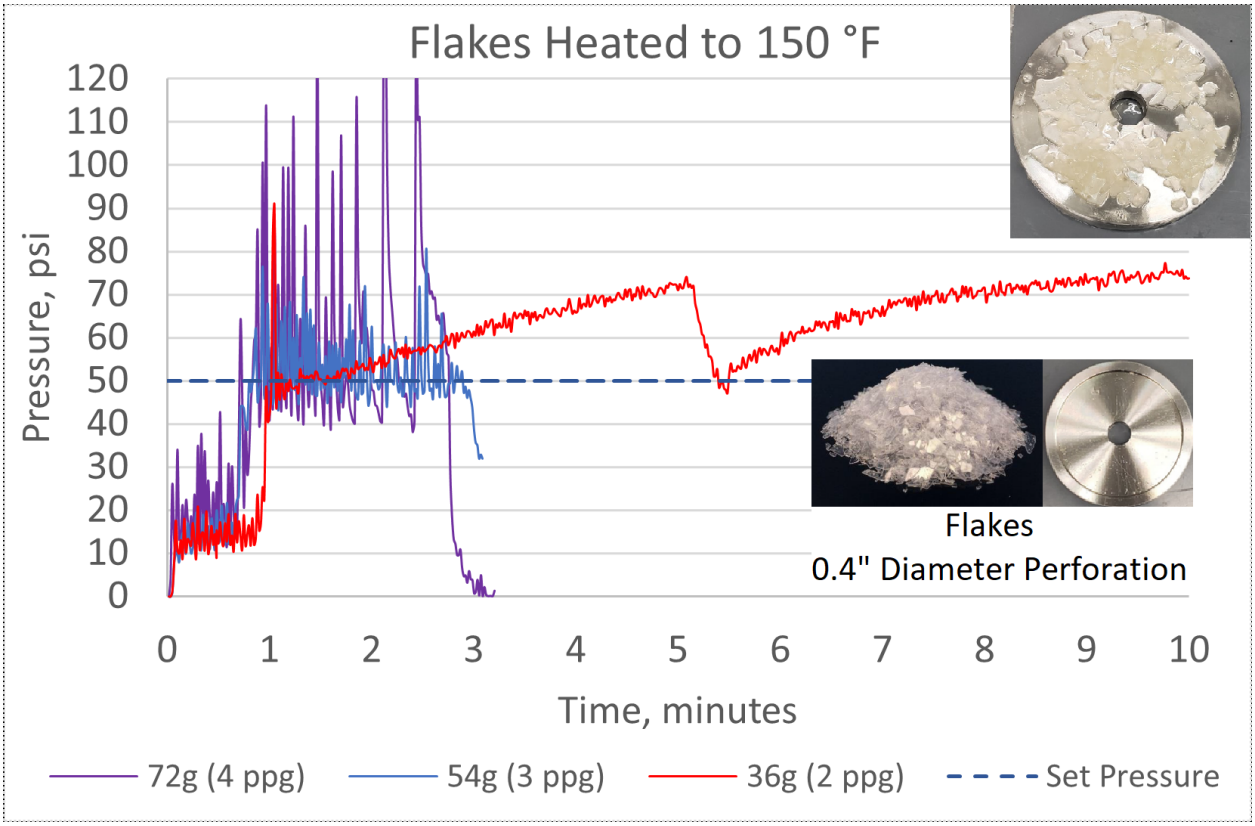

Figure 4.20 APPA results for three tests conducted using different mass of the flake diverter to plug the 0.4 in. perforation slotted disc. Initially, the 36 g flake sample was able to plug the 0.4 in. perforation disc. However, 5 minutes into testing, the pressure of the APPA cell started to decrease below the 50-psi set pressure, indicating a leak past the slotted disc. Later, the pressure started to build back up and stayed above 50 psi for the remainder of the test. Despite increasing the mass of diverters to 54 g and 72 g, the flake samples were not able to plug the 0.4 in. perforation. Moreover, looking at the image of the flakes (upper right) taken after the test was completed, the flake particulates never bonded together to form a solid plug.

Increasing the amount of flake diverter to 54 g (3 ppg) and 72 g (4 ppg), the pressure inside the APPA cell was not able to sustain pressures above the 50-psi set pressure. This indicates that the flakes were not able to plug the 0.4 in. perforation. Additionally, the flake particulates never bonded together to form a solid plug, Unlike the bead and the blend particulates.

Reviewing the tests conducted while heating the diverters to 150°F, it can be concluded that both bead and blend diverters preformed the best. Both bead and blend diverters were able to plug the 0.4 in. diameter perforation using as little as 18 g (1 ppg) of diverters. However, the flakes were not successful at plugging the perforation even with as much as a 72 g sample at a 4 ppg concentration.

4.5 Minimum Amount of Diverter Required to Plug Fractures and Perforations at Room Temperature

A few tests were conducted without heating the diverters to test their plugging performance below the glass transition temperature. These results are used to compare the plugging performance of the diverters at room temperature to their plugging performance above the glass transition temperature. The first few tests were done using 18 g of bead, blend, and flake diverters.

Using 18 g of each of the diverter samples to plug the 0.12 in. fracture width slotted disc, only the flake diverters were capable of plugging the fracture as seen in Figure 4.21. Comparing the results of the blend and bead diverters, the pressure response using 18 g of the blend diverters did not fluctuate as much as the pressure using the 18 g bead particulates. The blend diverters demonstrated a better flow resistance than the beads at room temperature, as expected. The blend diverters have lower pack permeability when compared to the one-size beads. However, the blend diverters were not able to sustain pressures above 50 psi during the test. Additionally, the bead sample had the most significant pressure losses among the three diverters and was unable to sustain pressures above 50 psi. Eventually, the floating piston made it to the top of the APPA cell and the

experiment had to be terminated for the bead and blend as they were not successful at plugging the 0.12 in. slotted disc at room temperature.

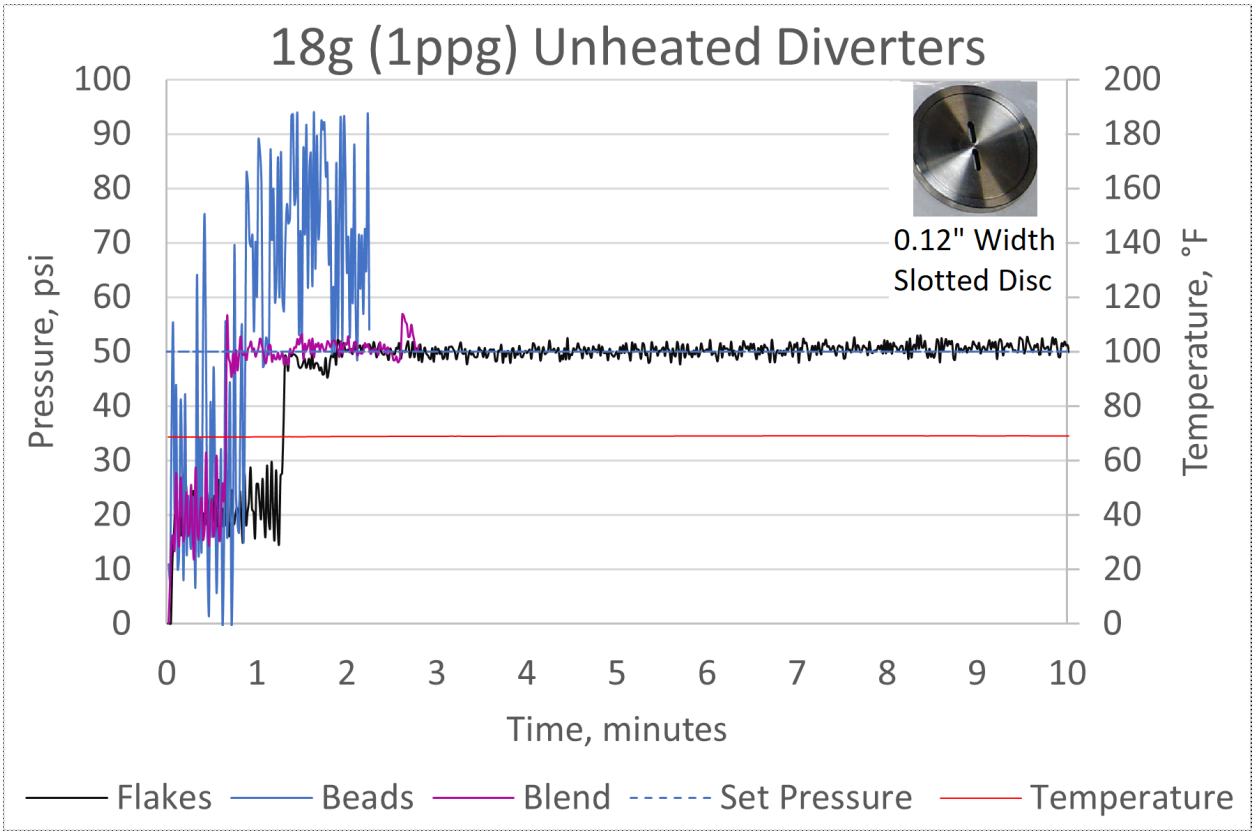

Figure 4.21 APPA Results for three tests conducting using 18 g (1 ppg) of each of the flake, bead, and blend diverters at room temperature. The flakes were able to pass the test plugging the 0.12 in. width slotted disc and sustaining the 50-psi differential pressure. Although the blend offered better flow resistance than the beads, neither the blend nor the beads were able to plug the 0.12 in. width slotted disc using the 18 g samples at room temperature.

To find out how much of the unheated beads diverters are needed to plug the 0.12 in. slotted disc, additional tests were conducted using different mass of beads. The collected data can then help in comparing and understanding the difference in the amounts of diverters required to plug a fracture if the diverters are below the glass transition temperature versus if the diverters are above the glass transition temperature. Based on the results presented in Figure 4.22, 36 g (2 ppg) of bead diverters was required to plug the 0.12 in. width slotted disc at room temperature.

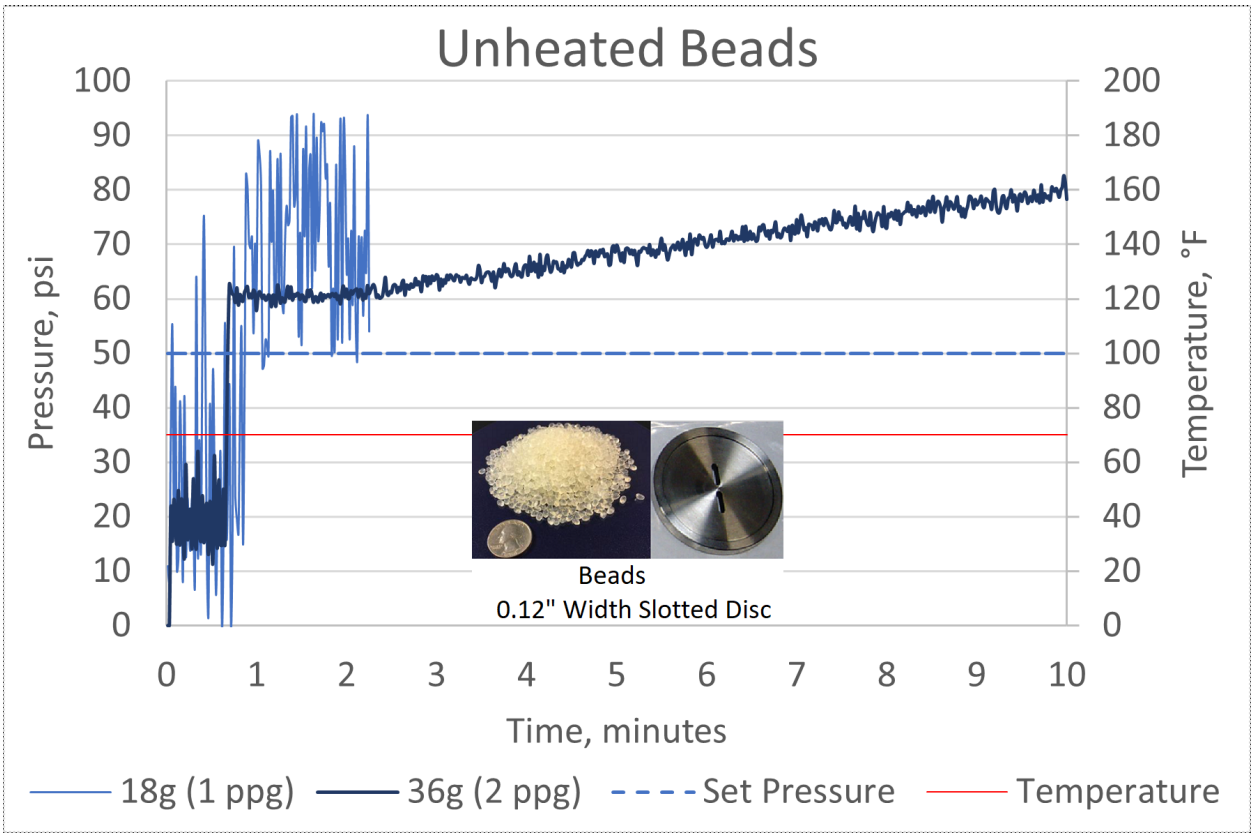

Figure 4.22 APPA results for tests conducted using different mass of bead diverters to find the minimum amount of beads required to plug the 0.12 in. width slotted disc at room temperature. The results show that a minimum of 36 g (2 ppg) of the bead diverter is required to plug the 0.12 in. width slotted disc.

The same test was conducted using the bead diverter at room temperature but while attempting to plug the 0.4 in. diameter perforation disc. Looking at Figure 4.23, a minimum of 144 g (8 ppg) of the bead diverter was required to plug the 0.4 in. perforation. The lower amounts of the bead diverter, including 36 g, 54 g and 72 g were not enough to achieve the flow resistance required to sustain 50 psi differential pressure for 10 minutes.

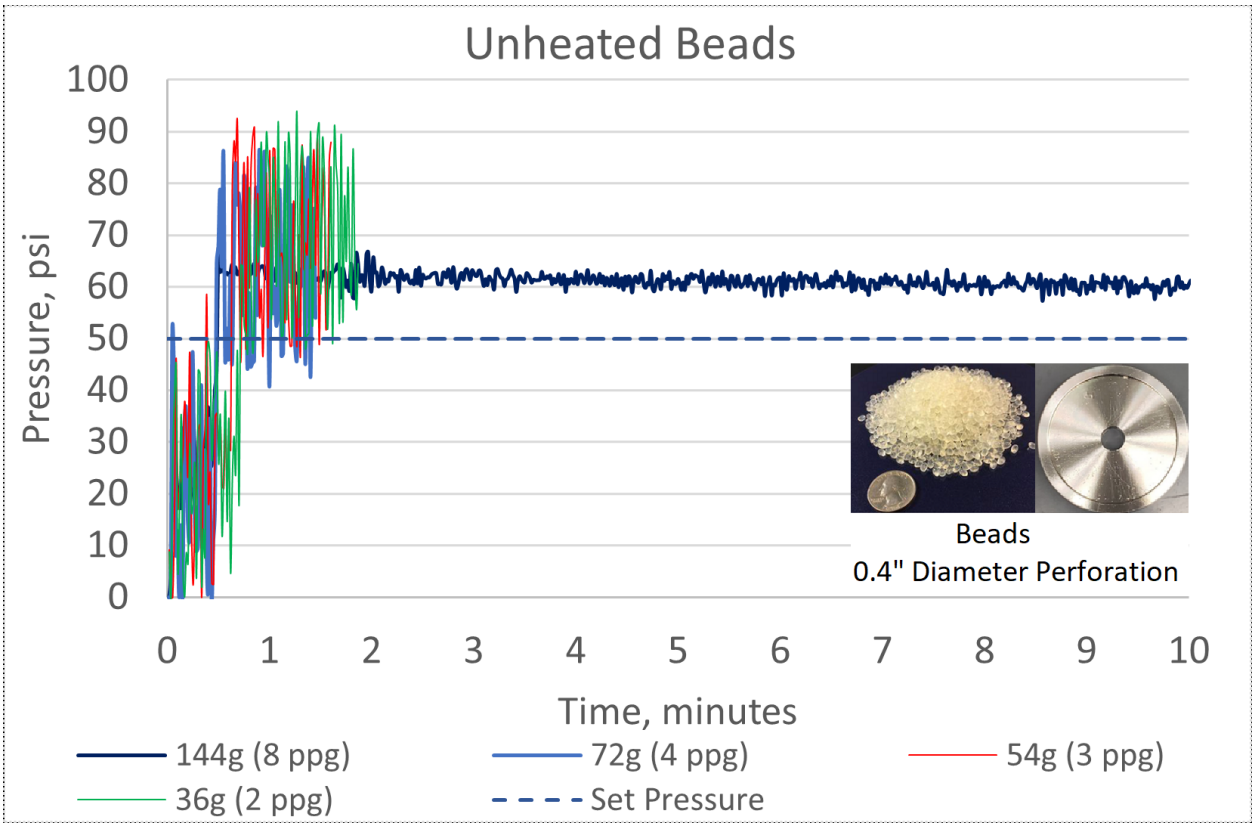

Figure 4.23 APPA results for the tests conducted on samples with different mass of bead diverters to find the minimum amount required to plug the 0.4 in. diameter perforation slotted disc at room temperature. The results show that a minimum of 144 g (8 ppg) of diverters is required to plug the 0.4 in. perforation.

4.6 Investigating Flowback Potential Within 24 Hours

One of the major issues with using biodegradable diverters is the uncertainty concerning their ability to degrade at rates fast enough to allow for flowback and production to commence soon after finishing the stimulation operation. To understand the

potential of flowback within 24 hours, a few tests were conducted on the bead, blend and flake diverters. Samples with different mass of diverters were mixed with 150 ml of water, including 36 g (2 ppg) and 9 g (0.5 ppg) and heated for 24 hours to 200°F. After heating the different samples, the APPA cell was pressurized to 50 psi to test whether the diverters will plug the 0.12 in. width slotted disc or not.

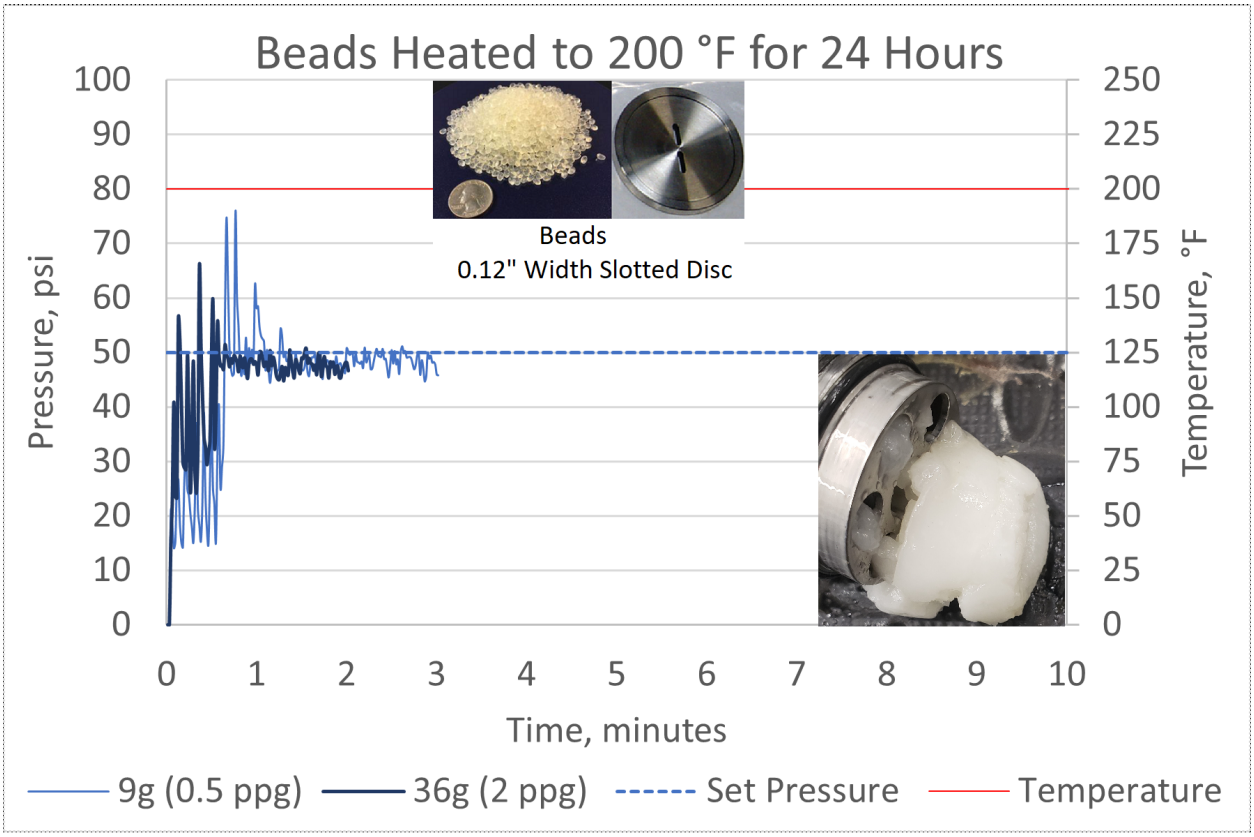

Figure 4.24 Results for two APPA tests conducted using 9 g (0.5 ppg) and 36 g (2 ppg) of bead diverters mixed with water and heated to 200°F for 24 hours to test the flowback potential. The bead diverters became a gum-like paste that is very pliable. This paste was pushed through past the slotted disc and made its way up into the LCM receiver (lower right). As seen on the pressure graphs, the beads were not able to plug the 0.12 in. slotted disc using the 9 g or the 36 g samples.

Looking at Figure 4.24, it can be seen that the beads were not able to plug the 0.12 in. width slotted disc for neither the 9 g or the 36 g samples. Additionally, the heated beads have softened and became a gum-like paste that was very pliable. This paste was pushed through the slotted disc and made its way up into the LCM receiver during testing as seen

in the picture taken after the test was completed. It was observed that there was a significant change in the particulate's mechanical properties such as strength and hardness. Moreover, once the resulted gum-like paste returned to room temperature, it stayed pliable and did not become solid again.

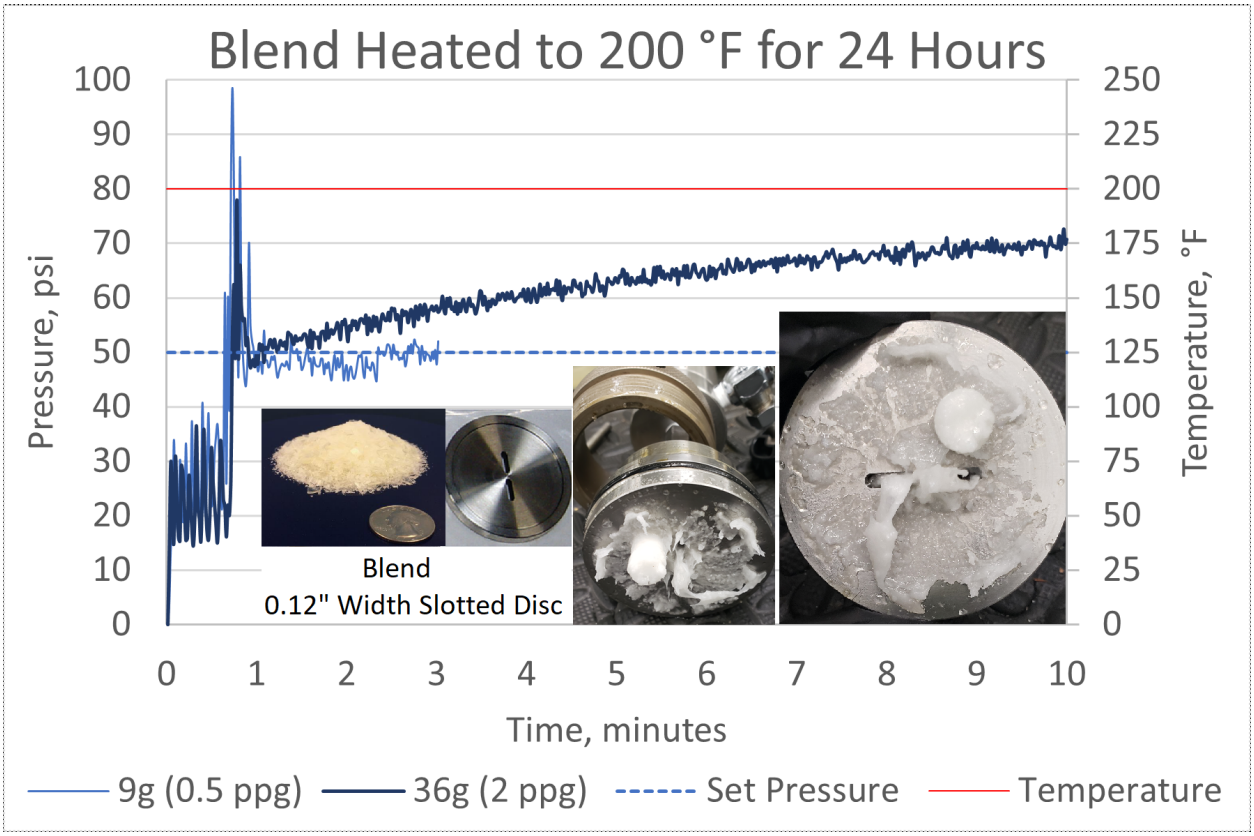

Figure 4.25 Results for two APPA tests conducted using 9 g (0.5 ppg) and 36 g (2 ppg) of blend diverters mixed with water and heated to 200°F for 24 hours to test the flowback potential. The blend diverters became a gum-like paste that is pliable. Low amount of paste was pushed through past the slotted disc. However, most of the blend diverters remained in the APPA cell during the test and the 36 g heated sample was successful at plugging the 0.12 in. width slotted disc.

The test was repeated while using 9 g and 36 g of the blend diverter. Looking at Figure 4.25, the test done using only 9 g of the blend diverter failed, and the amount was not enough to achieve an effective plug. However, the test that utilized 36 g of the blend diverter ended up plugging the 0.12 in. width slotted disc and was able to sustain the 50-psi differential pressure for 10 minutes. Additionally, the blend diverters softened and

became a gum-like paste that is pliable. The paste was being pushed through the slotted disc, however, only a minimum amount ended up moving past the 0.12 in. slotted disc. It was also observed that once the paste cooled down to room temperature, it was hardened again and became plastic-like, unlike the bead diverters that remained softened. However, it was observed that this plastic-like blend was softer than the cooled-down blend diverters that were heated to only 150°F for 60 minutes.

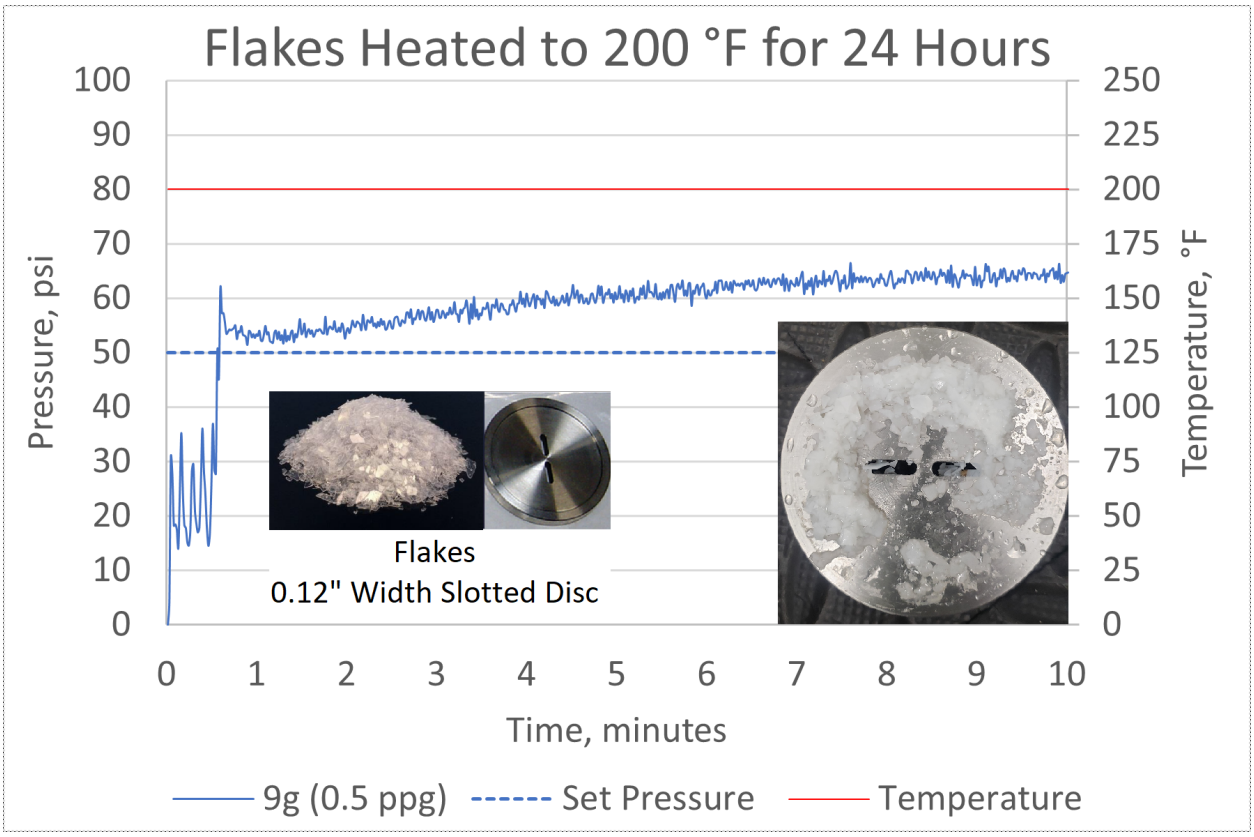

Figure 4.26 APPA results using 9 g of flake diverter mixed with 150 ml of water corresponding to 0.5 ppg concentration. The diverters were able to sustain the 50-psi differential pressure throughout the 10 minutes testing period. A picture of the flake diverter after the experiment was completed shows that the particulates did not bond together to form one solid plug. However, the 9 g of the heated diverters were able to plug the 0.12 in. slotted disc.

The test was repeated using 9 g of flake diverter. Looking at Figure 4.26, the 9 g heated sample was able to hold the 50-psi differential pressure inside the APPA cell. Unlike the bead and the blend diverters, the flake particulates never bonded together, nor did

they become paste-like. Although it was apparent the particulates started the hydrolysis process and became smaller in size, the degradation did not result in extreme transformation as did the blend and beads. The flakes ended up plugging the 0.12 in. width slotted disc using only a 9 g sample.

To summarize the flowback potential results, the flake diverter had the least potential for allowing flowback within 24 hours, followed by the blend diverter. The bead diverter on the other hand, preformed best as far as degradation and hydrolysis. Heating the bead and blend samples for 24 hours to 200°F had a visible effect on the diverter's mechanical properties. Both blend and bead particulates became gum-like paste that's pliable.

4.7 High-Pressure and Long-Term Tests

A few tests were conducted using the 0.4 in. diameter slotted disc to test the ability of the diverters to plug at higher pressures and for longer periods of time. Both blend and bead particulates were used for these experiments. However, since the flake diverters were not able to plug the 0.4 in. perforation, they were not used for this test. The diverters were heated to 150°F for 60 minutes, then gradually pressurized to 200 psi, and the pressure was held for 4 hours.

For the first test, 72 g of the bead diverters were heated to 150°F for 60 minutes then gradually pressurized to 200 psi. Looking at the pressure data in Figure 4.27, it can be seen that the diverters were able to hold the 200 psi set pressure for the entire 4-hour duration of the test. However, two hours into testing (around the 120-minute mark on the graph), the pressure momentarily fell below the 200-psi pressure. This minimal decrease in pressure was observed again four more times during the test. Looking at the image of the diverters taken after the test was completed, the formed plug can be seen being compressed through the 0.4 in. diameter perforation opening. Although minimal, these pressure losses seen are due to the diverters being squeezed into the opening of the slotted disc.

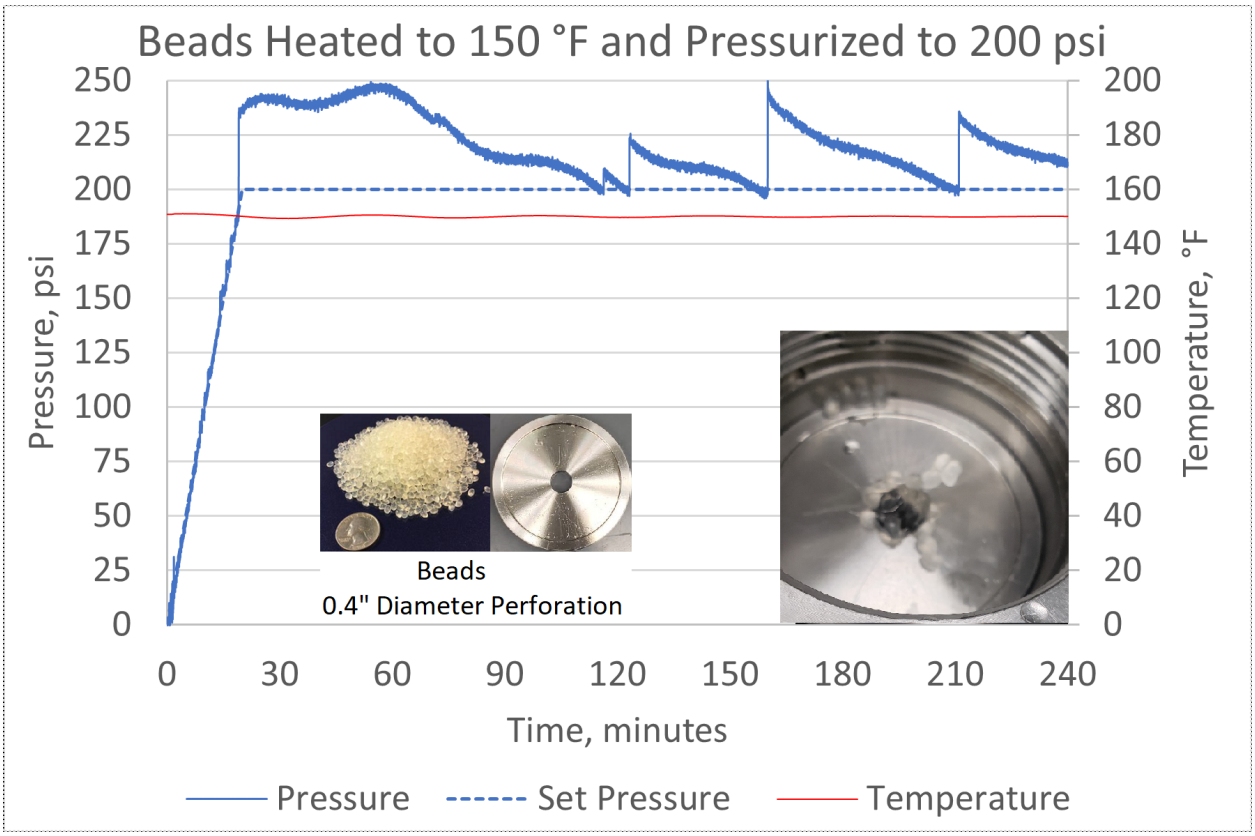

Figure 4.27 APPA results for the high-pressure and long-term test conducted using 72 g (4 ppg) of the bead diverter and the 0.4 in. diameter perforation disc. The sample was heated to 150°F for 60 minutes, and the pressure was gradually increased to 200 psi. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line represents the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The bead diverters held pressures above the 200-psi set pressure for the entire 4-hours duration of the test. However, 2 hours into testing, the pressure momentarily fell below the 200 psi-set pressure. This minimal decrease in pressure was observed again four more times during the test. Looking at the image of the diverters taken after the test was completed (lower right), the formed plug was being compressed through the 0.4 in. diameter perforation opening, which explains these pressure losses.

Next, 72 g of the blend diverters were heated to 150°F for 60 minutes then gradually pressurized to 200 psi and held under pressure for 4 hours. Looking at the pressure data in Figure 4.28, it can be seen that the diverters were able to hold pressures above the 200-psi set pressure for the entire 4-hour duration of the test. However, 60 minutes into testing, the pressure momentarily fell below the 200-psi set pressure. This minimal decrease in

pressure was observed again every 10-30 minutes during the remainder of the test. Looking at the image of the diverters taken after the test was completed, the formed plug was being compressed and squeezed through the 0.4 in. diameter perforation opening. Therefore, these pressure losses can be explained by the diverters being squeezed into the opening of the slotted disc.

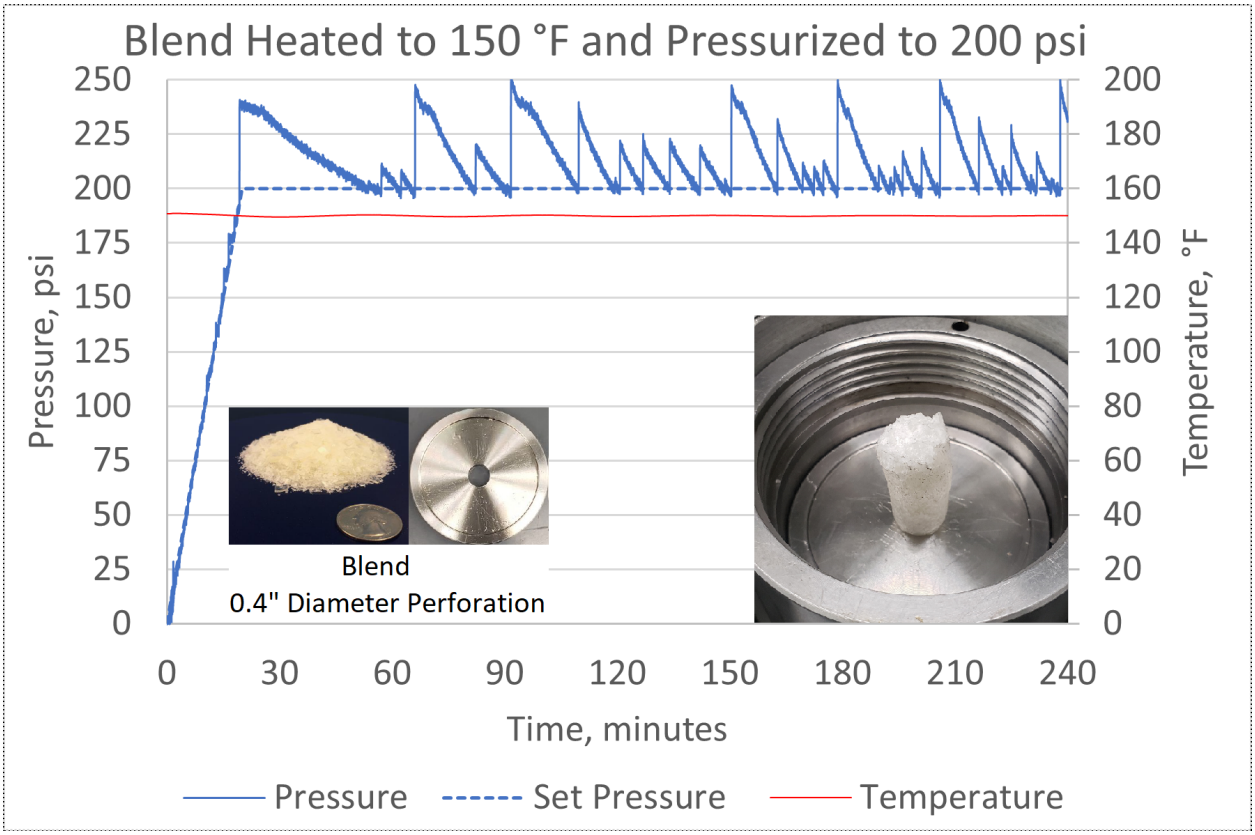

Figure 4.28 APPA results for the high-pressure and long-term test done using 72 g (4 ppg) of the blend diverters conducted on the 0.4 in. diameter perforation disc. The sample was heated to 150°F for 60 minutes, and the pressure was gradually increased to 200 psi. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line represents the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The blend diverters held pressure above the 200-psi set pressure for the entire 4-hours duration of the test. However, 60 minutes into testing, the pressure momentarily fell below the 200 psi-set pressure. This minimal decrease in pressure was observed again every 10-30 minutes during the remainder of the test. However, looking at the image of the diverters taken after the test was completed (lower right), the formed plug was being compressed through the 0.4 in. diameter perforation opening, which explains the observed pressure losses.

A few additional tests were conducted to ensure that the heated diverters can still plug the 0.4 in. perforation disc under 200 psi differential pressure using only 18 g of particulates. These tests include using 36 g (2 ppg) of the blend diverters as seen in Figure 4.29, and 18 g (1 ppg) of the blend diverters as seen in Figure 4.30. Both amounts of the blend diverters were able to sustain the 200-psi pressure for the 45 minutes of testing.

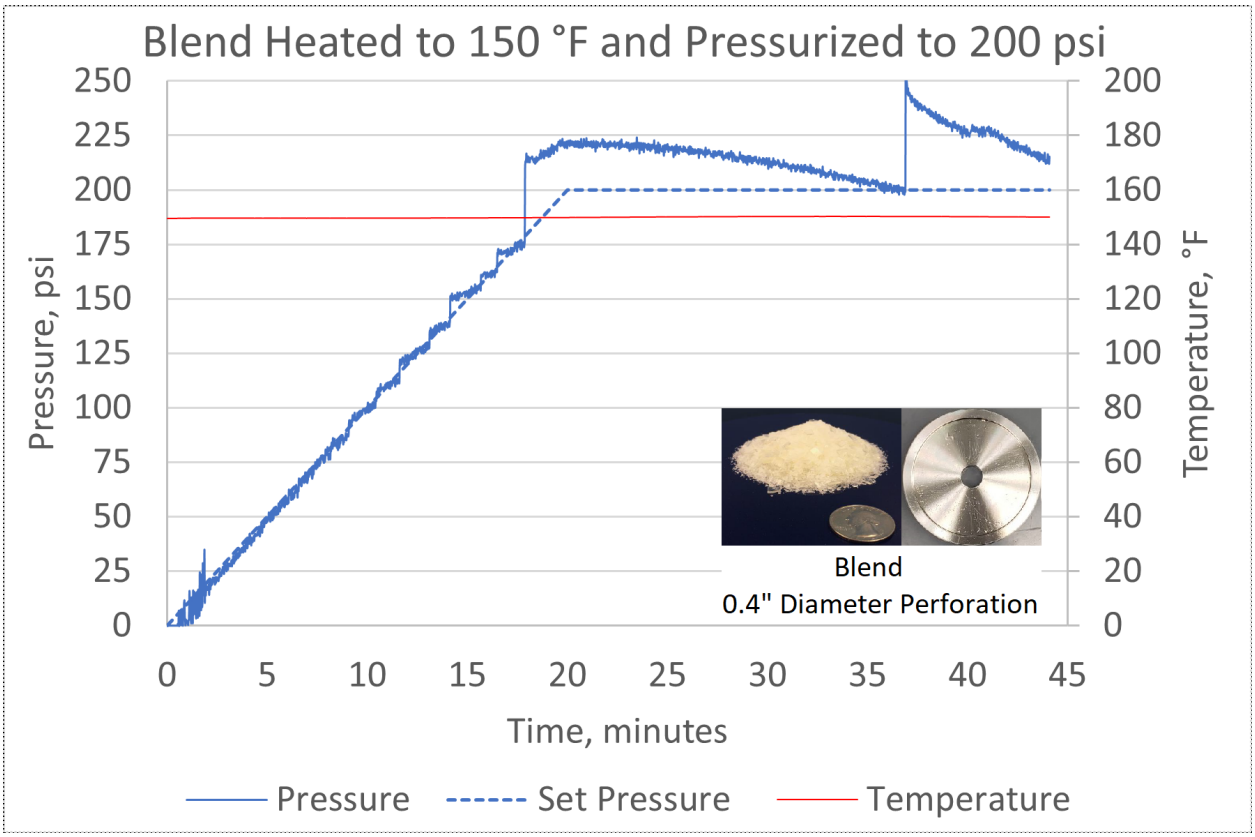

Figure 4.29 APPA results for 36 g (2 ppg) of the blend diverters tested using the 0.4 in. diameter perforation disc. The sample was heated to 150°F for 60 minutes, and the pressure was then gradually increased to 200 psi. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line represents the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The 36 g sample of the blend diverters was able to sustain the 200-psi pressure during the 45 minutes of testing.

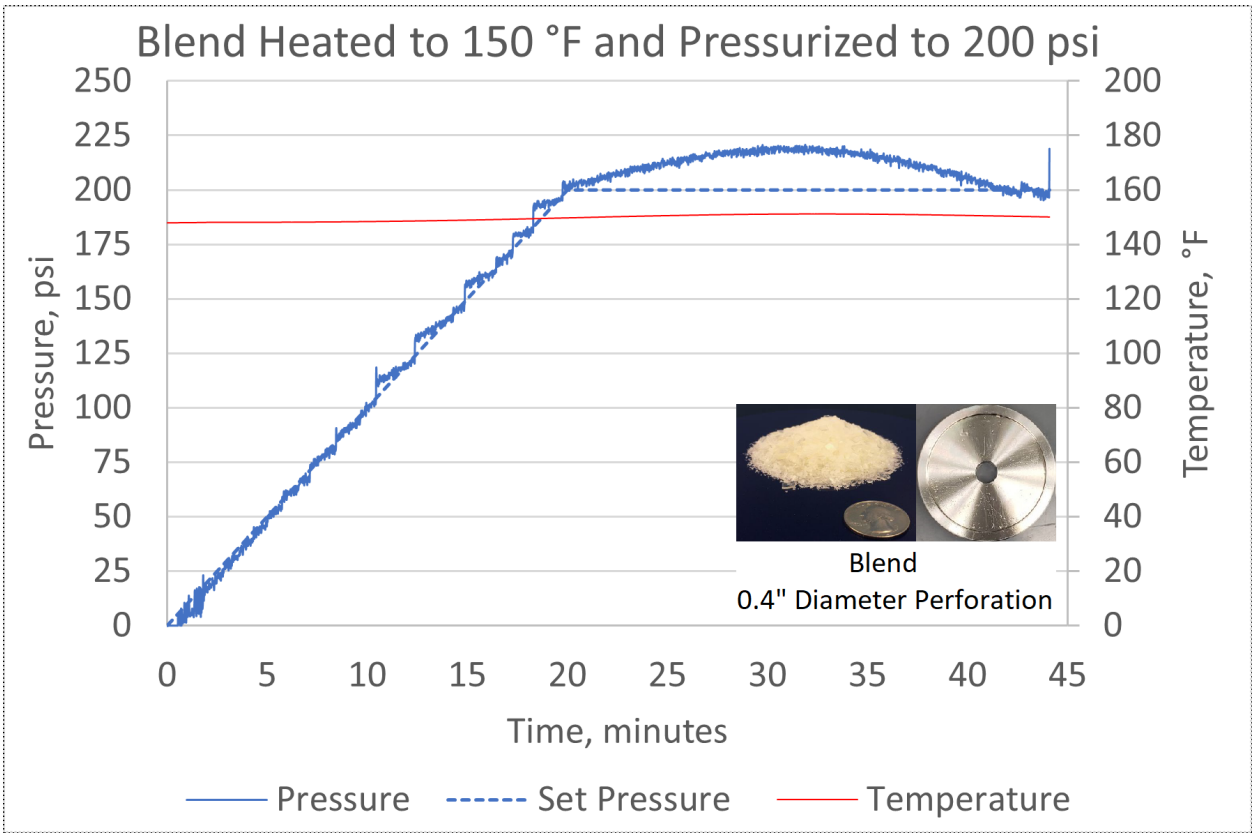

Figure 4.30 APPA results for 18 g (1 ppg) of the blend diverters tested using the 0.4 in. diameter perforation disc. The sample was heated to 150°F for 60 minutes, and the pressure was gradually increased to 200 psi. The dashed blue line represents the differential pressure that was set on the equipment, while the solid blue line represents the actual differential pressure achieved, and the solid red line represents the actual temperature of the APPA cell. The 18 g sample of blend diverters was able to sustain the 200-psi pressure during the 45 minutes of testing.

4.8 Confirming Repeatability of Results

To verify the repeatability of the data and results, seven repeatability tests were conducted. The data confirming the repeatability of the tests can be seen in Figure 4.31, Figure 4.32, Figure 4.33, Figure 4.34, and Figure 4.35. These tests include repeatability for heated diverters, tests conducted at room temperature, and the flowback potential tests. These repeatability tests also include experiments that used the 0.12 in. width slotted disc, as well as the 0.4 in. perforation disc. As shown in Figure 4.31, Figure 4.32, Figure 4.33, Figure 4.34, and Figure 4.35, the repeatability of the tests is very good, indicating the results obtained are representative.

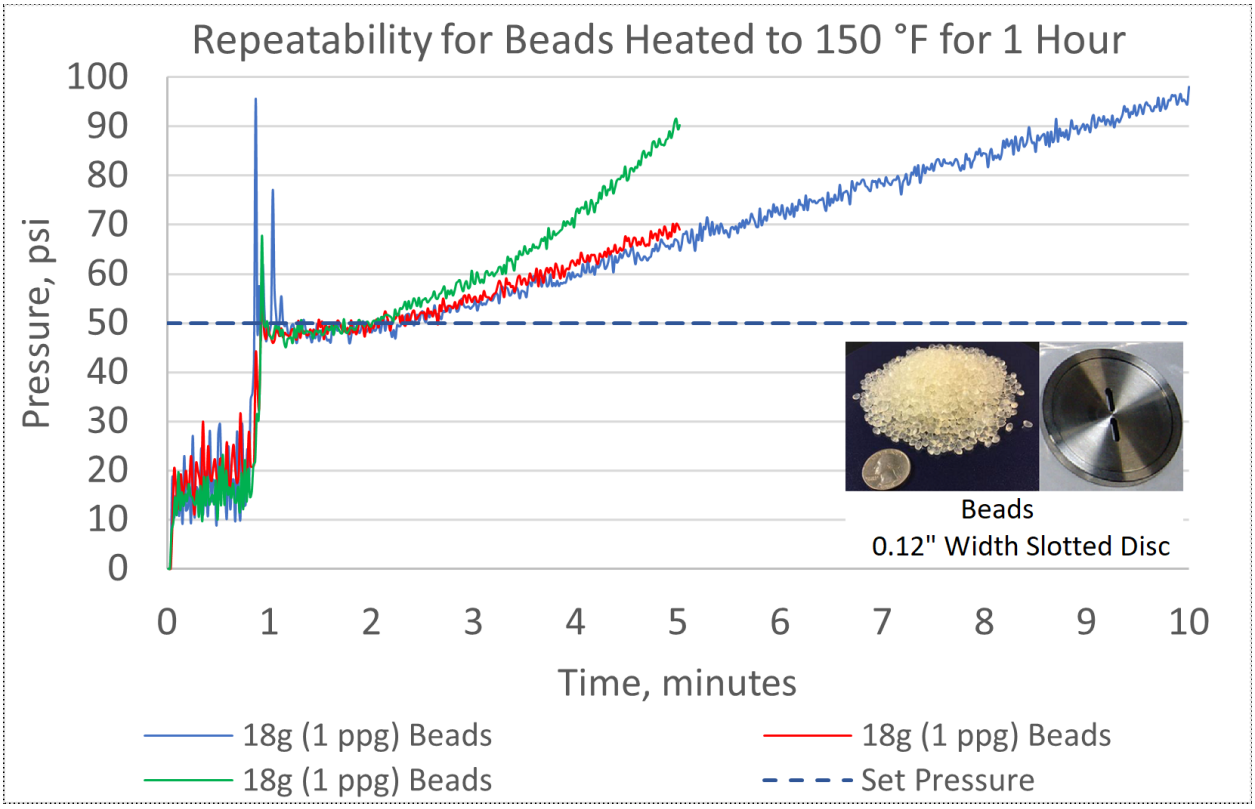

Figure 4.31 Two repeatability tests conducted for the test done using 18 g bead diverters that were heated to 150°F for 60 minutes to plug the 0.12 in. width slotted disc. The solid blue line shows the pressure response of the original test, while the red and green show the pressure responses of the two additional tests. All three pressure responses confirm the repeatability of the experiment.

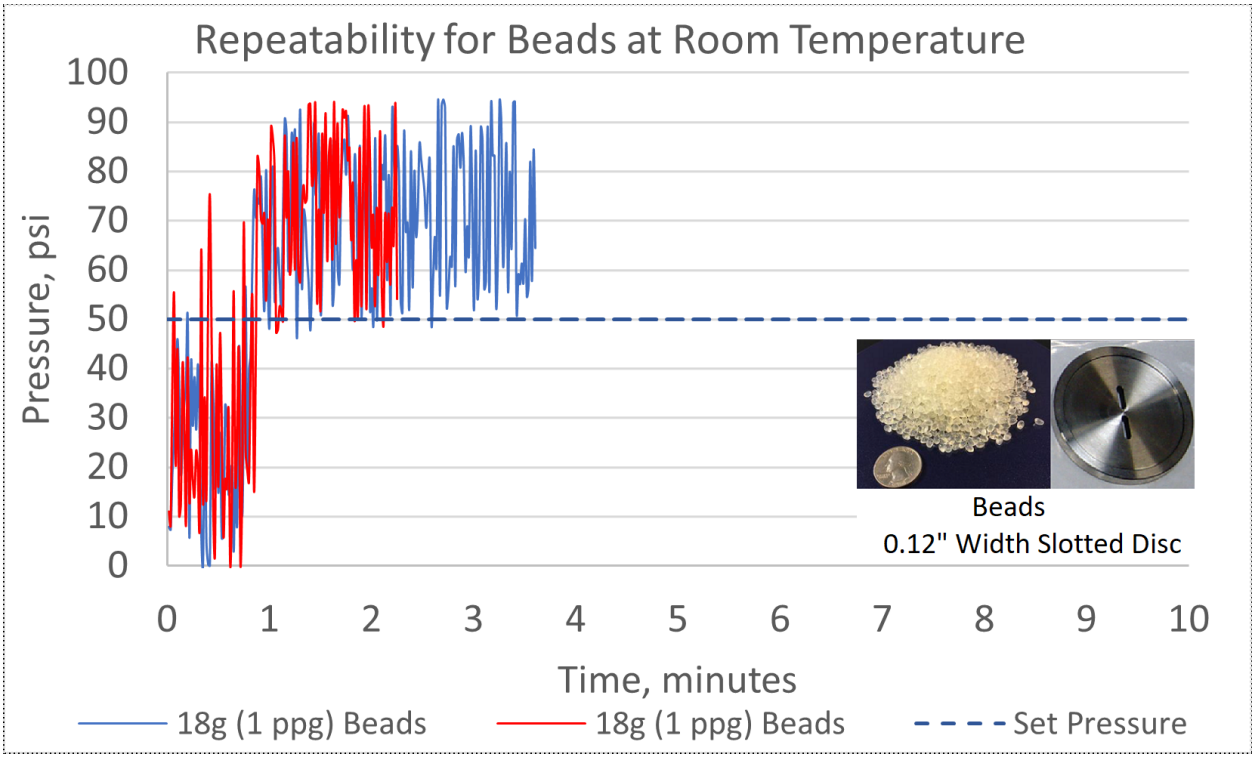

Figure 4.32 The repeatability test conducted at room temperature using 18 g bead diverters to plug the 0.12 in. width slotted disc. The solid blue line shows the pressure response on the original test, while the red line shows the pressure response of the repeated test. The data confirm the repeatability of the experiment.

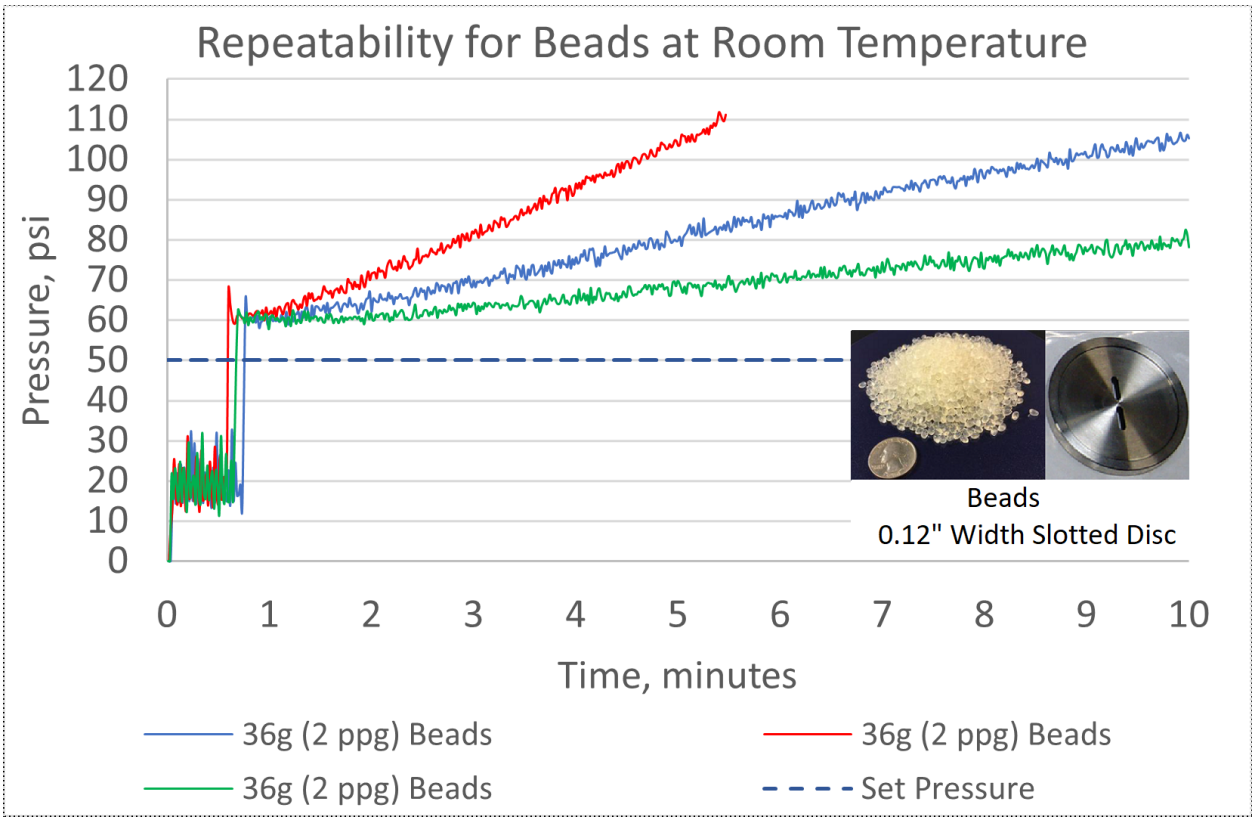

Figure 4.33 Two repeatability tests conducted at room temperature using 36 g of the bead diverters to plug the 0.12 in. width slotted disc. The solid blue line shows the pressure response of the original test, while the red and green show the pressure responses of the two additional tests. The data confirm the repeatability of the experiment.

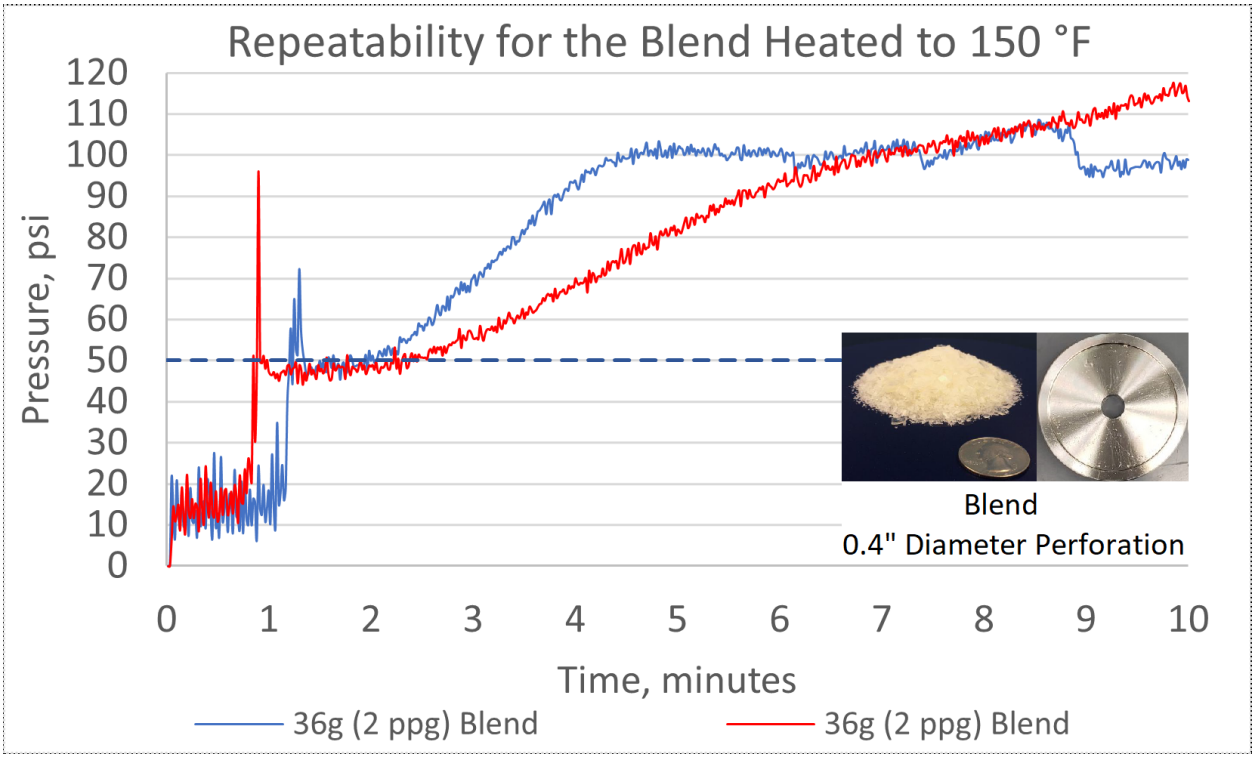

Figure 4.34 The repeatability test conducted for the 36 g of bead diverters heated to 150°F for 60 minutes to plug the 0.12 in. width slotted disc. The solid blue line shows the pressure response of the original test, while the red line shows the pressure response of the repeated test. The data confirm the repeatability of the experiment.

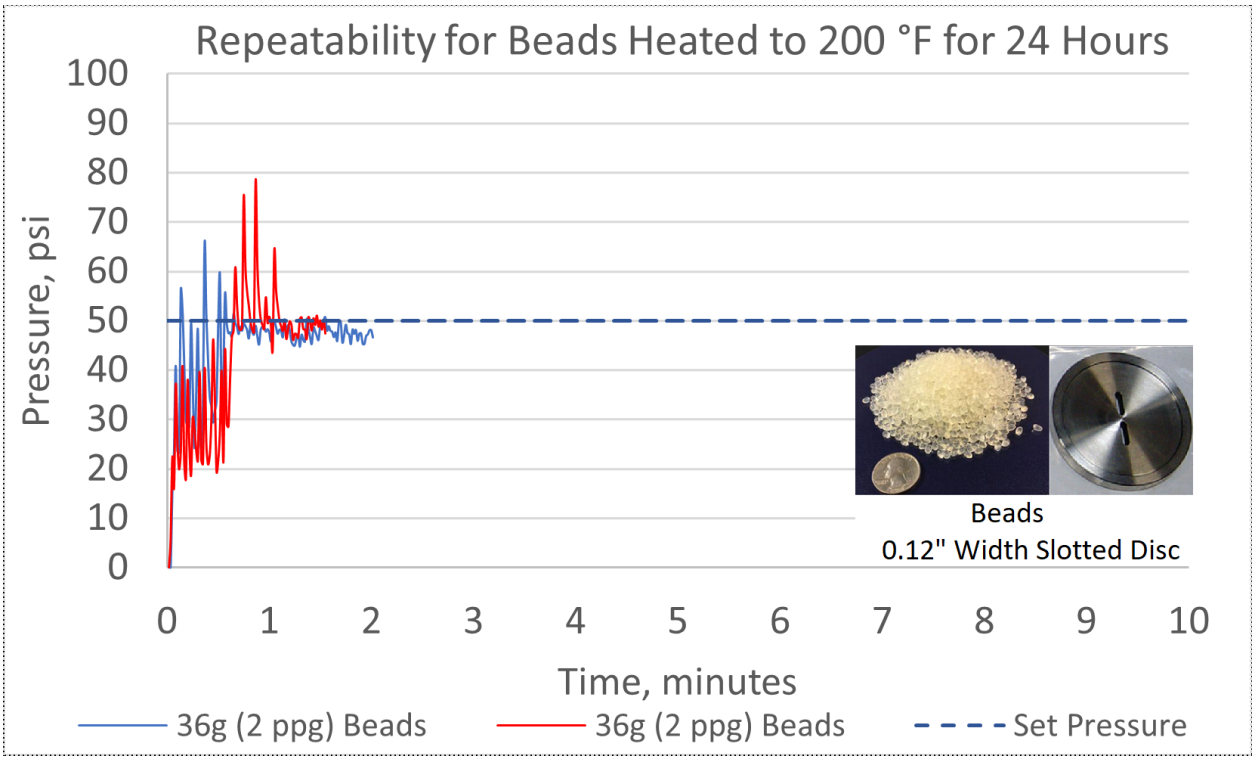

Figure 4.35 The repeatability test conducted using the 0.12 in. width slotted disc for the 36 g of bead diverters heated to 200°F for 24 hours to test the flowback potential. The solid blue line shows the pressure response of the original test, while the red line shows the pressure response of the repeated test. The data confirm the repeatability of the experiment.

CHAPTER 5
DISCUSSION AND ANALYSIS

Results from this work show that PLA particulate diverters have a significant advantage over conventional particulates. Their most notable advantage is their ability to deform above the glass transition temperature (T_g), creating a plug capable of sealing perforations and fractures. Taking advantage of their ability to deform above T_g not only causes better sealing performance, but also results in needing a significantly lower amounts of diverter. It was found that different shapes and sizes of diverter behave differently above T_g. Not accounting for the difference in behavior above T_g can lead to undesirable results and negative consequences in the overall effectiveness and efficiency of the hydraulic fracturing and refracturing treatments.

Data were reviewed and analyzed to draw conclusions and make recommendations on the following: the effect of glass transition temperature on the plugging performance of biodegradable diverters, the heating time required to form an effective plug, the minimum amount of diverters required to achieve an effective seal, flowback potential within 24 hours, the effectiveness of the plug under higher pressure and for longer periods of time, and the effect of the different shapes and sizes of particulates on plugging performance. Implications of this research's conclusions on field applications are also discussed. Additionally, conclusions from this work were related to some of the findings in the literature review as well as some of the behavior observed by operators in the field.

A summary of the test results can be found in Table 5.1. The collected pressure data were broken down into three categories and are interpreted in the following manner:

1. Pressure was not sustained before the piston made it to the top of the APPA cell. The particulate diverter was not able to form an effective plug under the selected testing variables and the results are labeled "no plug".

2. Pressure was sustained during some parts of test, but excessive pressure loss was seen, and the piston eventually made it to the top of the APPA cell. Although a plug was formed or was in the process of forming, it was not an effective plug. These results are labeled "ineffective plug".

3. Pressure was sustained throughout the length of the test. The results are labeled "effective plug".

Table 5.1 Summary of Testing Results.

Slotted Disc	Diverter	Diverter Mass (g)	Temperature (°F)	Differential Pressure (psi)	Test Results
0.04-0.1 in. Tapered	Blend	18	70-100	0-500	Effective plug
0.04-0.1 in. Tapered	Blend	18	100-150	0-500	Effective plug
0.04-0.1 in. Tapered	Blend	18	150-200	0-500	Effective plug
0.04-0.1 in. Tapered	Blend	18	200-230	0-500	Effective plug
0.04-0.1 in. Tapered	Flake	18	70	0-500	Ineffective plug
0.04-0.1 in. Tapered	Flake	18	70-100	0-500	Effective plug
0.04-0.1 in. Tapered	Flake	18	130	0-50	Effective plug
0.04-0.1 in. Tapered	Flake	18	150	0-500	Effective plug
0.04-0.1 in. Tapered	Flake	18	200	0-500	Effective plug
0.04-0.1 in. Tapered	Flake	18	225	0-500	Effective plug
0.12 in. Fracture	Bead	18	70	50	No plug
0.12 in. Fracture	Bead	18	150 / 10 min	50	Ineffective plug
0.12 in. Fracture	Bead	18	150 / 30 min	50	Effective plug
0.12 in. Fracture	Bead	18	150 / 60 min	50	Effective plug
0.12 in. Fracture	Bead	18	150	50 / 1-hour	Effective plug
0.12 in. Fracture	Bead	18	150	50	Effective plug
0.12 in. Fracture	Bead	18	150	50	Effective plug
0.12 in. Fracture	Bead	18	70	50	Effective plug
0.12 in. Fracture	Bead	9	150	50	Effective plug
0.12 in. Fracture	Bead	4.5	150	50	Effective plug
0.12 in. Fracture	Blend	18	150	50	Effective plug
0.12 in. Fracture	Blend	9	150	50	Effective plug
0.12 in. Fracture	Blend	4.5	150	50	Ineffective plug
0.12 in. Fracture	Flake	18	150	50	Effective plug
0.12 in. Fracture	Flake	9	150	50	Effective plug
0.12 in. Fracture	Flake	4.5	150	50	No plug
0.12 in. Fracture	Bead	36	70	50	Effective plug

Table 5.1 Continued.

Slotted Disc	Diverter	Diverter Mass (g)	Temperature (°F)	Differential Pressure (psi)	Test Results
0.12 in. Fracture	Bead	36	70	50	Effective plug
0.12 in. Fracture	Bead	36	70	50	Effective plug
0.12 in. Fracture	Blend	18	70	50	Ineffective plug
0.12 in. Fracture	Flake	18	70	50	Effective plug
0.4 in. Perforation	Flake	36	150	50	Ineffective plug
0.4 in. Perforation	Flake	54	150	50	No plug
0.4 in. Perforation	Flake	72	150	50	No plug
0.4 in. Perforation	Blend	18	150	50	Effective plug
0.4 in. Perforation	Blend	36	150	50	Effective plug
0.4 in. Perforation	Blend	36	150	50	Effective plug
0.4 in. Perforation	Blend	54	150	50	Effective plug
0.4 in. Perforation	Blend	72	150	50	Effective plug
0.4 in. Perforation	Bead	18	150	50	Effective plug
0.4 in. Perforation	Bead	36	150	50	Effective plug
0.4 in. Perforation	Bead	54	150	50	Effective plug
0.4 in. Perforation	Bead	36	70	50	No plug
0.4 in. Perforation	Bead	54	70	50	No plug
0.4 in. Perforation	Bead	72	70	50	No plug
0.4 in. Perforation	Bead	144	70	50	Effective plug
0.4 in. Perforation	Blend	72	150	200 / 4-hour	Effective plug
0.4 in. Perforation	Bead	72	150	200 / 4-hour	Effective plug
0.4 in. Perforation	Blend	36	150	200 / 4-hour	Effective plug
0.4 in. Perforation	Blend	18	150	200 / 4-hour	Effective plug
0.12 in. Fracture	Blend	9	200	50	No plug
0.12 in. Fracture	Blend	36	200	50	Effective plug
0.12 in. Fracture	Flake	9	200	50	Effective plug
0.12 in. Fracture	Bead	9	200	50	No plug
0.12 in. Fracture	Bead	36	200	50	No plug
0.12 in. Fracture	Bead	36	200	50	No plug

5.1 The Effect of Glass Transition Temperature and Heating Duration

One of the first things observed in the lab is the behavior of the biodegradable particulates at different temperatures. For example, using 18 g of the bead particulates mixed with 150 ml water and pressurizing the APPA cell to 50 psi without heating the mixture, the sample was not capable of plugging the 0.12 in. fracture disc. The pressure

drop for that experiment as seen in Figure 5.1 was substantial, and the test result was labeled "no plug". However, once another sample containing 18 g of bead particulates was heated and brought above the glass transition temperature (T_g), the plugging behavior of the particulates changed. The surface of the beads started to soften into a flexible and rubbery state. This surface deformation of the PLA particulates is due to the disintegration of the amorphous regions (the randomly arranged molecules) of the PLA. The amorphous regions in semi-crystalline polymers such as PLA, are usually the first to start to gradually degrade.

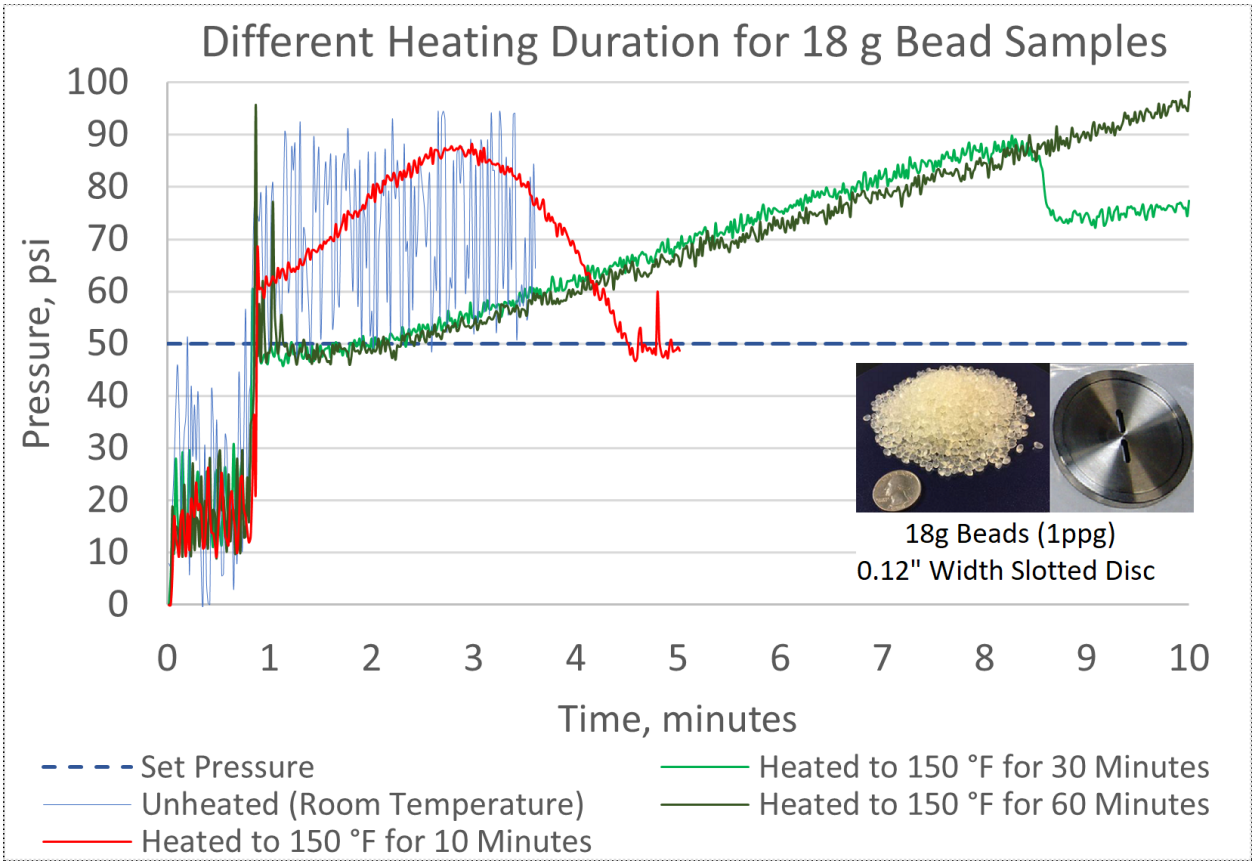

Figure 5.1 The effect of heating duration on PLA plugging performance. Samples containing 18 g of bead diverters were used to plug the 0.12 in. slotted disc.

After the mixture was pressurized to 50 psi, the softened and deformed surface caused the particulates to physically rearrange and bond together. Under pressure, this rearrangement and bonding caused the deformed surface to fill the empty pore space

between the particulates. This in turn resulted in the particulates forming an effective seal under minimum pressure. This formed seal offers a much better flow resistance for effective diversion as compared to the undeformed particulates that were tested at room temperature where they remained in their glassy and rigid solid state.

It did not take a long time for the surface of the bead particulates to start transitioning from their initial rigid and solid state at room temperature to the flexible and rubbery state above T_g. The surface of the particulates started to deform quickly, allowing the particulates to start bonding to each other. This was observed even for the 18 g bead sample that was heated to 150°F for only 10 minutes as seen in Figure 4.11. It is important to note that the diverters were not being exposed to the 150°F for the entire 10 minutes. The 10-minute period started from the time that the APPA heaters were set to 150°F. Therefore, there was a time lag until the heaters themselves reached the 150°F, and additional time lag until the APPA cell itself heated up to 150°F, before that temperature reached the particulates.

It is safe to conclude that the surface deformation of the particulates caused by the transitioning above T_g happen quickly. This is evident by the pressure response that shows the diverters starting to plug the slotted disc within minutes of being heated as seen in Figure 5.1. During this test, some pressure losses were seen 5 minutes into testing. This pressure loss could be due to the transitioning and physical rearrangement of the particulates as the pressure started to build-up inside the cell. In addition, looking at the image of the particulates after the test was completed (Figure 4.11), it is clear that a plug was in the processes of forming. However, a few particulates were still loose, which means that the surface of these particulates did not start to transition yet. Although 10 minutes was not enough for complete bonding of all particulates to achieve an impermeable seal, that time was enough to considerably decrease the permeability of the particulate pack and offer flow resistance that is superior to the flow resistance seen with the beads that were left at room temperature.

Using another 18 g bead sample and heating it to 150°F for 30 minutes, all the particulates in the sample bonded together to achieve an effective seal as seen in the image in Figure 4.12. Additionally, no decrease of pressure concerning the seal's effectiveness was observed in the pressure data. The image of the particulates after completing this test reveals two things: first, no visible empty pore space was observed between the particulates, and second, few particulates were squeezed inside the opening of the 0.12 in. width slotted disc. The deformation of the particulates under 50 psi pressure resulted in a plug that started to take the form of the fracture that it plugged. This was also observed and is more optically visible for the test that was pressurized to 50 psi for 1 hour as seen in Figure 4.14.

Heating the samples for 60 minutes as opposed to 30 minutes did not result in any significant changes in the pressure data or any observable changes in the formed plugs. It is concluded that the particulates start to gradually deform once they reach their T_g. As a result, their performance as diverting agents significantly improve once they reach their glass transition temperature.

Generally, when designing for the particulate diverter pill, the temperature grade of the biodegradable diverter is selected based on the reservoir geothermal temperature. This is done to ensure that the diverters degrade within an acceptable time frame after the stimulation operation is complete. However, the temperature grade of the biodegradable diverters is not usually selected for the plugging performance aspect of the particulates above T_g. Based on the results seen in this work, the recommendation is to include bottomhole operation temperature as a main criterion when selecting the appropriate temperature grade of the biodegradable diverters. The selected temperature grade should include a T_g that's within the range of the downhole operation temperature, which is generally lower than the reservoir geothermal gradient. This in turn can help in taking advantage of the superior plugging performance of the particulates above their T_g.

This surface deformation and bonding of particulates to form one plug was not only observed in the bead diverter, but in the blend diverter as well. However, this bonding was

not observed for the flake diverter. Figure 5.2 shows images taken of the bead, blend, and flake diverters after conducting the 50-psi APPA tests for the samples that were heated to 150°F for 60 minutes. Unlike the bead and blend particulates that bonded together to form one plug, the flake particulates never bonded under all testing conditions done in this work.

Figure 5.2 An image comparing the behavior of the bead, blend, and flake diverters above T_g. Both bead and blend particulates bonded and formed effective plugs, while the flake particulates did not bond and remained separate.

The different behavior of the flake diverter can be due to many factors. These factors could include the shape of the particulate, the surface roughness, the degree of the polymer's crystallinity, or the polymerization and manufacturing process of the PLA. For example, the flat and smooth surface of the flake diverter can cause the particulates to deform differently than the bead and blend particulates, which have relatively rougher surfaces. This is due to the relationship between surface roughness and wettability. The smooth surface of the flake results in lower wettability of the particulates, which can then affect and slow down the deformation and degradation of the flake. This results in poor adhesion that could explain why the particulates of the flake diverter never bonded together.

Safety and technical data sheets for the three diverters used in this work show that all three diverters have the same T_g (55°C), the same melting point (180°C), the same specific gravity (1.24), the same relative density (1.25), and they all contain more than 98% PLA

(DiverterPlus 2018). While the only differences include the physical appearance in shape, size, and surface roughness, different hydrolysis data, as well as different recommended use based on reservoir bottomhole temperature (where the flakes were suggested to be used in relatively higher temperatures). This data does not offer possible explanation for the different behavior of the flake, especially since the chemical composition is similar for all three diverters.

Although chemistry is not in the scope of this research, few things are worth mentioning in that regard. Research shows that how polymers are engineered, including the polymerization process, and the manufacturing process to obtain different physical characteristic, can influence their properties. These properties include but not limited to mechanical properties, physical properties, phase behavior, the polymeric structure, and the degree of their crystallinity (Qin 2016). Therefore, based on this knowledge and what has been observed in this lab, it is safe to conclude that not all PLA are created equal. Their shape, size, as well as how they are engineered and manufactured, influence how they behave above T_g.

5.2 Temperature During Hydraulic Fracturing and Refracturing Operations

Since the thermal properties of PLA and biodegradable particulates have a substantial effect on their plugging performance, it is important to discuss the changes of downhole temperature during hydraulic fracturing and refracturing operations. The large volumes of hydraulic fracturing fluid that are pumped at high rates cause the wellbore, as well as the stimulated reservoir volume, to cool down substantially during injection. Even after finishing the stimulation operation, the temperature can remain low for few hours, and at times for days, before returning to the original geothermal gradient.

A graph based on distributed temperature sensing (DTS) data from a study done by Sierra et al. (2008) gives an insight in how the temperature changes during a hydraulic fracturing treatment. Figure 5.3 shows temperature data obtained from DTS versus depth. Temperatures during different time intervals, as well as the geothermal gradient and a

simulated fracturing fluid temperature were plotted on the graph. It took 10 minutes and 52 seconds for the temperature to drop from 160°F geothermal temperature, to 90°F inside the perforation tunnel (seen around 9430 ft.). Additionally, it took 13 minutes and 12 seconds for the temperature inside the perforation tunnel to completely drop to the simulated fracturing fluid temperature of around 68°F (Sierra et al. 2008).

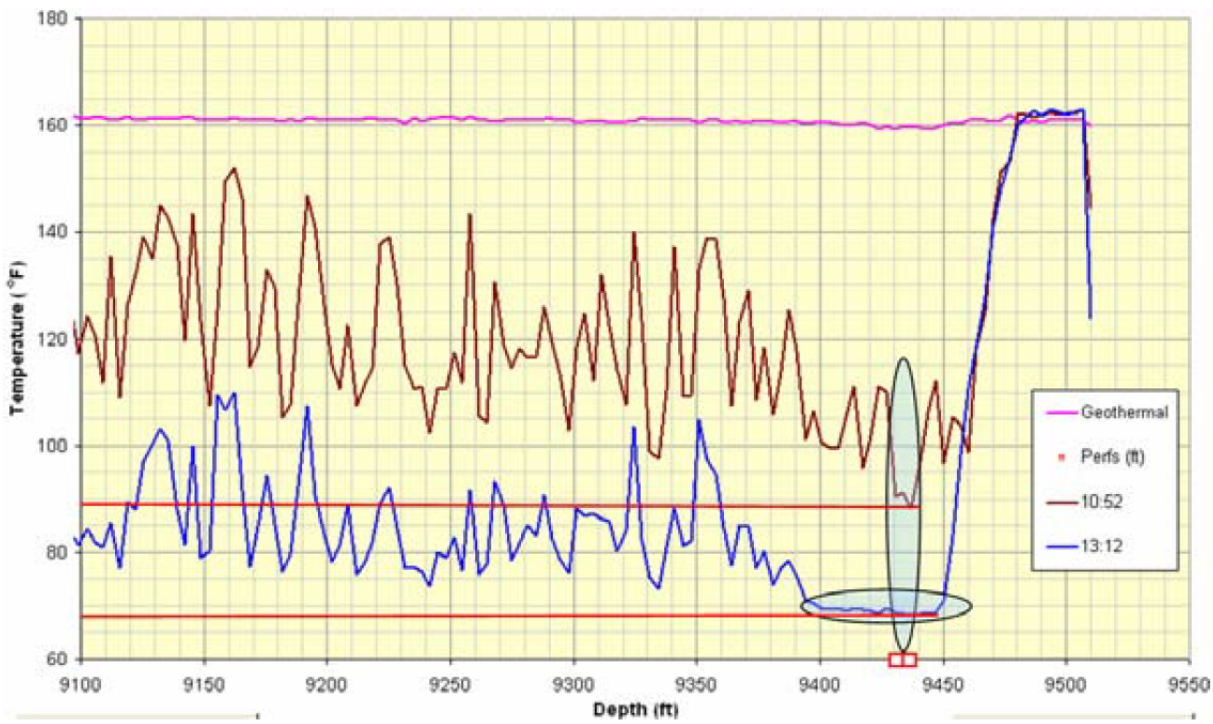

Figure 5.3 DTS data showing the cool-down effect during hydraulic fracturing operations. The recorded DTS data at different time intervals (in minutes and seconds), including (10:52) and (13:12), after initiating the fracturing of one of the stages, as well as the geothermal gradient and the simulated fracturing fluid temperatures are displayed on the graph (Sierra et al. 2008).

The quick and substantial drop in temperature, especially near-wellbore and inside perforation tunnels can prevent the particulate's from reaching their T_g. This can prevent or slow down the particulates from transitioning into a rubbery and deformable state that's responsible for their superior plugging performance especially during the time periods when this low temperature is reached during the fracturing operation. This in turn, can limit the

potential for achieving a better seal and thus, an overall more effective diversion, if the diverters don't achieve T_g and transition.

The severity of this temperature cool-down highly depends on the amount of fluid injected. During a multi-stage hydraulic fracturing treatment, the temperature inside the wellbore decreases more with each additional stage. Although the wellbore might be within a close range of the PLA's glass transition temperature during the initial few stages of the hydraulic fracturing treatment, the temperature can remain close to the stimulation fluid temperatures (surface conditions) for the remainder of the treatment and for a period after the operation is complete.

This means that the PLA pills that are dropped during the initial stages of the hydraulic fracturing or refracturing operations are possibly transitioning and deforming to achieve an effective seal inside perforation tunnels and near-wellbore fractures. This can also be the case for diverter pills that are dropped to seal off depleted fractures before commencing the refracturing operation. However, this may not be the case for the subsequent stages when temperatures downhole are well below T_g; and where division is possibly only occurring due to the flow resistance achieved by the low permeability of the diverter pack. This explanation is also in agreement with conclusions made from the field study done on diverters by Senters et al. (2018). One of the authors' conclusions is "In many cases diversion did open new clusters, but it came at the expense of reducing the total number of clusters treated during the later portion of the treatment" (Senters et al. 2018).

The decrease in temperature during a hydraulic fracturing treatment is usually more significant in near-wellbore regions, but not as significant in the far-field. This can make it easier to take advantage of the biodegradable plugging capabilities above T_g for far-field applications. Although the decrease in temperature is not as severe as near-wellbore, cooling still happens in the stimulated reservoir. Therefore, it is important to estimate this temperature drop in the stimulated reservoir prior to operations and select the PLA temperature grade for far-field applications accordingly.

The wellbore cool-down effect largely depends on the volume of the injected fluid. Acid stimulation treatments usually use a fraction of the fluid volumes used in multi-stage hydraulic fracturing operations. Therefore, this wellbore cool-down is not as extreme during acid stimulation treatments. In turn, this could explain why biodegradable diverters have been more successful for acidizing applications as opposed to hydraulic fracturing applications.

It is important to note here some of the observations made during the experimental phase of this work. After the particulates transitioned and formed a plug above T_g, the newly formed effective plugs became rigid once again after cooling down to room temperature. Additionally, the particulates remained intact and bonded together within the formed plug after they cooled down to room temperature. This means that if the particulates transition and form a plug, the formed plug can effectively divert the cool fracturing fluid. It is critical then to find a method to heat the biodegradable diverters downhole for few minutes to allow them to transition above T_g to take advantage of their enhanced performance and have effective diversion. This can be done after dropping the diverter pill and before starting the next hydraulic fracturing stage. This is especially the case for near-wellbore applications and during the latter stages of the stimulation treatment when downhole temperatures are significantly lower.

5.3 Determining the Amount of Diverter to Use

Some tests were conducted to help propose guidelines for the appropriate amount of diverter to plug perforations and fractures above T_g when PLA particulates transition into the deformable and rubbery state. These tests were done using the 0.12 in. width two-radial arms slotted disc that simulate a large fracture, and the 0.4 in. diameter slotted disc that simulate a perforation. The performed tests helped determine the minimum mass of particulates needed for each of the bead, blend, and flake diverters. Additional tests were conducted using the bead diverters at room temperature to compare the data with the tests done above T_g.

To plug the 0.12 in. fracture disc, only 4.5 g of the bead, 9 g of the blend, or 9 g of the flake was required for samples heated above T_g as seen in Figure 4.15, Figure 4.16, and Figure 4.17, respectively. The fact that a lower mass of bead diverter was cable of plugging the 0.12 in. fracture than blend diverter is contradictory to conventional wisdom. Blend has lower pack-permeability than beads due to the higher particle-size distribution. After all, this low permeability is the foundation for effective diversion of conventional particulates. This data further show that these particulates do behave differently above their glass transition temperature. In addition, it is safe to conclude here that above T_g, less mass of bead diverter is needed to achieve an effective plug compared to the mass required using blend or flake diverters. Both flake and blend diverters required double the mass needed for the bead diverter to sustain the 50-psi differential pressure above T_g. This in turn, gives the bead diverters an advantage over the other particulates.

To plug the 0.4 in. perforation, 18 g of the bead diverter was required above T_g as seen in Figure 4.19. However, 144 g of the bead diverter was required to plug that same 0.4 in. perforation at room temperatures as seen in Figure 4.23. The required mass of diverter at room temperatures was eight times the amount required to plug the same perforation at T_g. To further verify, the same test was done using the 0.12 in. fracture disc. Only 4.5 g of bead diverter was needed to plug the 0.12 in. disc above T_g, while 36 g of the bead diverter was needed to plug the same 0.12 in. at room temperature as seen in Figure 4.22. This also shows that an additional 8-fold of particulates is required if the diverters remain below T_g. A conclusion can be made here that the amount of diverter required can be decreased by 8-fold if the chosen diverters can transition downhole into their flexible and rubbery phase during the stimulation operation.

To put things into prospective, data obtained from this work is compared to current industry recommendations for the amounts of diverter needed. The 18 g of bead diverter that was needed to plug the 0.4 in. perforation is equal to 0.04 lb. This means approximately 0.04 lb per perforation is required if T_g is achieved. Additionally, the 144 g

of bead diverter that was needed to plug the same 0.4 in. perforation at room temperature, is equal to 0.32 lb per perforation. Current industry guidelines recommend starting with a minimum of 0.5 lb of particulates per perforation for cemented cased-hole completions, and possibly work up to 8 lb per perforation. Large near wellbore vugs and open hole completions usually requiring the higher end of that range. As discussed in the literature review chapter, the current industry guidelines are based on maximizing the flow resistance through permeability reduction of the diverter-pack.

The 0.32 lb per perforation obtained from this work to plug at room temperature is equivalent to industry recommendations that are based on fluid flow through porous media. Additionally, the mass found in the lab is within an acceptable range of what is used in the industry. Therefore, another conclusion can be made here that current industry recommendation can be eight times higher than what is needed in some cases. Especially for near-wellbore diversion during the initial stages of the hydraulic fracturing treatment when downhole temperatures are still relatively high enough to allow the biodegradable particulates to transition. Additionally, this could also be the case for far-field applications where the particulates are exposed to relatively higher temperatures that could also allow them to transition.

The use of these much higher volumes of diverter than needed can be very problematic to efficient diversion, and most importantly, to the overall success of the hydraulic fracturing treatments. If a plug is formed early on and the perforations are successfully sealed, then the additional particulates that are still being pumped can possibly plug the wellbore as well as other perforation clusters that need the hydraulic fracturing treatment. This can result in achieving the exact opposite goal for using the particulate diverters in the first place; causing an overall decrease in the stimulated reservoir volume and lower stimulation efficiency. This conclusion agrees with, and could explain, the inconsistent results seen by many operators regarding the effectiveness and placement of these biodegradable diverters. Therefore, a few calculations were made to develop guidelines

regarding choosing the appropriate mass off diverters to use when downhole temperatures are expected to be within the range of the glass transition temperature of the biodegradable diverters.

The mass-to-area ratios of the minimum amount of diverter required per cross sectional area of the opening that needs to be plugged were determined. This was done using the data obtained for tests done on both the 0.12 in. fracture slotted disc and the 0.4 in. perforation. The calculated cross-sectional area of the openings of the slotted discs are 0.0751 in^2 for the disc simulating a fracture and 0.1257 in^2 for the disc simulating a perforation.

The minimum amount of bead diverter required to plug the fracture is 4.5 g, while the minimum amount of bead required to plug the perforation is 18 g. The calculated mass-to-area ratio of diverters required per cross sectional area that needs to be plugged is found to be 0.13 lb/in^2 (19 lb/ft^2) for the fracture disc, and 0.32 lb/in^2 (45 lbs/ft^2) for the perforation disc. To account for particulate settling and other considerations, a 20% factor was applied to the calculated values. Therefore, the proposed recommendations is to start with 0.16 lb/in^2 (23 lbs/ft^2) for fractures and 0.38 lb/in^2 for perforations if T_g is achieved. However, for the cases when T_g cannot be achieved, current industry guidelines need to be used.

5.4 Flowback Potential

A few tests were conducted to assess the potential of flowback with a 24-hour period. These tests included heating all three diverters (bead, blend, and flake) to 200°F for 24 hours. After heating each sample, the APPA cell was pressurized to 50 psi to test if the different diverters can plug the 0.12 in. width slotted disc. A summary of the obtained pressure data as well as images taken of the samples after the test was complete can be seen in Figure 5.4.

For all three diverter samples that were heated to 200°F for 24 hours, it was observed that the properties of the diverters changed once again. Under these conditions, the beads

and the blend diverters became viscous fluid, that is gummy-like paste. However, this was not the case for the flake diverters. Even under the higher temperatures and longer heating duration, the flake diverter never bonded together nor became a viscous fluid. Instead, the flake particulates became more like a filter-cake as seen in the lower right image of Figure 5.4.

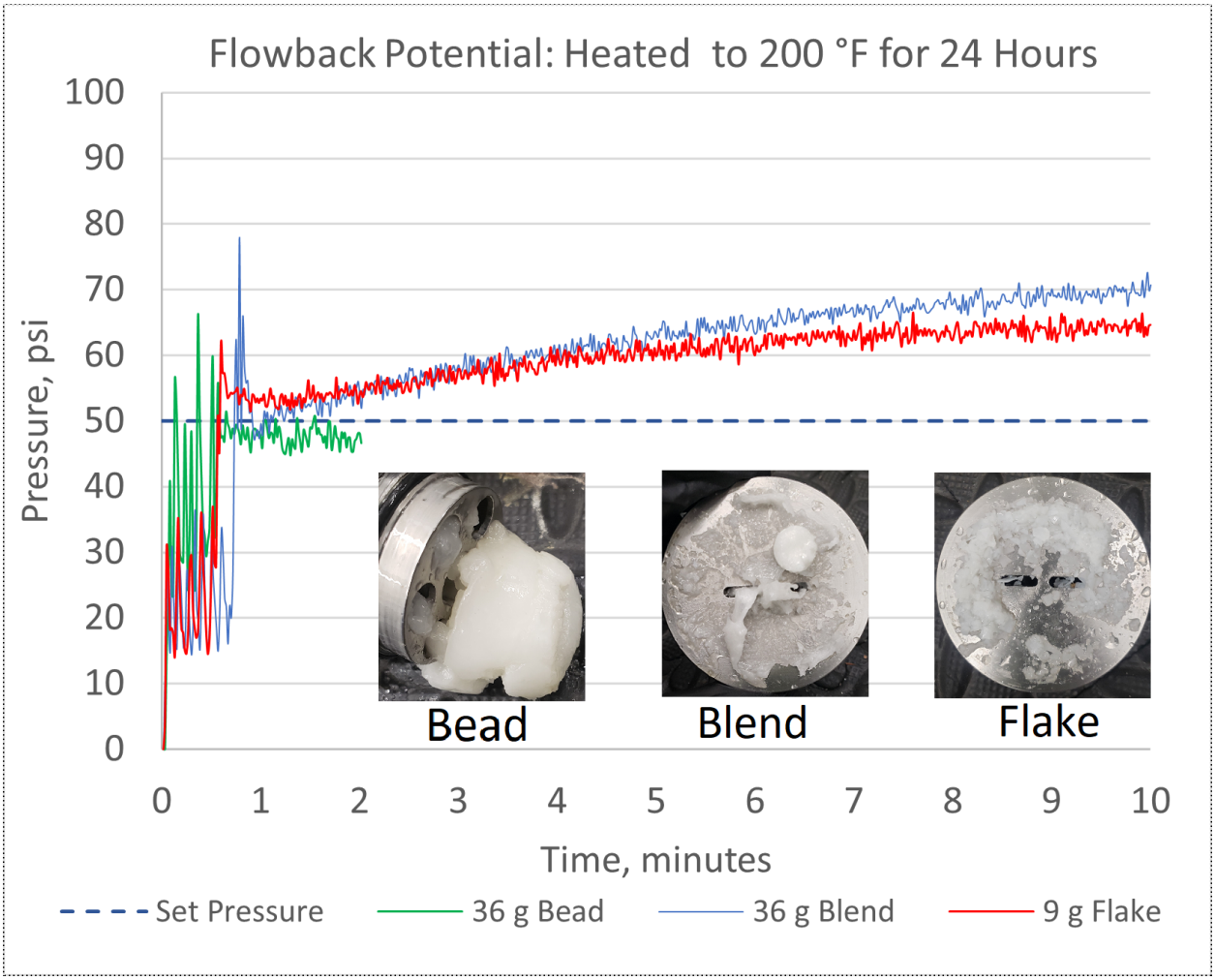

Figure 5.4 Flowback potential of the bead, blend, and flake samples heated to 200°F for 24 hours.

The gummy-like paste that resulted from heating the bead diverter for example, was able to flow past the 0.12 in. fracture width slotted disc under only 50 psi pressure. Not only did the 36 g of beads fail to plug the fracture disc, but the paste flowed from the

APPA cell, through the slotted disc, and into the LCM receiver during the test as seen in Figure 5.4. However, this was not the case for the blend sample. Although heating 36 of blend diverters to 200°F for 24 hours resulted in a gummy-like paste, this sample was still able to plug the fracture disc under the 50-psi pressure. Although the resulted blend paste was moveable, only a small fraction of that volume was displaced behind the slotted disc, while much of the paste remained in the APPA cell.

Samples from the resulting gummy-like paste for the bead and the blend were saved, and their behavior upon cooling back down to room temperature was observed. The paste from the bead diverter sample never hardened back and remained in that gummy-like paste form upon cooling down to room temperature. This however was not the case for the blend diverter. After cooling down, the blend diverter hardened again and became plastic-like. It was observed that it was easier for the cooled down blend (that was heated to 200°F for 24 hours) to bend compared to the cooled down blend samples that were only heated for 60 minutes to 150°F. This indicates a substantial reduction in their strength, but nonetheless, they still plugged the slotted disc.

As for the flake diverter, they behaved differently from the bead and the blend. Only 9 g of the flake diverter heated to 200°F for 24 hours could plug the 0.12 in. fracture. It is important to note that the flake particulates never bonded together under all experimental conditions done for this research. Additionally, the flake particulates remained in their solid form during this test. However, the sizes of the particulates were observed to have decreased indicating degradation as seen in Figure 5.4.

It is generally expected for the flowback from the zones that are plugged with biodegradable diverters to occur within hours or days as the particulates start to degrade. The reason behind this is the idea that partial degradation of individual particulates creates channels and flow paths for reservoir fluids to pass through. However, results from this work show different behavior. This study shows that particulates can still plug even at higher temperature. As the surface of the particulates start to degrade, they become

deformable and pliable taking on the shape of the area they plug.

Therefore, even during the early stages of partial degradation, the diverters are still capable of deforming further, keeping the areas plugged. This can occur until the volume of particulates that remains is lower than the volume necessary to cause an effective seal (as seen with the 9 g of blend sample) or until they become viscous fluid that is incapable of plugging (as seen with the bead diverters).

It was determined by the results of these experiments that excess volumes are currently pumped (by 8-fold) than required using current industry standards. This can add additional impact on flowback potential where larger volumes of diverter need to degrade. Additionally, the degradation process is further delayed due to the wellbore and reservoir cooling effect discussed in the previous section. Resulting in even longer periods of time before flowback can occur. All this can explain the long wait before flowback experienced by many operators.

The results obtained from the flowback potential tests conducted in this work further stress the importance of two conclusions made so far: 1) Selecting the temperature grade of the diverter based on the expected operation temperature and not based on the reservoir thermal gradient, and 2) utilizing a method to heat the diverters after they are pumped downhole. Doing so will result in using substantially lower amounts of diverter when T_g can be achieved during treatment. This will help solve the problem with the flowback delay that many operators are experiencing by using the optimum and lower volume of diverters. Having less volume of diverters means less volume that needs to degrade to allow flowback. Additionally, this will also help in taking advantage of the accelerated degradation rates that happen when the reservoir temperature is substantially higher than the glass transition temperature of the diverter. This is based on the discussed hydrolysis data in the methods and equipment chapter, as well as conclusions made by Gomaa et al. (2016b) that found temperature has more effect on dissolution rate than time. Thus, selecting the temperature grade of the diverters based on the relatively lower expected operation

temperature as well as heating the diverters after placement will help in having higher degradation rate and faster flowback.

To summarize the flowback potential results, heating the diverter for 24 hours to 200°F (a temperature that is lower than the melting temperature of all diverters) resulted in additional changes in their mechanical properties. Both blend and bead diverters became a gummy-like paste that is more pliable than the samples that were heated to 150°F for 60 minutes. The flake particulates on the other hand, started to degrade and became a filter-cake like substance capable of plugging the slotted disc using lower mass than the blend. However, these flake particulates never bonded together and behaved differently than beads and blend. Therefore, under this work's testing conditions, the flake diverter has the least potential for allowing flowback to happen within 24 hours, followed by the blend diverter. The bead diverter on the other hand, preformed the best, and was incapable of plugging the slotted disc even while using larger volumes.

5.5 High-Pressure and Long-Term Tests

A few tests were conducted using the 0.4 in. diameter perforation disc while pressurizing the cell to 200 psi for 4 hours. These tests were conducted on bead and blend diverters. Flake diverters were not used since they did not plug the perforation at 50 psi even when higher amounts were used. The diverters were heated to 150°F for 60 minutes then gradually pressurized to 200 psi. The pressure was then held constant at 200 psi for the remainder of the 4-hour experiment.

This experiment was done to test the ability of the heated particulates to hold a differential pressure that is within an average range of what is usually experienced during a hydraulic fracturing treatment in the field. Additionally, the samples were pressurized for 4 hours, which is also within a range for how long a fracturing stage typically takes to complete. These tests were done to ensure that the diverters can effectively plug when used above their glass transition temperature during a hydraulic fracturing treatment.
Figure 5.5 show the results for both the bead and the blend tests.

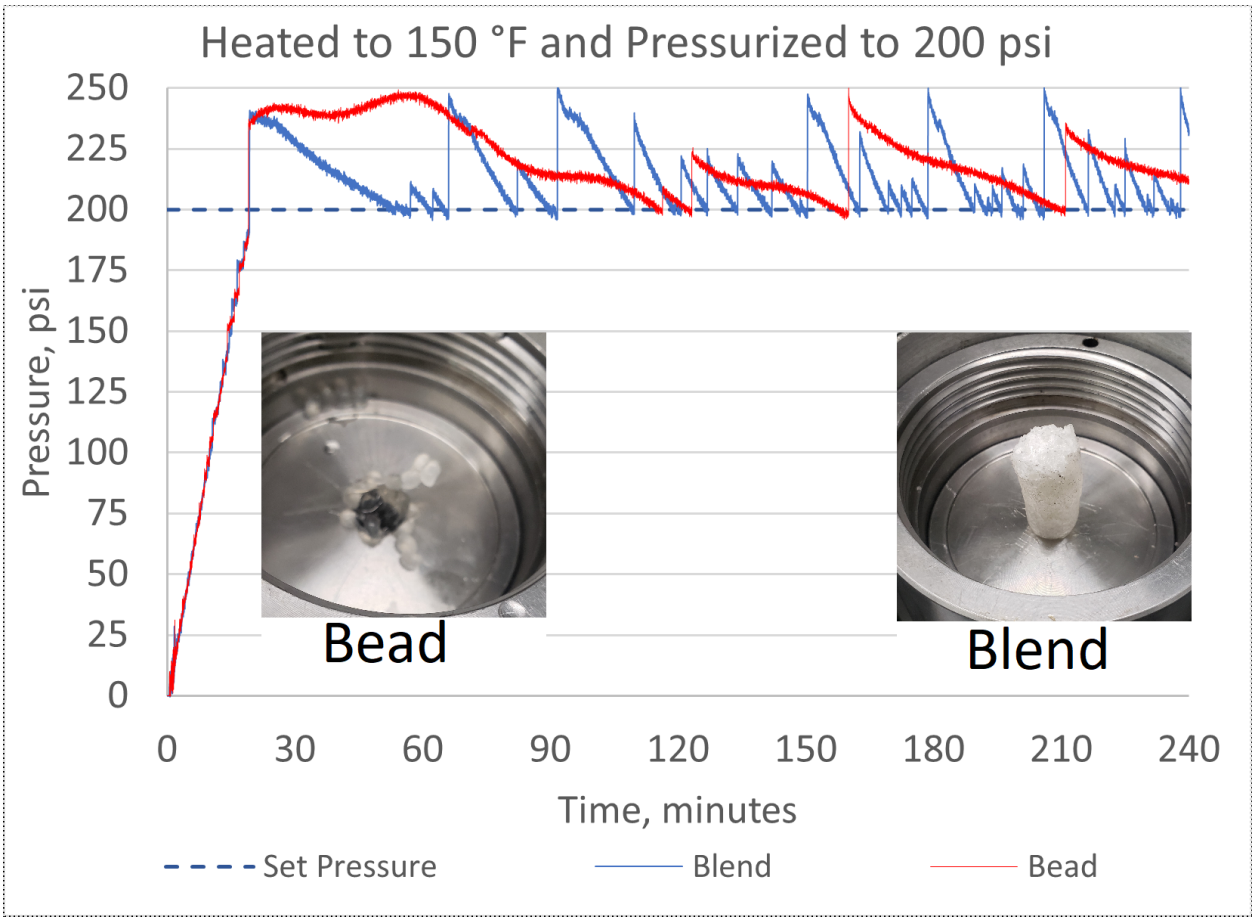

Figure 5.5 Test results for the high-pressure and long-term tests comparing the performance of bead and blend diverters above the glass transition temperature.

Looking at the pressure data in Figure 5.5, both particulates, the bead and blend, were able to withstand the 200-psi pressure and for the entire 4-hour duration of the experiment. This means that the plug formed from heating the particulates to a temperature above their T_g, can withstand the 200-psi differential pressures experienced during a hydraulically fracturing treatment, and for durations lasting for at least 4 hours.

The pressure for the test done using the blend diverter momentarily dropped below 200 psi. This pressure drop can be observed around the 60-minute mark on the graph. This decrease is observed to happen again every 10-30 minutes for the remainder of the test. However, this was a little different for the bead diverter. The pressure using the bead diverter momentarily dropped below 200 psi 2 hours into testing. This drop can be seen

around the 120-minute mark on the graph. The pressure drop using the bead diverter happened almost an hour after it was observed for the test done using the blend. Additionally, this minimal drop was only observed four times during the entire duration of the 4-hour test that was conducted using the beads. This drop was substantially less frequent than the pressure drop observed on the test done using the blend.

Looking at the images of both diverters taken after these tests were completed, the formed plugs were compressed and squeezed into the 0.4 in. perforation opening. After the tests were completed, the formed plugs did get stuck inside the APPA cell and inside the opening of the 0.4 in. perforation disc. This explains the minimal pressure losses seen for both diverters. Thus, higher differential pressures can result in additional compression in the formed plugs.

The resultant plugs were especially hard to remove from the slotted disc for the blend diverter. Larger volumes of the blend diverter made it past the slotted disc (lower right) as compared to the bead diverter where only few particulates squeezed past the perforation as seen in Figure 5.5 (lower left), further explaining the earlier and more frequent pressure drop seen with the blend compared to the bead diverter. This difference is most likely due to the smaller particulate size that make-up the bulk of the blend sample.

Smaller size particulates degrade faster than larger particulates, based on the study done by Gomaa et al. (2016b). This is due to larger area of the particulates that is in contact with the fluid. This leaves a larger volume in the core of the bead particulates in their solid and undeformed state where only the surface has deformed. While on the other hand, most of the fine particulate has deformed. This resulted in a plug that has an overall higher strength and is more stable for the bead than the blend.

Therefore, a recommendation is being made to use larger-size particulates for near-wellbore applications to plug perforations and larger fractures to ensure a stable and strong plug when using the diverter above their T_g. This recommendation is also in agreement with conclusions discussed in the literature review for conventional particulates.

Additional considerations should be made to ensure an optimized particulate-size to opening-size of perforation or fracture to ensure proper placement, based on the already established industry guidelines and recommendations.

5.6 Comparing Results for Different Shape and Size Particulates

Based on all the tests conducted for this research, different particulates behave differently above their glass transition temperature. The bead diverter preformed the best, followed by the blend, and last by the flake. Summarizing the previously discussed results, the following conclusions are made:

1. The bead diverter preformed the best for all the tests conducted above T_g.
2. Less amounts of the bead diverter are required to effectively plug above T_g as compared to both the blend and the flake.
3. For the flowback tests, the bead diverter has the most potential of allowing faster flowback to occur as compared to both the flake and the blend.
4. Both blend and bead diverters could plug the 0.4 in. perforation above T_g, while the flake diverter failed to plug even when higher amounts were used.
5. The bead particulates achieved a stronger and more stable plug under higher pressures and for longer periods of time than the blend above T_g.

Although blend diverters are more desirable to use for conventional particulates due to their lower pack-permeability, results from this work show that above T_g, the PLA bead particulates were the best performers across all tests conducted for this research. This conclusion can prove to be helpful in the field especially since flake and blend diverters have some issues with regards to pumping and placing the diverter pill.

Due to their irregular shape, the flake diverter can be hard to pump. Pumps that are used to for proppant during a hydraulic fracturing treatment are designed for the use of

spherical particles. A special pump that can handle the irregular shape of flake diverters may be required. On the other hand, the blend diverter contains particulates that have different sizes and different shapes. Different size particles travel at different velocities and have different settling behavior (Alotaibi and Miskimins 2020). This is based on what is known from proppant transport behavior. To pump a blend diverter pill containing different size and shape particulates and at the same rate and concentration can cause several issues. Some of these issues include the arrival of the particulates at different times and experiencing more severe settling. This is especially the case since the pump rate cannot be optimized for different particulate sizes. This in turn can make for an overall inefficient placement of the pill. Taking advantage of the superior performance of the bead diverters above T_g can help in mitigating many issues associated with using the flake or blend diverters.

5.7 Anomaly at Room Temperature

As previously discussed, the 18 g of the unheated bead sample was not capable of plugging the 0.12 in. fracture at room temperature as seen in Figure 4.22. Samples containing higher mass of the bead diverter were tested. Using 36 g in 150 ml water (2 ppg), the bead diverter was able to plug the 0.12 in. fracture disc at room temperature. As expected, the ability of this sample to plug using higher amount of bead can be attributed to the increase of the length (L) of the particulates-pack sample, causing an increase in flow resistance as governed by Darcy's equation for fluid flow through porous media.

For the test conducted using the 36 g bead sample, the data reveal a pressure anomaly. The pressure started to increase inside the APPA cell a little over 2 minutes into testing. Once the particulates reached the slotted disc (30 seconds into testing), they plugged the disc instantly. This is marked by the first green vertical line (left side) on Figure 5.6. The pressure then stabilized for almost 1.5 minutes at a 60-psi pressure as it was expected at room temperature. However, the pressure started to build up, as marked by the second green vertical line. This pressure build-up lasted for the remainder of the 10-minute test.

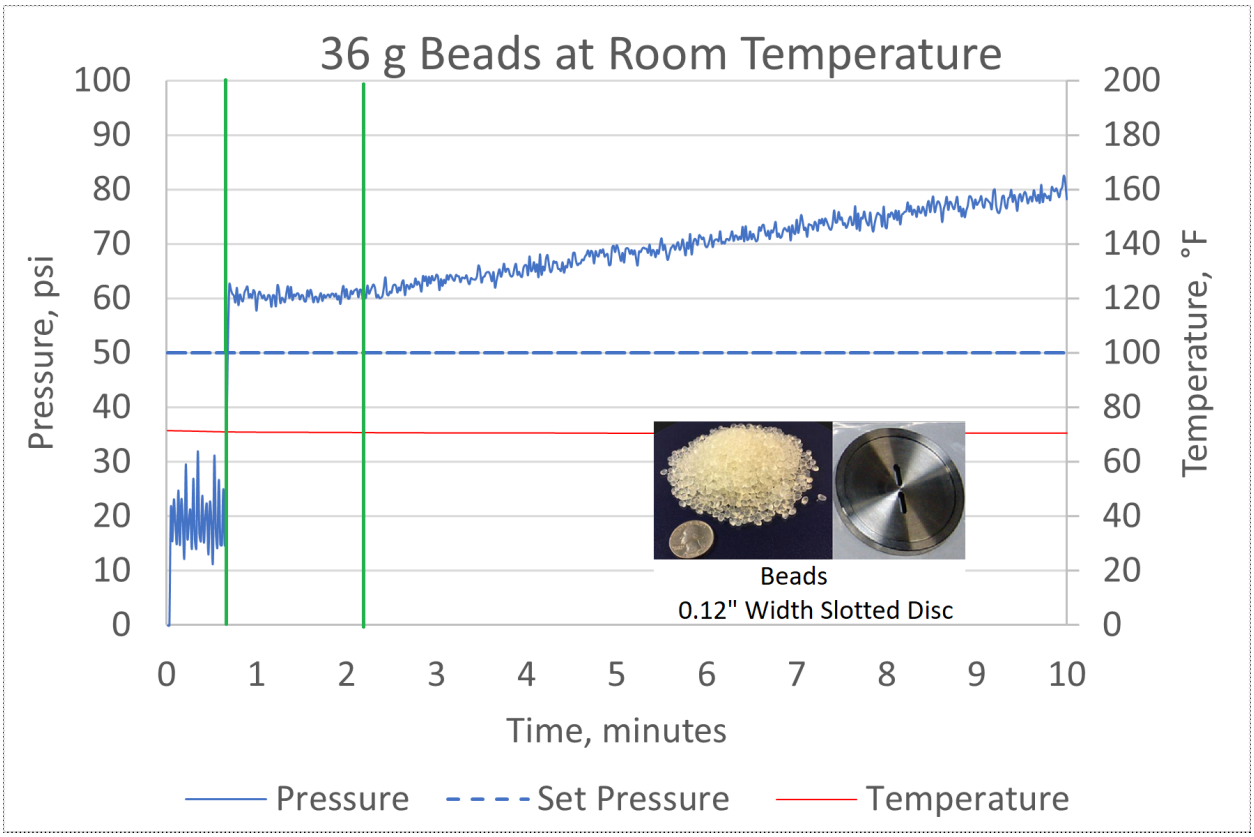

Figure 5.6 APPA results for the 36 g of unheated bead diverters plugging the 0.12 in. slotted disc. A pressure anomaly can be seen where the pressure inside the APPA cell was building up after almost 2 minutes into testing.

This observed pressure-increase inside the APPA cell happened without the equipment pumping any additional hydraulic oil. Since this test was done at room temperature, this pressure build-up cannot be attributed to thermal expansion of the fluid sample or the hydraulic oil, as in the cases for tests that were heated. Two repeatability tests were done using the same parameters to verify the results of this test. The pressure data obtained from the repeatability tests show similar behavior as seen in Figure 4.33.

In an attempt to understand this pressure behavior, research revealed that the PLA polymer can volumetrically swell in water. However, the degree of the swelling was not tested, and polymeric properties are not in the scope of this study. No final conclusions can be made regarding this anomaly as the reasons behind it could be due to volumetric

swelling or it could be due to possible human error. Especially since this pressure build-up was not observed for similar tests conducted using the 0.4 in. perforation disc as seen in Figure 4.23.

The degree of volumetric swelling of PLA could be one area worth investigating for future work. If such swelling is substantial under certain conditions, it should be accounted for when designing for PLA and biodegradable diversion. Such swelling can affect two important parameters, the amount of diverter to pump, and the size of the particulates to use. However, the only conclusion that can be made here is polymeric properties of PLA and biodegradable diverters have an impact on their plugging performance and should be studied and designed for accordingly.

CHAPTER 6

CONCLUSIONS, RECOMMENDATIONS AND FUTURE WORK

The experiments done for this research revealed that the plugging performance of biodegradable particulate diverters is highly influenced by temperature. The ability of biodegradable PLA diverters to deform above the glass transition temperature (T_g) results in an enhanced plugging performance, while utilizing significantly lower amounts of particulates with one-size distribution. The surface of the PLA particulates softens above T_g and becomes flexible and rubbery. This deformation causes the particulates to bond together and form a plug capable of sealing perforations and large fractures. This understanding can lead to more effective and efficient diversion, faster degradation and flowback, and an increase in consistent results in the field.

6.1 Conclusions on the Effect of Temperature

The following conclusions are made regarding the behavior and plugging performance of PLA diverters at different temperatures.

1. Below T_g:

    - Diverters are in their solid phase and are glassy and rigid.
    - Particulates remain separate, do not bond together, and do not form one solid plug.
    - Their plugging performance is similar to conventional particulates where diversion depends on the flow resistance achieved by lowering the pack permeability of the particulates.
    - Higher amounts of particulates are needed to achieve the appropriate flow resistance needed for diversion.

2. Above T_g and below T_m during the initial stages of transitioning:

    - Particulates undergo a deformation process and start transitioning into a rubbery state.
    - The deformation process happens quickly and within minutes of heating the diverters.
    - The deformation process begins with the softening of the particulates' surface.
    - This softened surface causes the rearrangement and bonding of the particulates to form one plug (only observed for the bead and blend diverters, not the flake).
    - Under minimum pressure (within 50 psi), the deformed surface fills up the empty space between the particulates resulting in an effective seal.
    - The formed plug offers an improved performance and sealing capabilities for effective diversion compared to the undeformed particulates under T_g.
    - The amount of diverter required to plug is reduced by 8-fold compared to the undeformed particulates under T_g.
    - Upon cooling down to room temperature, the particulates solidify again and remain bonded together, demonstrating their ability to remain intact during the cooler hydraulic fracturing treatment temperatures.
    - Current industry recommendations for the minimum amounts of diverters to use are at least eight times higher than what is required to form an effective plug above T_g.

3. PLA plugging performance at higher temperatures (70°F above T_g) and after 24 hours of heating:

    - Diverters start breaking down.
    - The particulates become gummy-like paste (observed for the bead and blend but not for the flake).

- Ineffective or less effective at plugging (depends on the shape and amount of diverter used).
- Eventually fully degrading and becoming liquid.

These conclusions can have many implications on field operations. By not accounting for the difference in phase behavior of the particulates at different temperatures, inconsistent plugging performance in the field can result during hydraulic fracturing treatments. This can have negative consequences resulting in low stimulation efficiency and a decrease in stimulated reservoir volume. Pumping higher volumes than needed can result in plugging the wellbore and other perforation clusters that need the fracturing treatment. This can happen where the particulates are exposed to temperatures that are within the range of T_g. Examples for when this can happen include near-wellbore diversion during the initial stages of the fracturing treatment and in far-field diversion. Additional implications include prolonged periods of time before flowback can occur until a substantial volume of the diverter degrade.

6.2 Conclusions on the Effect of Shapes and Sizes Above The Glass Transition Temperature

Particulates with different shapes and sizes behave differently above T_g resulting in a different plugging behavior and effectiveness. The bead diverter performed the best for all experiments conducted above T_g followed by the blend, while the flake diverter performed poorly. Some of the advantages of using the bead diverters compared to the blend and the flake include:

- Lower amounts (up to 50% less) of the bead diverter are required to form an effective plug compared to both the blend and the flake.
- Both bead and blend diverters could plug the 0.4 in. perforation above T_g, while the flake diverter failed to plug.

- Under higher pressure (200 psi) and for longer periods of time (4 hours), the bead particulates achieved a stronger and more stable plug than the blend.

- Flake particulates had different transitioning and degradation behavior than the bead and the blend diverters. Flake particulates never bonded under all testing conditions done in this work, possibly due to the smooth surface that effects the wettability of the particulates.

- The bead diverter has the most potential for allowing faster flowback, followed by the blend and the flake. For the flowback experiment, both the blend (using 36 g) and the flake (using 9 g) plugged the 0.12 in. fracture slotted disc while the bead diverter was incapable of plugging (using 36 g).

- Using bead diverters can have the following implications on field operations:
  1) Simpler particulate diversion design.
  2) Mitigating issues related to severe settling from pumping blend diverters that have different size particulates.
  3) Mitigating issues related to pumping the irregular shape of flake diverters.

6.3 Design Guidelines and Recommendations

The advantages of the biodegradable particulate diverters above the glass transition temperature are significant. These advantages include enhanced plugging performance and substantial decrease in the amounts required to achieve effective seal for diversion. Correctly designing for these particulates based on their phase behavior above T_g, will not only help with taking advantages of their enhanced and efficient plugging capabilities, but will also help in mitigating many issues currently experienced by many operators, including inconsistent diversion results and prolonged time before flowback.

However, all these advantages can be limited during the latter stages of the hydraulically fracturing treatments. This is especially the case for near-wellbore

applications when downhole temperatures substantially decrease due to the wellbore cooling effect of the stimulation fluids. This decrease can prevent the diverters from reaching T_g while downhole. Therefore, it is critical to investigate and employ methods to heat these diverters downhole for a few minutes to allow them to transition during these latter stages of hydraulic fracturing treatment.

Based on the results and conclusions of this research, the following recommendations and design considerations above T_g are made:

1. Select the temperature grade of the biodegradable diverter based on estimated bottomhole operation temperatures and not the reservoir temperature. Doing so will result in:
    - Ensuring the transitioning of the particulates to take advantage of their enhanced plugging capabilities.
    - Using lower amounts of particulates and increasing efficiency.
    - Achieving faster flowback when using lower amount of diverters, and by taking advantage of the accelerated degradation rates that happen when the glass transition temperature of the diverter is substantially lower than the reservoir temperature.
2. Select one size (single distribution) coarse bead particulates for near-wellbore applications. The size of particulates should be optimized based on the already established industry guidelines. This will result in:
    - Effective, stable, and strong plug.
    - Lower amounts of particulates needed.
3. Determine the minimum amounts of diverter to use based on the cross-sectional area of the opening that needs to be plugged. When operation temperature is in the range of T_g, start with 0.16 lb/in^2 (23 lbs/ft^2) for fractures and 0.38 lb/in^2 for perforations.

A 20% factor is already included in these numbers to account for settling and other considerations.

4. For the cases when the temperatures of the diverters downhole cannot be brought above T_g, current industry guidelines for conventional diverters can be used.

6.4 Recommendations for Future Work

The following are few areas of interest that can help in further understanding biodegradable particulate diverters to effectively utilize them in field applications. The recommendations for future work include:

1. Investigate polymeric properties of PLA to further understand other parameters that can affect and induce the phase behavior changes of the particulates downhole.

2. Investigate particulate transport and placement in horizontal wells. Proper particulate transport and placement is of critical importance to the overall effectiveness of diversion and still poorly understood especially in horizontal well applications.

3. Investigate the possibility of combining limited entry diversion methods with biodegradable particulates.

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