

OILFIELD TRACER ANALYSIS AND APPLICATION FOR HYDRAULIC
FRACTURE DIAGNOSTICS

A Thesis

by

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ABSTRACT

From the mid-1950s, tracer tests have been conducted in oilfield for various applications such as determining residual oil saturation, identifying barriers or high permeability zones in reservoirs, and providing the information on flow patterns. While the utilization of tracer technologies for conventional oilfield development is mature, the use of tracers in unconventional hydraulic fracturing operations is relatively new. Limited number of research studies has been done on using novel tracer technologies for hydraulic fracture diagnosis.

The objectives of this tracer research include: (1) review the usage of tracer in literatures for traditional oilfield development; (2) investigate the advantages and disadvantages of novel proppant tracer technology for unconventional oil and gas development; (3) evaluate a chemical fluid tracer method of monitoring oil/water movement for hydraulic fracture diagnostics; (4) introduce a novel fluid tracer approach to ‘tag’ and monitor hydraulic fracturing fluid.

This research discusses the common tracer usage for traditional oil and gas development. Each type of tracer comes with its own strengths and weaknesses. Comparing the pros and cons of different tracer technologies based on their chemical nature and commercial availability helps identify the most ‘suitable’ tracers for specific oilfield investigations.

For unconventional oilfield development, novel tracer technologies to track both proppants and fluids for hydraulic fracture diagnosis have been developed over the years.

Proppant tracer techniques allow for the detection of proppant location while fluid tracers can be used to estimate production contribution and detect fracture communication in multi-stage hydraulic fracturing. Based on the tracer analysis, suggestions on how to design and conduct a tracer test using novel tracer technique are provided.

In the last part of this research, a novel fluid tracer approach is introduced to ‘tag’ and locate fracture fluid. Gadolinium-based tracer is recommended as an appropriate indicator of fracture fluid. Comparing the pulsed neutron log data before and after the fracture job gives an indication of the fracture fluid location along the wellbore.

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NOMENCLATURE

C_f	volumetric concentration of fractures
M_i	molecular weight of the compound
q_p	production rate
Σ_a	the Σ of shale formation after injecting GdCl_3
Σ_t	the initial Σ of shale formation
C	measured concentration of tracer
c_{Gd}	number of Gd atom in 1cm^3 GdCl_3 solution
c_i	number of i atom in 1cm^3 GdCl_3 solution
M	total injected tracer mass
m	recovered tracer mass
M_{Gd}	molecular weight of Gd
N_A	Avogadro constant
Σ	macroscopic capture cross-section
σ_{Gd}	atomic neutron capture cross-section of Gd atom
Σ_{Gd}	macroscopic capture cross-section of GdCl_3
σ_i	atomic neutron capture cross-section of i atom
N	neutron population
t	time
v	velocity of the thermal neutron
Φ	porosity

ρ	density
c.u.	capture unit, $1 \text{ c. u.} = 10^{-3} \text{ cm}^{-1}$
barn	unit of cross-sectional area, $1 \text{ barn} = 1 \times 10^{-24} \text{ cm}^2$

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CHAPTER 1

INTRODUCTION

1.1 Background

An extensive variety of substances have been used as tracers in different scientific disciplines and industrial practices, including traditional oilfield development, hydrological application, groundwater flow investigation, and geothermal evaluation. As a general rule, a traditional oilfield tracer refers to those substances that can flow with the injected fluid or solids, to indicate the presence of the tagged fluid or solids, the flow direction or velocity in porous medium.

In the early 1900s, aqueous-phase tracers were originally used in hydrology to qualitatively understand the movement of underground fluids. From the mid-1950s, reservoir engineers began to apply tracer tests to understand fluid flow pathways and fluid dynamics in waterflood projects. Waterflood is a method of secondary recovery in which water is injected into the reservoir formation to displace residual oil. The heterogeneity of the reservoir plays a decisive role in the flow pattern of the fluid in the reservoir, and it has a great influence on the production of oil, water and gas. In order to identify and determine the degree of reservoir heterogeneity, it is necessary to simulate the tracer flow in the reservoir and fit it with the measured tracer data. The flow of tracers between injection wells and production wells can clearly indicate the characteristics of the target reservoir between these wells. Brigham et al. (1965) proposed a method for predicting the flow characteristics of water flood tracers in a five-spot well pattern, which analyzes the

tracer peak concentration and transit time for tracer arrival. The tracer test is to inject the tracer slug from the water injection well, and then monitor its production from the surrounding production wells, and draw the curve of the tracer production concentration over time. The interpretation of tracer data has developed quantitatively, and its applications have become more and more extensive.

A significant amount of field applications for both inter-well tracer test (IWTT) and single well tracer test (SWTT) have been performed. Cooke (1971) designed an inter-well tracer test to characterize oil distribution in a reservoir. Both passive and partitioning tracers were used to determine the residual oil saturation. Tomich et al. (1973) developed the first field application of a SWTT to measure the residual oil saturation in a watered-out formation. Ethyl acetate was used as the primary tracer during injection. It is considered a partitioning tracer because it is soluble in both water phase and oil phase. Then a portion of the primary tracer interacts with formation water to form ethanol, which is the secondary tracer that only follows the water phase. The difference in breakthrough time of two tracers is quantitatively related to the residual oil saturation.

To further interpret the tracer data, the method of moments can be applied as a useful analytical method to analyze residual oil saturation. Maroongroge (1994) analyzed partitioning tracers by using moment analysis method and two-dimensional streamline modelling. Jin et al. (1995) used the method of moments to estimate the mean residence time of tracers and the residual oil saturation. Given the recovered tracer concentration data, the first temporal moment can be used to determine the oil saturation. Since then, a tracer test has become a successful tool for reservoir description and characterization, such

as determining swept pore volume, delineating fluid preferential path in reservoir (Robinson et al., 1988; Tang and Harker, 1991; Asakawa, 2005).

Tracer tests in reservoir characterization has proven itself to be an effective diagnostics tool. Sustained interest in optimizing production from hydraulic fracturing in the recent past has motivated the use of tracer technology to trace the movements of fracture fluid and proppants in unconventional fractured reservoirs. To this end, some novel tracer technologies emerged to provide better understanding of hydraulic fracture characteristics. Palisch et al. (2016) proposed a novel tracer method utilizing gadolinium (Gd) compound to locate proppant in the near wellbore region. Zhang et al. (2018) developed the latest electromagnetic (EM) proppant tracer technique for far field proppant detection.

1.2 Research objectives

Numerous analyses of tracer tests and abundant tracer data can be found in the literature, but only a limited number of publications review the tracer selection and tracer test design. While tracer methods for water tracing in reservoir characterization is well established, the tracer technologies designed for unconventional hydraulic fracturing diagnostics is relatively new. For this reason, one focus of this research is to review the published literature of tracer usage for both traditional and unconventional resource development. Each type of tracer comes with its own strengths and weaknesses. Comparing the pros and cons of different tracer technologies based on commercial availability, previous field applications and economic considerations, we can identify the

most appropriate or suitable tracer method for specific applications. In the end, a novel tracer method is proposed for fracture fluid tracing.

The objectives of this tracer analysis research can be split into the following parts:

- 1) review the usage of tracer in literatures for traditional oilfield development.
- 2) investigate the advantages and disadvantages of novel proppant tracer technology for unconventional oil and gas development.
- 3) evaluate a chemical fluid tracer method of monitoring oil/water movement for hydraulic fracture diagnostics.
- 4) introduce a novel fluid tracer approach to ‘tag’ and monitor hydraulic fracturing fluid.

1.3 Chapter Layout

Chapter 2 presents a literature review on common tracer usage for traditional oil and gas development. The criteria for a substance to be used as a tracer is that it should be distinct from other substances naturally occurring in the environment; non-toxic, environmentally friendly; inert / physically and chemically stable; cost effective, etc. The substances commonly used as tracers can be grouped into following types: dye tracers, radioactive tracers, gas tracer, alcohols, anionic and cationic tracers (Zemel, 1996; Cheung et. al., 1999).

Chapter 3 discusses some newly emerging proppant tracer technology for hydraulic fracture evaluation. It investigates the unique approaches applied in different novel tracer techniques and introduces methods to interpret the results. Radioactive (RA)

proppant tracer and gadolinium (Gd) proppant tracer can be used for near-well proppant detection while electromagnetic (EM) proppant tracer can be used for far-field proppant detection in the fracture (Bartuska et. al, 2012; Palisch et. al., 2016; Zhang et. al., 2018). Logging techniques are required to locate proppant in the near wellbore region. Spectral gamma ray log should be run to detect RA tracers and pulsed neutron log is run to locate Gd tracers. These two types of proppant tracer technology are limited by the depth of investigation of the logging tool, which typically ranges from 18 to 24 inches into the formation. For EM tracers, electrically conductive proppants are used and detected by measuring the electric- and magnetic-fields both before and after pumping the proppants, thus giving information about proppants distribution in far-field fractures (up to 175 ft into the formation).

Chapter 4 introduces the use of chemical fluid tracer injection. This chemical tracer technology can be used to ‘tag’ water, oil and gas within fractures. Chemical tracers are soluble in one specific target phase and travel with the carrier fluid (King and Leonard, 2011; Catlett et al., 2013; Goswick and LaRue, 2014). Both water tracers and oil tracers are pumped with fracture fluid. Water tracers follow the water phase while oil tracers partition into the oil phase upon contact. For a chemical tracer test, unique water and oil tracers can be injected to tag each single stage in the fractured well and monitor tracer production. By collecting flowback fluid samples, the production profile can be evaluated from single well tracer test and fracture communication can be identified from inter-well tracer test (Li et al., 2016). Combined with pressure data and production data, tracer

response curves can be analyzed to investigate stage inflow contribution, fracture fluid recovery, tracer mean residence time and swept pore volume.

Chapter 5 proposes a novel fluid tracer approach of utilizing chemicals with high neutron capture cross-section (Σ) to ‘tag’ and monitor hydraulic fracturing fluid. Two fracture fluid tracing programs have been designed in support of tracer monitoring.

CHAPTER 2

TRADITIONAL OILFIELD TRACER

2.1 Introduction

Water-phase tracer has been used in the oilfield as a powerful diagnostic and measurement tool for many years. With the continuous advancements of secondary and tertiary oil recovery technologies, tracers can be applied in more applications for different research objectives. Therefore, the requirements for oilfield tracer should be considered in more details.

The use of water-phase tracer technology in inter-well tracer tests can provide reservoir engineers with direct evidence that the injected fluid has flowed from injection wells to production wells or between two observation wells, clearly indicating fluid flow paths and connectivity of the target reservoir.

For waterflood projects, water is injected into the reservoir formation to displace residual oil. When a tracer test method is used for waterflood projects, a water tracer slug is usually injected during the water injection process, and the tracer serves as a stable marker of the injected water. After injection into the formation, the tracer is transported conservatively with the water phase. The water tracer can be detected by collecting the samples of produced water. The concentration of the recovered tracer can be determined through either on-site or off-site analysis depending on the interpretation method and instruments used for a certain type of tracer.

If the oil reservoir is considered to be a homogeneous single layer, convection and diffusion will cause the output concentration of the tracer gradually increase towards a maximum concentration. Then the concentration will gradually decrease, and the shape of tracer concentration output curve resembles a single peak curve. However, actual oil reservoirs are often multi-layered and heterogeneous, and the actual tracer response curves have various shapes. The measured tracer response curve is a set of discrete concentration data points sometimes including several peaks, as shown in Figure 2-1.

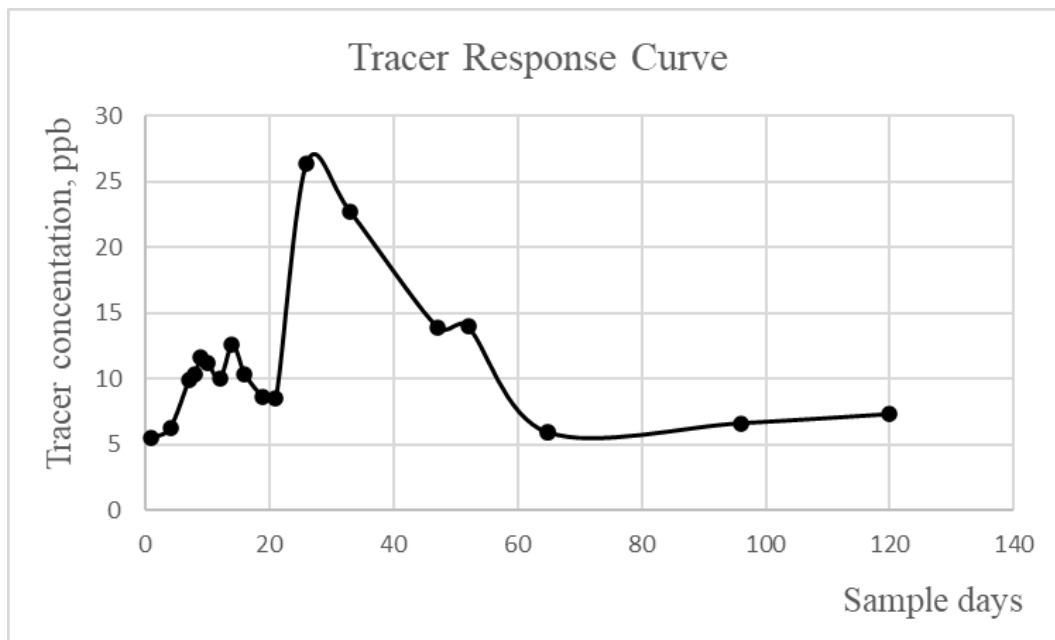


Figure 2-1 Tracer Response Curve

In summary, after the advancement from qualitative analysis to quantitative interpretation, the waterflood tracer technology has matured and is gradually developing

into other new fields (Wanger, 1977). The main research objectives of the previous waterflood tracer tests can be categorized as below:

- Investigate the distribution coefficient of injected fluid and its swept volume;
- Determine the connection between injection and production wells;
- Indicate the distribution characteristics of natural fractures within a rock reservoir;
- Evaluate the advancing speed of the waterflood front;
- Evaluate sweep-improvement treatments;
- Examine the heterogeneity of the reservoir and the distribution of residual oil saturation;
- Identify directional flow trends and delineate reservoir barriers;
- Determine the connectivity of the flow paths within or between layers;
- Describe the physical and chemical properties of rocks and fluids in the reservoir;
- Investigate the change of relative flow velocity with different injection fluids.

2.2 Tracer Selection Criteria

The tracer selection will be dependent on the goals and objectives of the project. Suitable tracers must be validated through laboratory testing. In an effort to make a successful tracer, the substance selected should meet the following requirements:

- Stable and inert chemical properties
- Non-absorbent
- Non-partitioning or partitioning depending upon application
- Good compatibility with the reservoir fluids

- Not naturally present
- Easily detectable
- Low or non-toxic
- Commercially viable
- Reasonable cost
- Stay in the desired phase and follows the ‘tagged’ objects

Using the right tracers for the right applications is crucial to getting flow knowledge and the research target of a project. The misuse and misunderstanding of tracer properties have provided a lot of room for failed project and incomplete data.

The stability of tracers in reservoir as well as after being produced is critical. If there are interactions with the reservoir environment, there will be an impact of the test results due to tracer losses. Stability is the key of success. A number of factors can affect tracer stability, such as chemistry of the injected fluid, and exposure to high temperature. These factors can be problematic for many compounds thought to be good tracers. Exposure to high temperature can significantly impact project outcomes due to a poor thermal stability of tracers. Equally, tracers need to be designed to be phase specific in most cases. If only the oil or gas phase should be traced at one time, it should be a warning sign that tracer is partitioning into a different phase.

2.3 Tracer Types

At present, there are various types of tracer being used in the oil and gas industry and different ways to group those tracers Zemel, 1996 described three groupings of tracers:

natural, radioactive, and chemical. Other classifications are determined by different properties or functions of the tracers. Alternatively, the physical state of the intended target phase (solid, liquid, gas) allows tracers to be grouped into the categories: proppant, liquid and gas. Lastly, the partition coefficients of tracers permits their characterization as partitioning tracers and non-partitioning tracers (also referred to as conservative or passive tracers).

In this section, five types of commonly used tracers in oilfield development are introduced:

- Dye tracers
- Radioactive tracers
- Water-soluble alcohols
- Anionic and cationic tracers
- Gas tracers

Table 2-1 summarizes the tracer groupings described above.

Table 2-1 Different Tracer Groupings

Zemel (1996)	Traget Phase	Partition Coefficient	This Research
Natural Radioactive Chemical	Proppant Liquid Gas	Partitioning Conservative/Passive	Dye tracers Radioactive tracers Water-soluble alcohols Anionic and cationic tracers Gas tracers

2.3.1 Dye Tracers

In the early stage of fluid tracing, dyes were commonly used tracers in the oil industry to track water flow. Examples of the frequently used substances include fluorescent molecules such as Fluorescein, Eosin, and Rhodamine (Lichtenberger, 1991; Zemel, 1996; Khalil and Oliveira, 1999).

Dyes have been used in oilfield tracer applications for years due to a number of advantages: they are inexpensive to purchase, easily handled and detected, and rapidly analyzed.

Dyes are not considered as ideal tracers because of their retention in pore spaces within reservoirs. When using these compounds, tracer retardation is typically observed by absorption onto reservoir rock surface, which results in a lower tracer peak concentration and a delayed tracer breakthrough, as shown in Figure 2-2. A significant delay would be problematic for tracer detection. Regardless, dyes can still be used as satisfactory markers if a quick breakthrough is expected within a fractured rock reservoir where travel times are commonly short, or the project aims to determine only the flow path and direction.

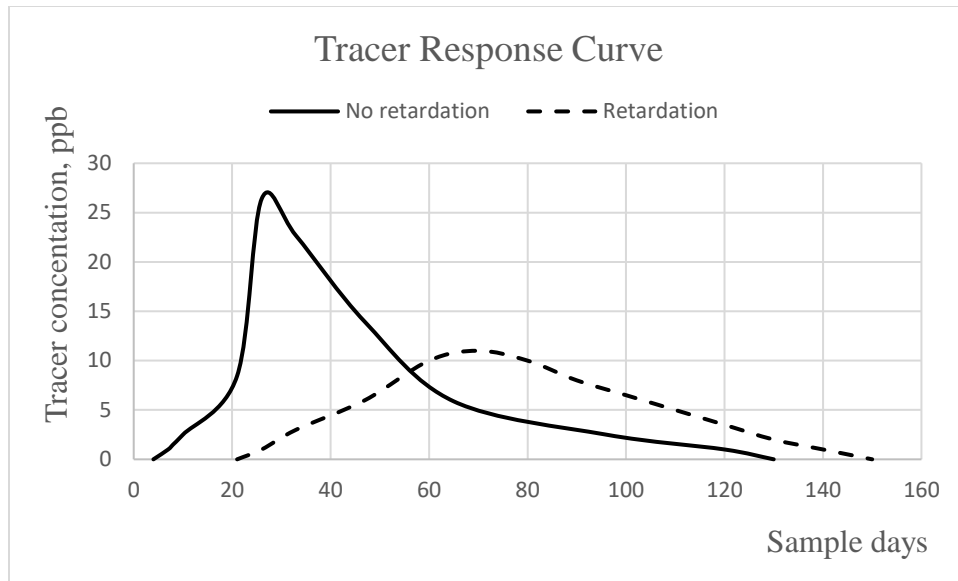


Figure 2-2 Effect of Retardation

Fluorescein is an organic compound that is slightly soluble in water. It is available in powder form as an orange dye with a yellowish-green fluorescence. Melo et al. (2005) successfully used fluorescein as one of the selected tracers for evaluation of polymer injection applications in Brazil. The recovered concentration of fluorescein tracer from multiple producers was analyzed to characterize the reservoir heterogeneities and identify polymer absorption. Khisamov et al. (2009) also reported the use of fluorescein in tracer surveys carried out to investigate the flow characteristics of a carbonate reservoir. A relatively high fluorescein recovery of 82.1% was measured in producing wells. These surveys prove the potential of fluorescein to be used as successfully tracer.

Fluorescein can usually be detected by fluorimetry, a fluorescence spectrophotometry technique. It uses a rather simple instrument called a fluorometer with very low limits of detection. Its portable feature allows for on-site analysis. The limit of

detection is as low as 0.3 ng/mL for fluorescein (Hutchins et al., 1991; Kleimeyer et al., 2001).

Different rhodamine dyes are used as oilfield tracers, including rhodamine WT, rhodamine B and sulfo-rhodamine. The most widely used compound in the oil industry is rhodamine WT. It is a fluorescent and a xanthene dye (Smart et al., 1976). The rhodamine family of dyes is generally non-toxic when used at low concentrations except for rhodamine B. It is reported genotoxic, which is not suitable for water tracer applications (Behrens et al., 2001). Rhodamine dyes fluoresce and therefore can also be detected easily and inexpensively by fluorimetry.

However, there are certain factors affecting the stability of dyes. As described above, they may sometimes be lost during a field test, exhibit absorption onto the formation rock surface, perform less conservatively, or be bio-degraded by bacteria or other organic matters (Lichtenberger, 1991; Cheung et al., 1999; Melo et al., 2005). For instance, Magal et al. (2008) investigated the feasibility of using fluorescein as conservative tracer through laboratory surveys. The surveys confirmed that fluorescein shows strong absorption onto clay minerals and thus it would be a concern if there's significant content of clays within the target zone.

These dyes also suffer from degradation when exposed to light. So before pumping the dye tracers, they should be prepared and stored properly to avoid light exposure. In terms of thermal stability, laboratory test shows that fluorescein and rhodamine WT remain thermally stable up to 200°C. When tested up to 100°C for a month duration,

fluorescein and rhodamine WT exhibit only slight losses due to thermal degradation (Horne, 1985; Adams and Davis, 1991; Rose and Adams, 1994).

2.3.2 Radioactive Tracers

Radioactive salts are popular with a variety of investigations in the petroleum industry. From the early 1940's, radioactive materials have been used in logging techniques for formation evaluation. Radioactive tracers are commonly chemical compounds that emit gamma or beta rays, which can be detected at very low concentrations. Samples can be analyzed using counting techniques, such as liquid scintillation counter for beta-emitting isotopes and NaI(Tl) scintillation radiation detector for gamma ray emitters.

The selection of suitable radioactive tracers to use for specific research purposes depends on multiple factors: commercial availability, cost, solubility, radioactive intensity and half-life. The term half-life is defined as the time required for one-half of the atoms of a radioactive material to decay to a non-radioactive isotope, or the time it takes for the gamma or beta ray emission to decrease by half. Half-lives for different radioactive isotopes vary dramatically from a few microseconds to thousands of years. Radioactive elements for oilfield applications are generally short-lived isotopes. These typically used radioactive substances include Iodine 131 (^{131}I), Tritium (^3H), Cobalt 60 (^{60}Co), Sodium 22 (^{22}Na), and Chlorine 36 (^{36}Cl).

Among all the radioactive elements, tritium (^3H) is generally considered one of the most suitable conservative water tracers. ^3H is a beta emitter with a relatively long half-

life of 12 years. It is available in the form of a water molecule as tritiated water (HTO). HTO can be utilized as an ideal water tracer because its physical and chemical behaviors resemble a normal water molecule, and it poses less radioactive hazard than other tracers in the radioactive species (Wheelet et al., 1985). In terms of detection limit, the response from using HTO shows a wider range between the lowest detectable value and the highest peak concentration compared to other radioactive elements. Additionally, the cost for detection and analysis of HTO tracer is inexpensive (Beier and Sheely, 1988; Hutchins et al., 1991).

Other radioactive materials such as Iodine 131, Cobalt 60 and Chlorine 36 have been used in oilfield applications as conservative water tracers. These tracers have no or low reaction with the reservoir fluids or formation rock. They can also be detected easily at very low concentrations, measured and analyzed inexpensively. But compared with HTO, their gamma ray emissions have a higher hazardous threat to both environment and operational staff. In addition, the half-life of these radioactive elements is relatively short, normally on the order of days. Therefore, the preparation and handling of these radioactive isotopes should be considered more cautiously (Bjornstad, 1991; Bjornstad et al., 1994).

Before the 1990s, radioactive elements were commonly used for tracer applications in oil and gas industry. Kelldorf (1970) utilized several radioactive isotopes, such as Iodine 131, Cobalt 60, Iridium 192, and Scandium 46 for waterflood applications to determine flow paths and well connectivity in Wason San Andres field, West Texas. Stiles et al. (1983) successfully applied HTO for enhanced oil recovery (EOR) application

in a CO₂ tertiary pilot in the Means San Andres field, leading to detection of dual-permeability zones.

With a very low limit of detection and the ease of measurement, they are considered advantageous because only a small injection volume of tracers is required. However, safety and environmental regulations on the use of radioactive tracers must be followed in oilfield investigations. Their inherent radiation hazard indicates extra caution is needed when considering using radioactive tracers. Since the 1990s, Cobalt has not been used widely as a result of safety concerns (Lichtenberger, 1991).

2.3.3 Gas Tracers

Gas tracers are suitable compounds that remains in the gaseous state under reservoir conditions and therefore can be used as a stable indicator of the movement of gas in porous media. It is mainly used in gas injection miscible flooding and steam flooding projects. The most commonly used gas tracers include tritium, sulfur hexafluoride, perfluorocarbons, chlorofluorocarbon (freon) and krypton.

Since the 1960s, radioactive gas tracers began to be used on site in oilfield development. For instance, tritium gas tracers, such as tritiated alkanes, or tritium itself have been widely used in the field because they are relatively inexpensively to detect and do not impact the logging procedure. However, under the safety regulations and requirements for ecological and environmental protection, the use of radioactive gas tracers requires higher levels of care and therefore labor in terms of preparation, handling,

and disposal. Therefore, radioactive gas tracers have been gradually replaced (Zemel, 1996).

From the 1980s, with the advancement in gas tracer technique, chemical gas tracers have gained in popularity. The ideal chemical gas tracer should be insoluble in water, corrosion resistant, chemically stable, and can be detected even at low concentrations. It should also have low reactivity or adsorption with the reservoir fluids and formation rocks. Some gas tracers can also be in liquid state under standard surface condition. After injection they will be in gaseous state under reservoir conditions. Compared with radioactive tracers, chemical gas tracers are a very low-cost tracer tool.

Nowadays, chemical gas tracers have been widely used in oil fields. There are compounds such as perfluorocarbons, sulfur hexafluoride and freons. Chromatographic analysis is often used to detect chemical tracers.

Compounds such as chlorofluorocarbon (freon) are typical chemical gas tracers. The minimum detection volume fraction for freon is around 1.25×10^{-11} (ft³/ft³). Freon will partition into the oil phase and impact the refining process of crude oil. Therefore, the concentration of freon gas tracer should be restricted when they are applied to the field (Liu, 2015). However, the excessive use of freon compounds will destroy the atmospheric ozone layer, and its use is highly regulated. According to the Environmental Protection Agency, freon will no longer be made or imported to the United States, starting January 1st, 2020. As a result, freon is no longer considered an available tracer due to environmental considerations.

Sulfur hexafluoride (SF₆) is a synthetic inert gas. When used as a gas tracer, the minimum detection volume fraction can be as low as 5.0×10^{-14} (ft³/ft³). Pure sulfur hexafluoride is a colorless, odorless, non-toxic and non-flammable gas with stable chemical properties. So it is considered a suitable gas tracer for high temperature downhole environments especially in steam flooding applications. A large number of field practices have proven that sulfur hexafluoride interacts with the oil phase present in the formation. The extent of partitioning into the oil phase is relatively large, which results in a smaller proportion of SF₆ tracer in produced gas. Therefore, it is not recommended to use sulfur hexafluoride as a tracer for wells that have larger spacing or higher oil volume (Liu, 2015).

Perfluorocycloalkane is a kind of cyclic hydrocarbon derivatives, in which the fluorine atoms are used to replace hydrogen atoms in hydrocarbon cycloalkanes, and its general molecular formula is C_xF_{2x}. Among these hydrocarbon derivatives, perfluorocycloalkanes containing six to nine carbon atoms are suitable for use as gas tracers in oilfield. These tracers are in liquid state under surface condition and will be in gaseous state under reservoir conditions. Perfluorocycloalkanes are not naturally occurring substances. Therefore, the background concentration in the formation can be ignored. These compounds have strong thermal stability. They are physically and chemically inert, non-flammable, non-toxic, and their unique ring structure is very sensitive to electron capture detection, leading to a minimum detection volume fraction as low as 10⁻¹⁶ (Begley et al., 1988; Liu, 2015).

2.3.4 Alcohols, Anionic and Cationic Tracers

Alcohols such as methanol, isopropanol, ethanol, and propanol can be used as conservative water tracers for certain applications in oilfield developments. They are inexpensive to purchase and analyze, thermally stable, and highly soluble in water. These alcohols can also be easily detected and analyzed by gas chromatography (GC) or spectrophotometry with a very low limit of detection on the level of $\mu\text{g/mL}$ (Cayias et al., 1990; Lichtenberger, 1991). Therefore, these water-soluble alcohols have drawn petroleum engineers' attention for the use as tracers in oil industry for several decades.

However, according to Hutchins et al. (1991), these alcohols are organic compounds that will interact with formation rock and fluids, and partition into the oil phase. The partitioning effect into oil will increase with a higher molecular weight of the alcohol compound. Additionally, alcohols are likely to be toxic (CH_3OH) and methanol or ethanol may suffer from microbial degradation (Zemel, 1996). In downhole environment, alcohols can be already existing in the formation due to the usage of other chemical additives which may bring in alcohols. As a result, the tracer response curve and interpreted trend of result may be flawed. These drawbacks will limit the application of alcohol tracers to specific research objectives, for example, inter-well tracer tests to determine residual oil saturation.

For anionic and cationic tracers, commonly used substances include Chloride (Cl^-), Bromide (Br^-), Iodide (I^-), Nitrate (NO_3^-) and Lithium (Li^+). The halides, Cl^- and Br^- , are naturally occurring in reservoir environment due to the existence of saline or brine compositions in formation water. They can be used as conservative water tracers in the

form of sodium salt and be purchased at a very low cost. They have proven efficient as conservative tracer with low retention or reactivity with formation fluids or rock (Benson and Bowman, 1994). As natural tracers, they can be applied to determine flowback efficiency and identify the fraction of the waterflood water from originating formation water. Different from Cl^- and Br^- , I^- has a lower natural presence in formation water and a relatively higher cost. These anionic tracers can be detected and analyzed by ionic chromatography (IC) or high performance liquid chromatography (HPLC) technique (Lichtenberger, 1991; Yanagisawa et al., 2002). The detection limit of IC technique is about $1 \mu\text{g/mL}$ for Br^- and I^- . However, background noise in the formation should be taken into accounts for these tracers. They are not applicable in the case of high salinity formations which requires larger quantities of tracer during water injection (Hutchins et al., 1991).

Other tracers, such as Thiocyanate anion (SCN^-), Nitrate anion (NO_3^-) and Lithium cation (Li^+), have also been reported for use as oilfield tracers in the past. But nowadays these compounds are not considered suitable tracers because they are susceptible to chemical instability, retention and bacterial degradation under reservoir conditions (Zemel, 1996).

CHAPTER 3

NOVEL PROPPANT TRACER

3.1 Introduction

Hydraulic fracturing proppant is normally a solid material made of sand or artificial ceramic materials. During a fracturing treatment, proppant is added in fracturing fluid and the proppant laden fluid is injected under high pressure into the formation to create fractures. Proppants are therefore placed inside the induced hydraulic fractures to keep them from closing and to maintain high conductivity.

Tracers, as an effective diagnostic tool in traditional oilfield development, have also greatly interested the industry for use of fracture diagnostics in unconventional oil and gas investigations. A variety of novel proppant tracer techniques have emerged in recent years to investigate the physical property of fractures, including radioactive (RA) proppant tracer, gadolinium (Gd) proppant tracer and electromagnetic (EM) proppant tracer. These techniques allow for proppant detection in the fracture because the tracer materials are embedded inside the proppants. In addition, there have already been successful field practices and promising results that prove their efficiency and reliability as applicable tracer tool for hydraulic fracture diagnostics.

3.2 Radioactive Proppant Tracer

Radioactive proppant (RA) tracer can be used to evaluate stage isolation and proppant distribution along the perforated interval, identify propped fracture

communication between wells, and better understand fracture geometry. The three radioactive isotopes used as taggants inside the proppant grain are Scandium (Sc), Iridium (Ir), and Antimony (Sb). Each of the radioactive isotopes (Sc, Ir, and Sb) releases a gamma ray containing its own energy when it decays, which can be identified as a unique signature. Therefore, these isotopes can be detected by gamma ray spectrometry, which requires running a spectral gamma ray log to locate proppants in the fractures (Scott et al., 2010). RA proppants are commercially available in 40/70 mesh size with a specific gravity of 2.65. The properties of the tracer isotopes are shown in Table 3-1.

Table 3-1 Tracer Properties of Radioactive Isotopes

Isotope	Symbol	Half-life	Particle Size	Specific Gravity
Iridium	Ir-192	74 days		
Scandium	Sc-46	83.8 days	40/70 mesh	2.65
Antimony	Sb-124	60.2 days		

The use of radioactive materials as proppant tracers are normally for near wellbore diagnostics in unconventional oilfield applications. They are limited to a few feet of depth of signal because the gamma rays will be absorbed by dense materials such as steel, cement, reservoir rocks and fluids. As a result, the data interpretation is limited to near wellbore region depending on the depth of investigation of the logging tool, which typically ranges from 18 to 24 inches.

For long horizontal well diagnostics, the three different isotopes are pumped into different stages to create their unique signature response. A field example of spectral gamma ray log result is shown in the Figure 3-1 (Bartuska et al., 2012). RA tracers are normally designed to be injected alternatingly into each different stage along the perforated interval. Different colors correspond to their unique signature from each RA proppant tracer.

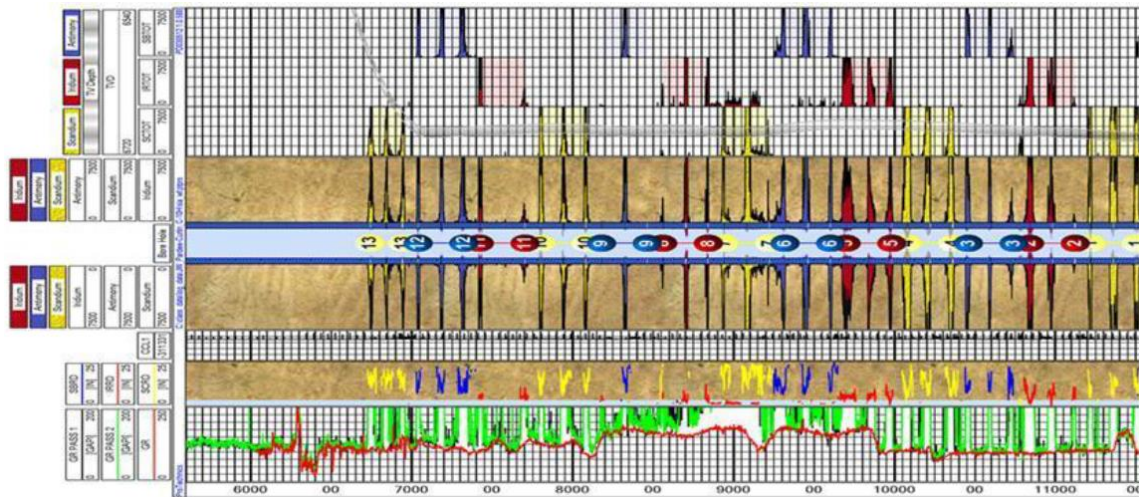


Figure 3-1 Example of spectral gamma ray log result (Red represents Iridium, blue represents Antimony and yellow represents Scandium)

For example, the enlarged sections shown in Figure 3-2 from the spectral gamma ray log interpretation show a comparison of proppant coverage between different design of perforation clusters. The stage on the left indicates only one perforation cluster contained RA proppants while the stage on the right shows signs of RA proppants in all three clusters (Figure 3-2).

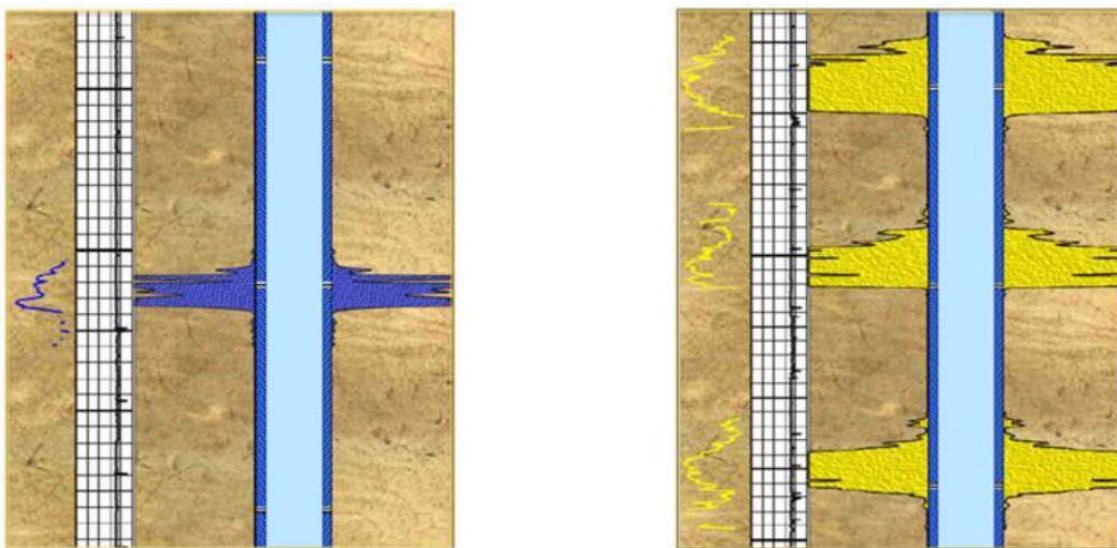


Figure 3-2 Enlarged section 1 (Bartuska et al., 2012)

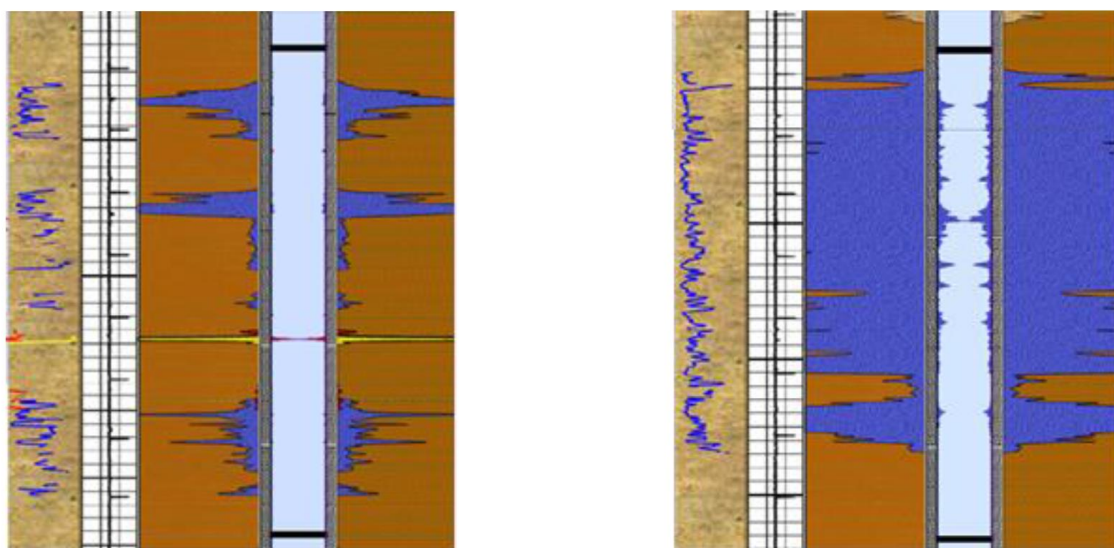


Figure 3-3 Enlarged section 2 (Bartuska et al., 2012)

Another example from Figure 3-3 indicates proppant communication between two neighboring stages. As shown in the wellbore part, the black bars are the boundaries of the stage intervals. RA proppant tracers were injected into the stage on the left while no

tracers were pumped into the stage on the right. However, the spectral gamma ray log results show the tracer signals spreading across the next stage. This proves a high interconnectivity between neighboring stages at this location of the wellbore.

In this way, locating the RA tracers can identify proppant communication between stages, near wellbore proppant placement of the lateral, cluster connectivity and proppant coverage within each cluster. Additionally, RA tracer can also be applied for possible proppant communication between primary and offset wells. Following the fracturing treatment of a primary well, a spectral gamma ray log can be run in adjacent offset well to determine if proppant communication exists within certain well spacing.

While the RA tracer technique provides direct measurement of proppant distribution across a long perforated interval, its applications are still limited by half-life decay of radioactive isotopes and the depth of investigation of logging equipment. Most importantly, main concerns for using RA proppant tracers are related to environmental protection, and health and safety management during the use and disposal.

3.3 Gadolinium Proppant Tracer

Gadolinium (Gd) proppant tracer is a new technique that utilize non-radioactive materials as taggant inside the proppant grain. The unique aspect of gadolinium compounds is that they have very high neutron capture cross-section, which is a desirable property of formation evaluation for petro-physicists. The macroscopic neutron capture cross-section, also referred to as Sigma (Σ), is an important nuclear parameter for borehole

neutron measurement in oil bearing formations. Table 3-2 shows the Sigma of different formation rocks and elements.

Table 3-2 Sigma of Common Formation Rocks and Elements

Substance Name	Macroscopic Capture Cross-section (c.u.)	Element Name	Capture Cross-section (b)
Sandstone ($\Phi=15\%$)	12.4	H	0.33
Limestone ($\Phi=15\%$)	14.8	Na	0.53
Dolomite ($\Phi=15\%$)	12.8	Cl	33
Shale	35 - 55	B	759
Crude Oil	18 - 22	Gd	49000

According to Zhang et al. (2017), gadolinium (III) oxide (Gd_2O_3) was selected as non-radioactive taggant integrated to ceramic proppant grains. Gd_2O_3 is an inorganic compound and the most widely used form of gadolinium materials. Gd tracer has a great advantage over radioactive isotopes because it has no hazards in the handling and injection of tracer during a fracturing treatment, which fully complies with environmental or logistical regulations. Once embedded in the proppant grain, Gd_2O_3 remains physically and chemically stable throughout the tracer application.

To measure formation sigma and detect the presence of Gd proppant tracer, pulsed neutron logging technique is required. Pulsed neutron logging is a formation evaluation method that uses pulsed neutron sources to emit a neutron beam with an energy of 14.1 MeV into the formation with a certain pulse width and repetition period. These fast neutrons interact with the nuclei of the formation element as they inelastically scatter. Fast neutrons rapidly slow down and then become 0.025eV thermal neutrons. During diffusing

of thermal neutrons, capture reaction with the nuclei of the formation elements occurs and gamma rays are emitted. The pulsed neutron logging tool measures the emitted gamma rays and the time required for fast neutrons emitted into rock formations to slow down and finally be captured, which can be used to interpret Sigma (van der Hoeven et al., 2017).

$$N = N_0 e^{-\Sigma v t} \quad (3.1)$$

Where,

N is the neutron population,

v is the velocity of the thermal neutron,

t is time, and Σ is the macroscopic capture cross-section.

At any given time, the captured gamma ray intensity is proportional to the neutron density surrounding the logging instrument. Applying this equation, the measured neutron populations and time can provide quantification of the macroscopic capture cross-section, Sigma.

In unconventional oil and gas development, to locate the Gd proppant tracer, a pulsed neutron log is commonly run both before and after the fracturing treatment. The log before a fracturing job serves as a background survey, which records the data of baseline Sigma in both formation and borehole. After the fracture operation, a pulsed neutron log is run again to measure the increased Sigma in the fractured interval of formation and borehole. Comparing the corresponding log data before and after the fracture job gives an indication of the Gd proppant tracer location along the perforated

interval. An increase in Sigma indicates the presence of Gd proppant in the fractures.

Figure 3-4 shows a field example of pulsed neutron log for a horizontal well.

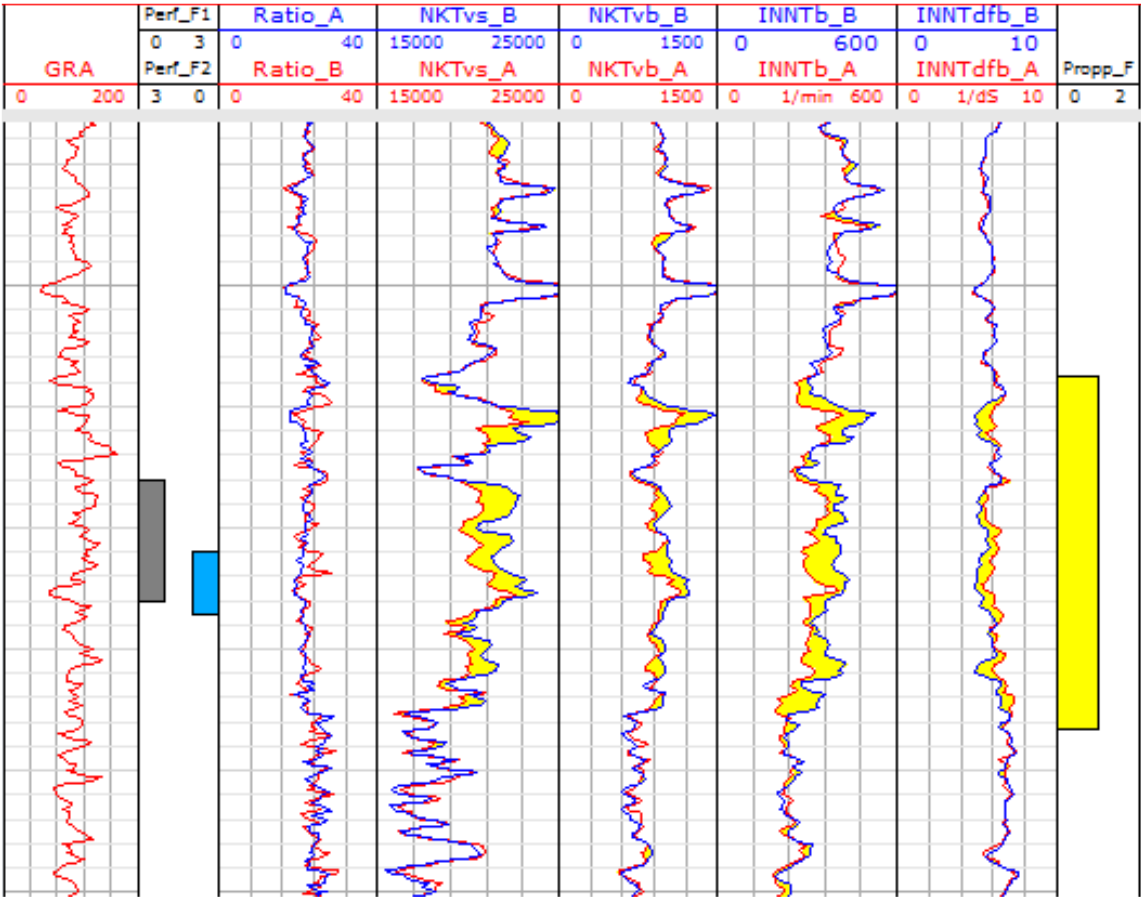


Figure 3-4 Example of Pulsed Neutron Log Result (Zhang and Smith, 2017)

In this example, track 2 (counting from the right side) shows the overlay of pre-fracture vs. post-fracture thermal neutron decay slope log, which is directly related to the formation sigma. The yellow shading on this track of the log data clearly indicates the location of Gd proppants. The amount of yellow shading is indicative of the magnitude of the Gd proppant signals (Zhang and Smith, 2017).

According to Carbo Ceramics, Gd proppant tracer is commercially available as a low-density form of ceramic grains with a 40/70 mesh size. The use of Gd tracer allows for evaluation of perforation efficiency and detection of proppant location in near wellbore fractures. By running a pulsed neutron log in the adjacent offset well, proppant communication between wells can be determined if proppants from the primary well have traveled to the near wellbore region of the offset well. This non-radioactive proppant tracer eliminates the concerns of environmental regulation in terms of preparation, storage, handling, injection, and disposal of radioactive materials. However, the application of Gd proppant tracer is also limited to the depth of investigation of the logging tool, which is normally within a few feet close to the wellbore depending on different instruments. Compared to the three radioactive isotopes, the Gd proppant tracer is limited in its availability of only one unique material. Therefore, for long horizontal well with multiple stages, it cannot create unique tracer signature for individual stage to determine proppant communication between neighboring stages (Zhang et al., 2017; Zhang et al., 2018).

3.4 Electromagnetic Proppant Tracer

Most recently, a novel tracer technology for far-field proppant detection has greatly interested the oil industry. The two previously described tracer methods, RA tracer and Gd tracer, require logging technique in their application. Therefore, the availability of these two proppant tracers is limited by depth of investigation of the logging tool, typically ranging from 18 to 24 inches. For electromagnetic (EM) proppant tracer, it allows for determination of proppant location in the far-field of the fractured well.

Different from RA or Gd proppant tracer which the taggants are integrated inside the proppant grain, EM tracer method put the taggants on the proppant grain surface. This is accomplished by placing a metallic coating on a low-density ceramic proppant grain. As a result, the specialty detectable proppant is made highly electrically conductive. Additionally, the stability under reservoir condition, flow characteristic, and strength of the synthetic EM tracer satisfy the need of a suitable proppant.

A high contrast in electrical conductivity between the EM proppant tracers and other substances in surrounding environment makes detection possible. The detection procedure involves having a combination of two different techniques: a surface array of multi-component receivers for magnetic and electric field sensing and a downhole source tool for electrical current injection.



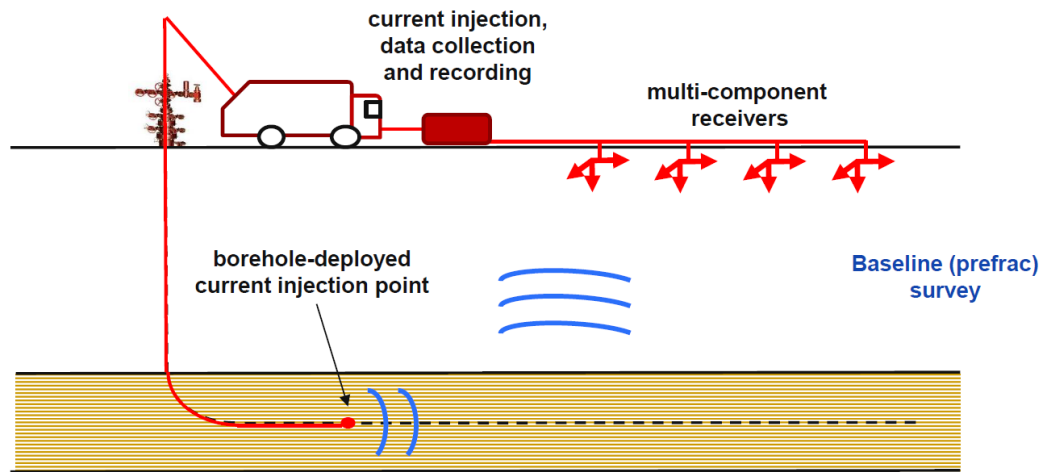
Figure 3-5- Surface array of multi-component receivers, including magnetic and electric field sensors (Palisch et al., 2016).



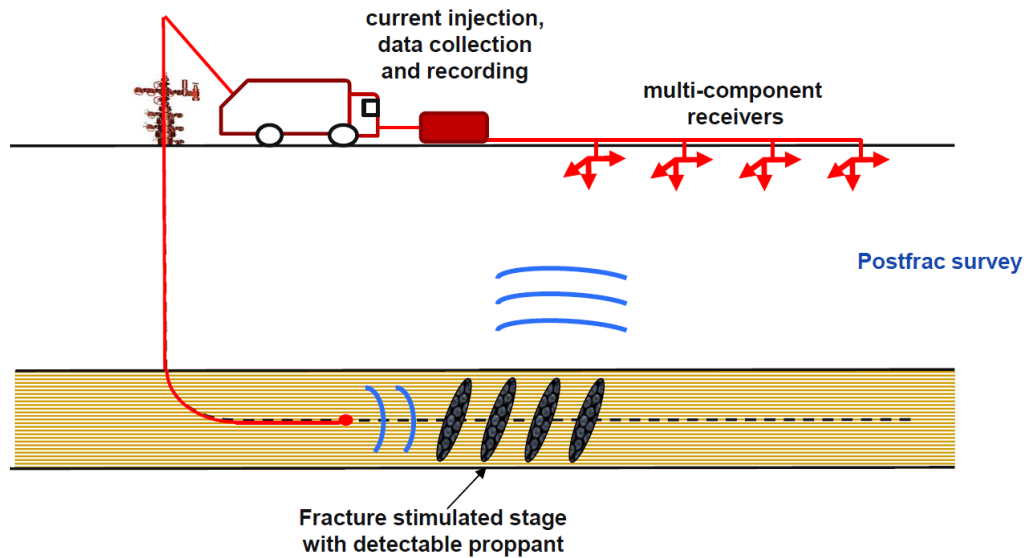
Figure 3-6 A downhole electrical current injection tool (Palisch et al., 2016).

Connected to an electric-line unit, the downhole source tool of electric current is placed above the perforations along the wellbore. Therefore, electric current can be injected as close as possible to the induced fractures. The high electrical current, at least 10 amps, is conveyed through the steel casing and transmitted to the electrically conductive EM proppants inside fractures. A surface receiver array consists of multiple sensors and it allows for an electric and magnetic field be detected at surface.

This EM proppant tracer method is made successful by coordinating with standard plug-and-perf operation and deploying high electric current downhole to produce corresponding electric and magnetic fields. These subsurface fields have interactions with the detectable proppants and as a result secondary electric and magnetic fields are created to propagate outward from adjacent wellbore. The electric and magnetic field are sensed by measuring the electrical or magnetic potential difference between two orthogonal sensors on the surface receiver array.



(a)



(b)

Figure 3-7 Field test sequence (Palisch et al., 2017)

Similar to the Gadolinium proppant tracers, for EM method two surveys of measuring EM characteristics should be carried out to yield the best results. Pre-fracture survey provides the baseline EM data of geologic formation and EM native noise before

fracture job and the post-fracture survey shows the difference in EM properties from the proppant laden fractures and surrounding formation. A stronger contrast between the fractures and surrounding formation will be favorable in terms of data acquisition after the fracture job. The EM data difference between the pre-fracture and post-fracture survey will give an indication of the presence of EM proppant tracer within induced fractures.

After EM data was recorded, a 3D finite difference algorithm that solves Maxwell's equations governing EM physics can be applied for numerical simulation (Palisch et al., 2017). The difference in pre-fracture and post-fracture EM data is then inverted and visualized in 3D in a fracture modeling software.

The first field case of EM proppant application was conducted in the Delaware Basin (Palisch et al., 2016). As shown in the figure, the EM data was processed on a grid spacing of 10 meters and the EM proppant location was determined. From this proppant image, the propped fracture height is around 155 ft, and the propped fracture length is approximately 175 ft (Figure 3-8).

As one of the most up-to-date proppant tracer technologies, EM proppant tracer is still under continuous development to be more applicable for oilfield investigations. Although preliminary results were promising, the reliability of EM proppant tracer is limited by the number of successful field applications. Up to now, only a few field cases were reported and published in the literature (Palisch et al., 2016; Palisch et al., 2017; Haustveit et al., 2019; Palisch et al., 2020).

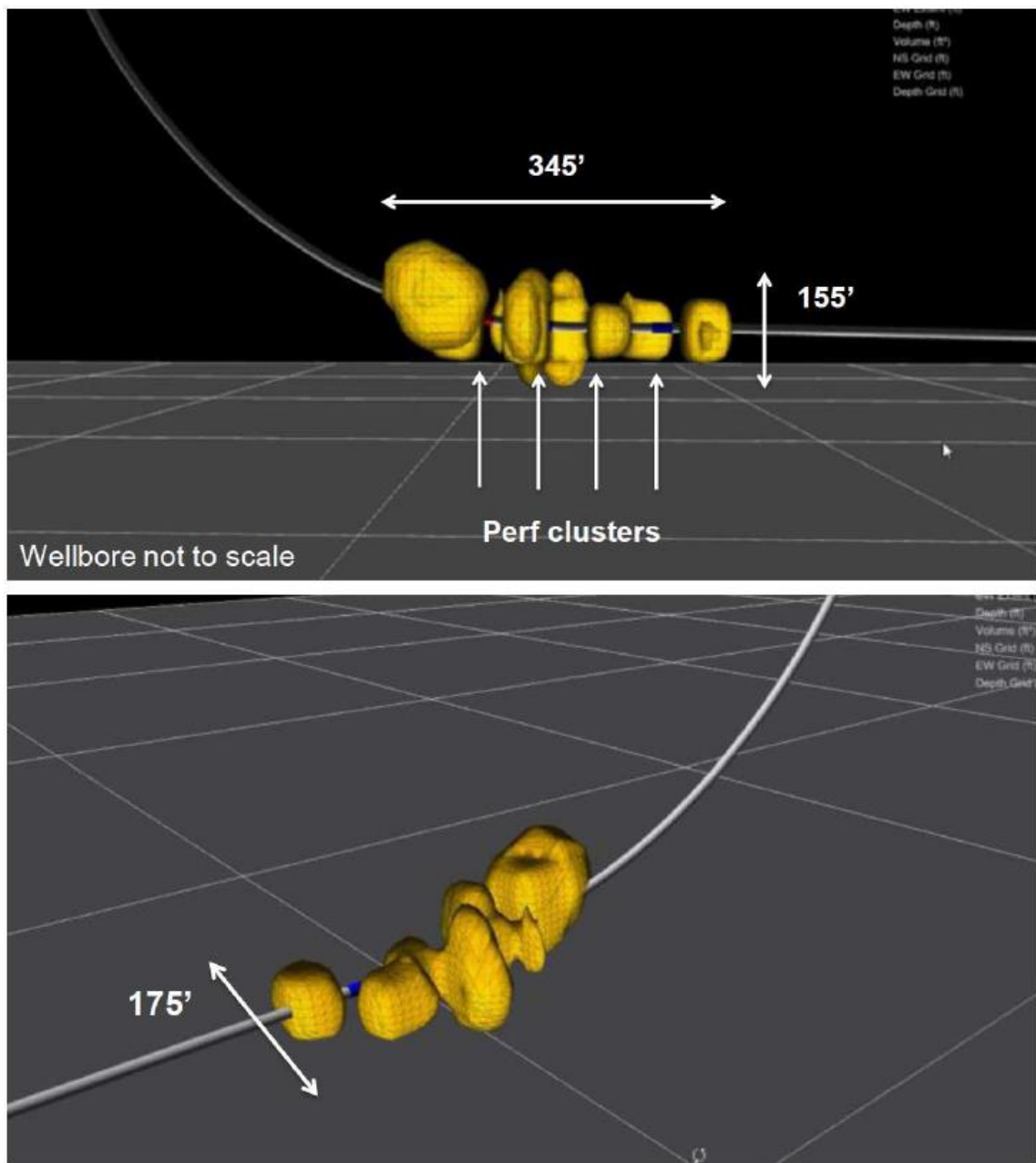


Figure 3-8 Output of EM proppant image (Palisch et al., 2017)

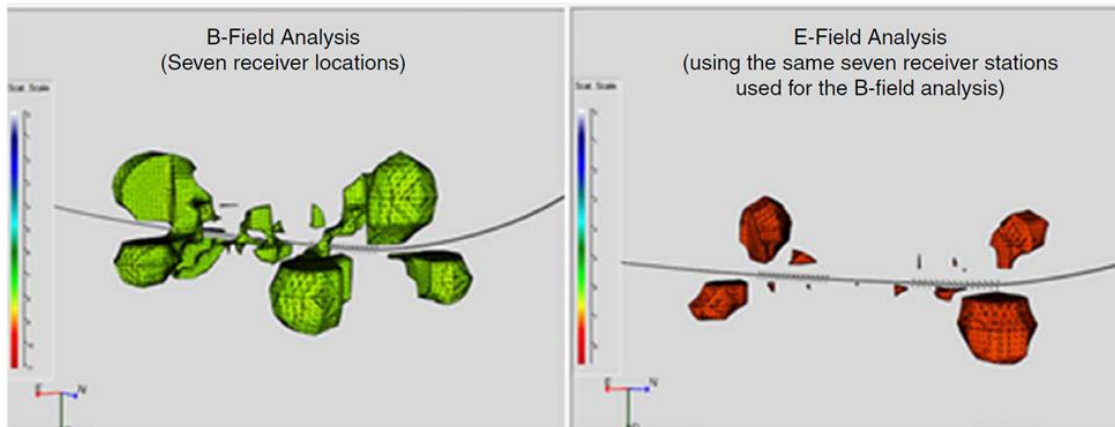


Figure 3-9 Comparison between proppant image results from magnetic field (B-field) and electric field (E-field) (Palisch et al., 2017)

Additionally, comparison between the magnetic and electric field data shows a significant difference in the output result of propped fracture volume (Figure 3-9). The reason for the inconsistency may be the insufficient number of magnetic field sensors. Enhancing numerical techniques for data processing, noise filtering and applying novel algorithms will also help refine the proppant location result. Apart from that, the major disadvantage concerning the usage of the EM proppant is the high cost of proppant itself. Subsequent tests should be designed to further validate this novel technique, including optimizing the receiver array distribution at the surface, increasing electric current amplitude and the electrical conductivity of the EM proppant.

CHAPTER 4

CHEMICAL FLUID TRACER

4.1 Introduction

Chapter 2 covers the traditional fluid tracer usage for oilfield investigations in the past. In this chapter, present-day fluid tracer in hydraulic fracture applications will be discussed. Using the right tracers for the right applications is crucial to getting flow knowledge and the research target of a project. From the 1990s, chemical tracer technology has greatly interested the oil and gas industry due to their unique advantages over traditional tracers (Adams et al., 1992; Bjornstad et al., 2001). For example, chemical fluid tracers present obvious advantages over radioactive tracers: no tool intervention into the well and no radiation hazards.

These oil or water soluble chemical tracers are conservative tracers. Their conservative properties allow for characterizing well communication and quantifying production. They are non-toxic and environment friendly. Water soluble tracers do not interact with the reservoir rock or partition into oil phase. Oil soluble tracers will partition into oil phase once in contact. They travel with the host fluid and are only soluble in the desired phase due to hydrophilic or hydrophobic chemical nature, which makes the tracing of fracture fluid or hydrocarbon in hydraulic fracture possible. This allows for better understanding of the network that is being produced and quantification of the fractional flow.

4.2 Tracer test design and data collection

A chemical tracer test involves injection of unique chemical tracers into fracture fluid and monitoring tracer production. For a long horizontal well with hydraulic fracture stimulation, multiple stages are the essential design to create larger surface area of formation rock in contact with the wellbore. Therefore, considering the multi-stage fracture stimulation that is planned, it is favorable to have a wide range of different tracers to enable the injection of a unique tracer into each stage.

Commonly used water phase tracers are the halogenated boronic acids and fluorinated benzoic acid (FBA). With zero affinity for the hydrocarbon phase, these water phase tracers allow for the tracing of fracturing fluid. They are injected continuously throughout the treatment at a constant concentration (Serres-Piole et al., 2012).

On the other hand, substances that are used as oil phase tracers are halogenated hydrocarbons and bromo-fluorobenzene. These oil phase tracers stay immiscible as a form of emulsion when being injected with fracturing fluid throughout the proppant-laden portion of the treatment. Due to their hydrophobic chemical nature and a strong affinity for the oil phase, oil tracer will be forced out of their emulsion in the fracturing fluid and partition into the oil phase on contact.

According to ProTechnics, there are more than 50 unique tracers commercially available for both water phase and oil phase. With large numbers of unique tracers available, the unique signature from over 50 traced stages can be provided.

Sampling strategies should always be challenged to ensure that they satisfy the requirements of intended research objectives. Chemical fluid tracers can be used for long-term production profiling if designed carefully. Higher sampling frequency at the beginning of production is often required. It is better to collect more samples early on as not to miss important data points or miss a critical flow channel. A common mistake is not collecting enough samples. In the event there is a discrepancy from expectations when the well is placed on production, more samples can be analyzed for comparison. Also, with more available collected samples, simply skipping those that are not needed can create a huge saving for the project. Further refinement to the sampling strategies can be made as tracer concentration data presents itself.

Nowadays advanced analysis techniques are used to measure the tracer concentration from the collected sample. Typically, high performance liquid chromatography (HPLC) or gas chromatography (GC) can be applied to carry out tracer analysis. Individual components within a flowback sample can be chromatographically separated and then analyzed using primarily mass spectrometry. With the recent advancement, mass spectrometry technique allows for molecule to be divided into one or two pieces or even further. And now they can be detected at very low limit of detection, which is in the ranges from parts per billion (PPB) to parts per trillion (PPT) level (Banerjee et al., 2020).

Utilizing oil or water soluble tracer to monitor fluid movement can help evaluate the swept pore volume and complexity of flow in unconventional reservoir. These phase specific chemical tracers now shed light on individual phase production of oil, water and

gas. The lower limits of quantification, non-hazardous nature, and quantitative capabilities have changed the oil and gas industry and how it measures production, gains efficiency and speeds technology development.

4.3 Analysis Methods

The ability to capture useful tracer data is often linked to the analytical capabilities of what is being measured. The misunderstanding of tracer properties will result in failed project and incomplete data.

Sometimes raw data from chemical tracer is acquired but not understood. If the tracer analysis depends on recovered concentration file (PPB) alone, it does not take produced volume and injected tracer mass into account. This will cause confusion in the tracer interpretation. A misleading trend in production can have significant impact on the interpretation.

Stage 2	Stage 2a	Stage 3	Stage 4	Stage 5	Stage 5a	Stage b	Stage 6	Stage 6a	Stage 7
IWT 100 ppb	IWT 1100 ppb	IWT 1800 ppb	IWT 2000 ppb	IWT 2200 ppb	IWT 1300 ppb	IWT 2400 ppb	IWT 1700 ppb	IWT 2000 ppb	IWT 2100 ppb
11	5	58	1	37	7	6	237	40	685
27	6	71	4	1	9	11	21	25	10
11	4	66	12	27	227	380	190	180	5
14	5	70	13	22	198	358	192	197	7
12	6	34	15	30	193	376	181	166	5
19	17	30	54	62	224	242	80	70	4
65	75	43	166	116	242	180	68	58	0
40	41	36	121	105	248	189	72	64	3
39	40	50	128	164	164	216	97	82	0
38	34	59	133	174	149	174	87	71	0
39	33	29	139	179	105	152	60	52	0
28	33	41	149	183	121	121	41	38	0
44	41	33	157	211	131	105	38	35	0

Figure 4-1 Tracer concentration raw data (Asadi et al., 2008)

When evaluating the mass recovery and taking volumes into account, relative stage or segments, phase, and production trends can be established to quantify the production from different stages or segments, inter-well fracture communication, primary and offset well relationships. Normalized tracer mass percentages and production data are required to interpret the production profile or communication over time.

If concentration data of a certain tracer is given at a sampling time, the recovered tracer mass can be determined knowing the density of produced fluid and the cumulative produced volume over sampling period (Equation 4.1).

$$m = \rho \int_0^T q_p C dt \quad (4.1)$$

where,

q_p is the production rate,

C is the measured concentration of tracer,

m is the recovered tracer mass,

ρ is the density of produced fluid.

Mass percent calculation example of water phase tracer:

Volume of produced water, $V_w = 1000$ bbl

Density of water, $\rho_w = 1 \frac{\text{g}}{\text{mL}}$

Concentration, $C = 100$ ppb = $100 \frac{\mu\text{g tracer}}{\text{kg water}}$

Recovered tracer mass, $m = 1.6 \times 10^{-4} \cdot C_1 \cdot \rho_w \cdot V_w = 16$ g

Mass percent recovery = m/M

where,

M is the total injected tracer mass,

The mass recovery of tracer helps to deliver the flow knowledge of a stimulation project. With the mass information, tracer data can be used to analyze flow patterns, quantify zonal contribution, examine reservoir capacity, and determine fracture complexity. Summation of tracer producing from a stage over time reveals overall stage contribution and single stage flow contribution trends.

Comparison between each unique tracer mass recovered allows fractional flow from each stage or segment to be measured. If the exact location of a tracer injected is known, production from that location can be confirmed. This is based on the assumption that the tracer mass percent recovery will be directly proportional to the flowback fraction of produced fluid coming from the position tracer was put in.

When water or oil phase tracers are injected in a known location, the amount of tracer flowing back to the surface from each stage within a well will show proportional behavior to the water or oil volume produced from that stage. Putting a unique tracer in the stage means that the tracer is just tagging what is being produced in that stage. Essentially, these phase specific tracers are measuring the fraction of flowback water or removable oil from that stage or section to wellbore.

Depending on the tracer availability and scope of the research project, single well tracer test can be designed by matching the number of unique tracers and total amount of stages or segments. Best case scenario is to have unique tracer injected into each stage to provide higher resolution. If there are more wells or more stages in the project design, chemical tracer test will be limited by the number of available unique tracers. In this case, the neighboring stages can be grouped into one segment and unique tracers are pumped

into each segment. As shown in Table 4-1, for Well A each unique tracer is designed to be injected into each stage. In Well B, two stages are grouped into one segment with one unique tracer. Therefore, more stages or more wells are covered in the tracer test.

Table 4-1 Comparison between tracer test design

Heel		Well A						Toe
Stage 8	Stage 7	Stage 6	Stage 5	Stage 4	Stage 3	Stage 2	Stage 1	
CFT 8	CFT 7	CFT 6	CFT 5	CFT 4	CFT 3	CFT 2	CFT 1	
OFT 8	OFT 7	OFT 6	OFT 5	OFT 4	OFT 3	OFT 2	OFT 1	

Heel		Well B						Toe
Stage 8	Stage 7	Stage 6	Stage 5	Stage 4	Stage 3	Stage 2	Stage 1	
Segment 4		Segment 3		Segment 2		Segment 1		
CFT 4		CFT 3		CFT 2		CFT 1		
OFT 4		OFT 3		OFT 2		OFT 1		

Similar to the traditional tracer tests, chemical tracer can also be used for single well tracer test and inter-well tracer tests. If there are adjacent offset wells, the extent of hydraulic fracture communication can be determined from inter-well tracer test. Putting unique tracers into each offset well will be able to differentiate recovered tracer and determine production communications. Figure 4-2 shows the fracture communications between offset wells from water phase tracer results.

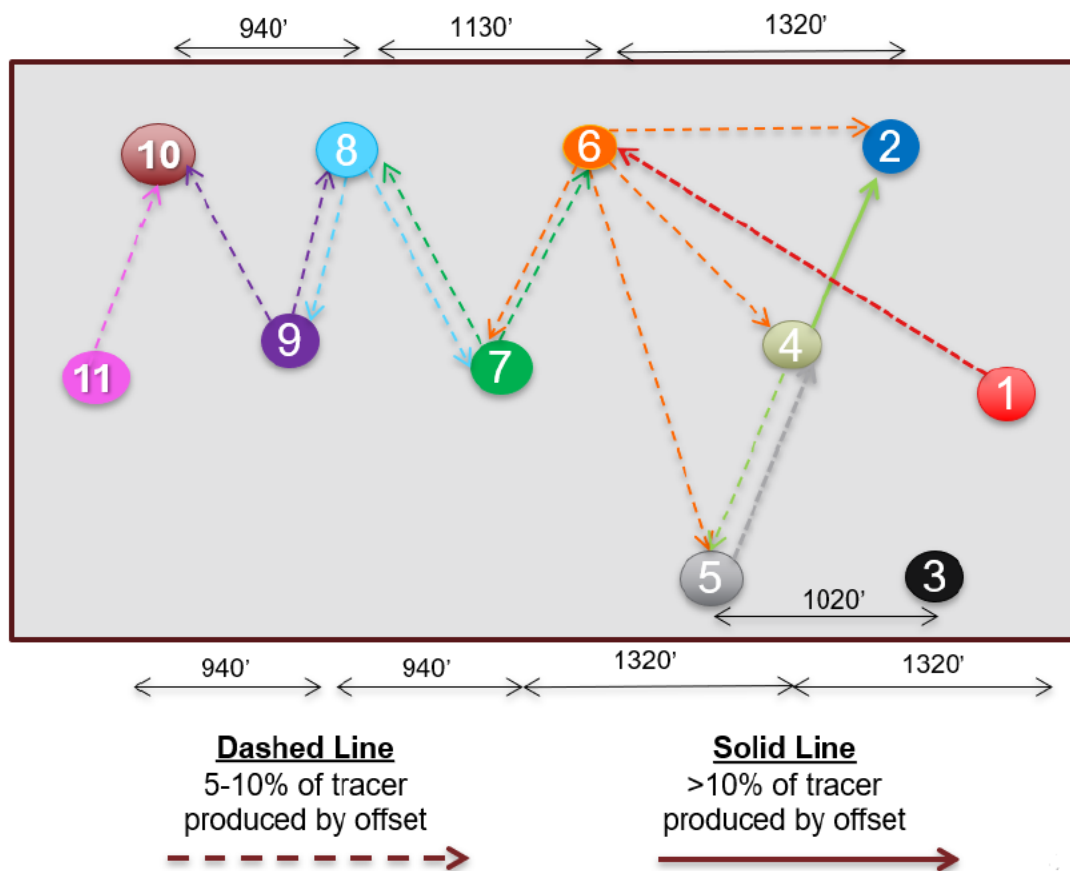


Figure 4-2 Communication summary of inter-well tracer test (Banerjee et al., 2020)

CHAPTER 5

GADOLINIUM FLUID TRACER

5.1 Introduction

In chapter 3, rare earth element gadolinium (Gd) is discussed as a suitable tracer material for proppant tracing. The previous study (Zhang and Smith, 2017) based their criteria for selection on gadolinium (III) oxide (Gd_2O_3) as non-radioactive taggant integrated to ceramic proppant grains.

In this chapter, a novel fluid tracer method is proposed to locate the distribution of fracture fluid near the wellbore. Extremely high capture cross-section (Σ) elements, such as boron (B) and gadolinium (Gd), are most capable of capturing thermal neutrons in the formation. Therefore, water soluble form of chemical tracers containing these two elements will be of great potential. When a certain amount of these neutron tracers penetrates the formation, it will change the macroscopic capture cross-section of formation significantly.

5.2 Tracer Selection and Analysis Method

Two tracers appropriate for the fracture fluid tracer test are gadolinium chloride ($GdCl_3$) and borax ($Na_2B_4O_7$). Both chemical compounds are water soluble and can be used as conservative water tracer. When injected downhole, they can both be detected by running a pulsed neutron log. This is the same logging technique as the gadolinium proppant tracer, and more details about pulsed neutron logging are introduced in Chapter

3. However, gadolinium has an extremely high neutron capture cross-section (Σ) of 49,000 barns among other rare earth elements, which is 65 times higher than the Σ of boron and more than 1,000 times higher than the Σ of chloride. In order to achieve the same Σ difference when tracers are injected into formation, a much larger quantity of borax ($\text{Na}_2\text{B}_4\text{O}_7$) is required compare to gadolinium chloride (GdCl_3). Therefore, considering the tracer preparation, storage, and operational efforts, GdCl_3 is selected as the more appropriate fracture fluid tracer in terms of the ease of handling.

Gadolinium is placed in a water-soluble form by dissolving GdCl_3 in fracturing fluid to tag and monitor its movement. GdCl_3 is a hygroscopic solid (Figure 5-1). It should be stored under a desiccated condition at room temperature. The solubility in water is 94.65g/100mL at 25°C (Saeger and Spedding, 1960).

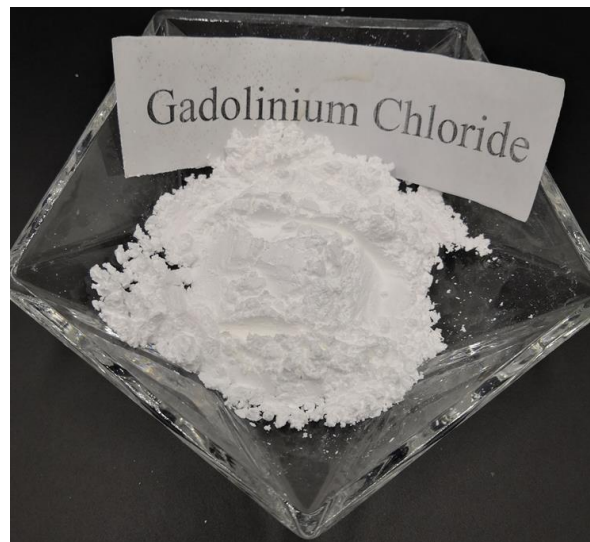


Figure 5-1 GdCl_3 at room temperature

Table 5-1 Chemical properties of GdCl₃

Molecular Weight	Storage	CAS Number	Solubility in Water
263.61	Desiccate	10138-52-0	94.65 g/100mL, 25°C

Fracturing fluid containing GdCl₃ solution can be detected by running a pulsed neutron log. The interpretation procedure requires running pulsed neutron logging before and after the injection of fracture fluid to reflect the change of Σ in the formation, which is the same detection method as the Gd proppant tracers. Pre-fracture pulsed neutron log provides the baseline data of formation Σ . There will be a high Σ contrast between the matrix and induced fractures containing GdCl₃ tracer. After the post-fracture log is recorded, any differences in Σ will be indicative of the presence of fracture fluid.

The macroscopic cross section Σ can be calculated for a mixture of materials or a solution using the atomic density of each component. The macroscopic capture cross-section of GdCl₃ solution is calculated by:

$$c_i = \frac{\rho N_A}{M_i} \quad (5.1)$$

$$\Sigma = \sum_{i=1}^n c_i \sigma_i \quad (5.2)$$

where,

n is n kinds of atoms in the GdCl₃ solution,

Σ is the macroscopic cross-section of the GdCl₃ solution,

c_i is the numbers of i atom in 1cm³ GdCl₃ solution,

σ_i is the atomic neutron capture cross-section of 1 atom,

ρ is the material density,

M_i is the molecular weight of the compound.

Example of calculating the macroscopic capture cross-section of 1,000 parts per million (ppm) GdCl_3 solution:

The macroscopic cross-section of Chloride (Cl) is too small and can be ignored, Equation 5.2 becomes:

$$\Sigma = \Sigma_{Gd} = c_{Gd} \sigma_{Gd} \quad (5.3)$$

The molecular weight fraction of Gd in GdCl_3 is given by:

$$\frac{M_{Gd}}{M_{Gd} + 3M_{Cl}} = \frac{157.25}{157.25 + 3 \times 35.45} = 0.5965 \quad (5.4)$$

The density of Gd in 1,000 ppm (0.1%) GdCl_3 solution:

$$\rho = 0.1\% \times 0.5965 \times 1 \frac{\text{g}}{\text{cm}^3} = 5.965 \times 10^{-4} \frac{\text{g}}{\text{cm}^3} \quad (5.5)$$

From Equation 5.1:

$$c_{Gd} = \frac{\rho N_A}{M_{Gd}} = \frac{5.965 \times 10^{-4} \frac{\text{g}}{\text{cm}^3} \left(6.022 \times 10^{23} \frac{\text{atoms}}{\text{mole}} \right)}{157.25 \frac{\text{g}}{\text{mole}}} = 2.28 \times 10^{18} \frac{\text{atoms}}{\text{cm}^3} \quad (5.6)$$

From Equation 5.2:

$$\begin{aligned}\Sigma_{Gd} &= c_{Gd} \times \sigma_{Gd} = 2.28 \times 10^{18} \frac{\text{atoms}}{\text{cm}^3} (49000 \text{ barns}) \left(\frac{1 \times 10^{-24} \text{ cm}^2}{1 \text{ barn}} \right) \\ &= 0.1119 \text{ cm}^{-1}\end{aligned}\tag{5.7}$$

From Equation 5.3:

$$1 \text{ c. u.} = 10^{-3} \text{ cm}^{-1}\tag{5.8}$$

$$\Sigma = c_{Gd} \sigma_{Gd} = 112 \text{ c.u.}\tag{5.9}$$

where,

Σ is the macroscopic cross-section of the GdCl_3 solution,

Σ_{Gd} is the macroscopic capture cross-section of Gd,

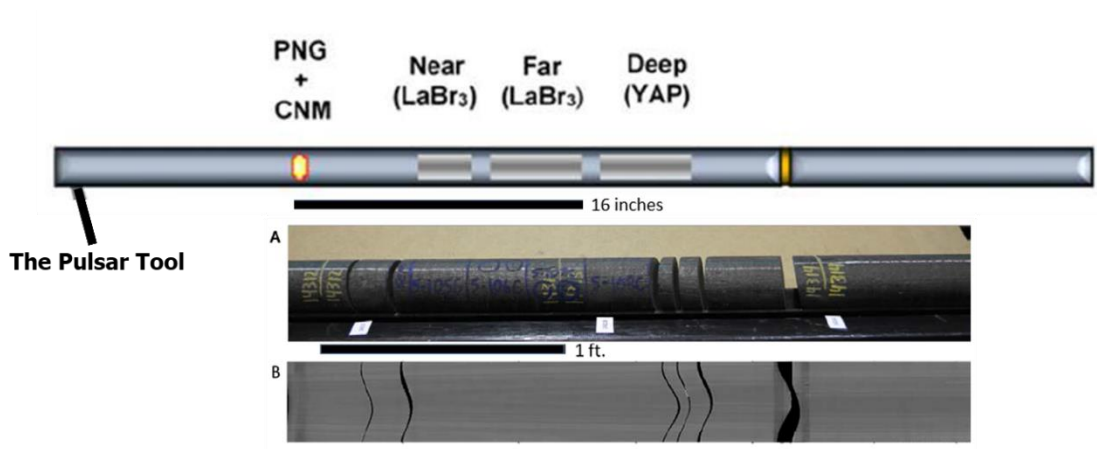
c_{Gd} is the number of Gd atom in 1 cm^3 GdCl_3 solution,

σ_{Gd} is the atomic neutron capture cross-section of Gd atom,

N_A is the Avogadro constant,

M_{Gd} is the molecular weight of Gd.

Details about the pulsed neutron logging technique are discussed in Chapter 3. The neutron source from the logging tool emits fast neutrons into formation. Fast neutrons interact with the elements in formation, eventually slow down and become thermal neutrons and release gamma rays during diffusing.



A: dipping fractures in core. **B:** the same section of CT image as an unwrapped circumferential image.

Figure 5-2 Illustration of Detection Technique (Adapted from Raterman et al., 2017)

As shown in Figure 5-2, the pulsed neutron logging tool averages response over 16 inches along the wellbore. This resolution is defined by the source-detector spacing (the Pulsar Tool from Schlumberger).

From Figure 5-3, comparison between the two pulsed neutron logging results shows the change of Σ in 1150 – 1200 m section of a vertical well doped with boron tracer (Wang et al., 2000). Qualitative evaluation can be made from the logging interpretation result. A strong water produced interval is identified at the depth of 1186 m in this well.

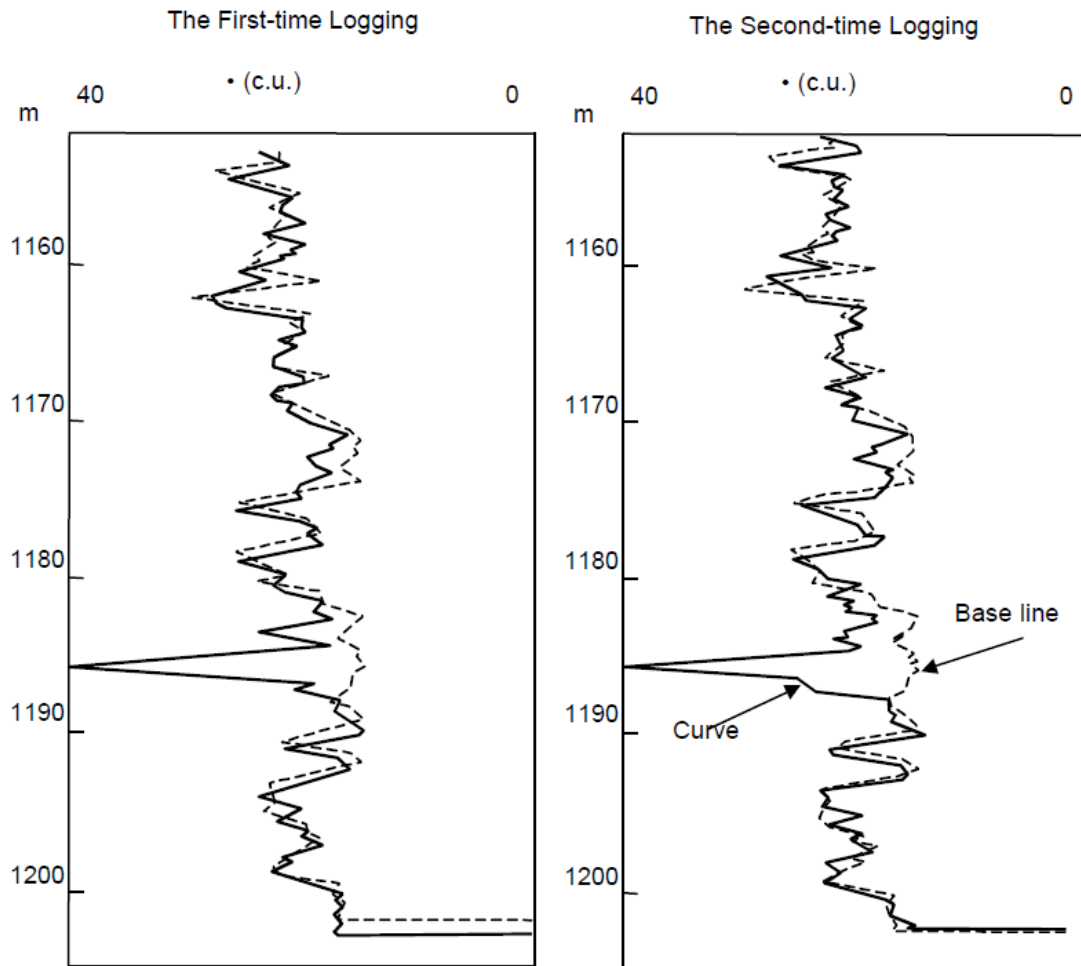


Figure 5-3 Example of Pulsed Neutron Logging Result (Wang et al., 2000)

5.3 Tracer Test Design

From Figure 5-2, CT image shows dipping fractures in core (Rateman et al., 2017). Similarly, after a fracture treatment, there will be narrow induced fractures containing GdCl_3 tracer separated by matrix without tracer. The pulsed neutron log acquired after the injection of GdCl_3 tracer reflects the change of Σ in formation. Considering the volume fraction occupied by fractures, the macroscopic capture cross-

section Σ_a from post-fracture log obeys the volume-weighted average Σ mixing law for fractured formations:

$$\Sigma_a = C_f \Phi \Sigma_{Gdcl_3} + (1 - C_f) \Sigma_t \quad (5.10)$$

$$C_f = \frac{\text{Fracture Volume}}{\text{Volume of Investigation}} = \frac{\text{Fracture Width}}{\text{Resolution of Logging Tool}} \quad (5.11)$$

The Σ change after injecting $GdCl_3$ is expected to be:

$$\Delta \Sigma = \Sigma_a - \Sigma_t = C_f (\Phi \Sigma_{Gdcl_3} - \Sigma_t) \quad (5.12)$$

where,

C_f : the volumetric concentration of fractures,

Φ : porosity in the fractures,

Σ_t : the initial Σ of shale formation before injecting $GdCl_3$, assumes 40 c.u.,

Σ_a : the Σ of shale formation after injecting $GdCl_3$.

A higher contrast in Σ will be favorable in this specific application. The goal of the tracer test is to identify fracturing fluid doped with $GdCl_3$ tracer at a concentration between 2000 to 3000 ppm.

The worst-case scenario:

Considering the fracture properties of 0.1 inch fracture width and 30% fracture porosity:

If there is only 1 fracture within the volume of investigation, using 2,000 ppm GdCl₃ tracer solution,

$$\Sigma_{Gdcl3} = \frac{2000\text{ppm}}{1000\text{ppm}} \times 112 \text{ c. u.} = 224 \text{ c. u.} \quad (5.13)$$

The Σ change is (From Equation 5.6):

$$\Delta\Sigma = C_f(\Phi\Sigma_{Gdcl3} - \Sigma_t) = \frac{0.1}{16} \times (30\% \times 224 - 40) = 0.17 \text{ c.u.} \quad (5.14)$$

Similarly using 3,000 ppm GdCl₃, the Σ change is expected to be 0.38 c.u.

$$\Delta\Sigma = C_f(\Phi\Sigma_{Gdcl3} - \Sigma_t) = \frac{0.1}{16} \times (30\% \times 336 - 40) = 0.38 \text{ c.u.} \quad (5.15)$$

2,000 ppm GdCl ₃	
Fractures	$\Delta\Sigma$ (c.u.)
1	0.17
2	0.34
3	0.51
4	0.68
5	0.85

3,000 ppm GdCl ₃	
Fractures	$\Delta\Sigma$ (c.u.)
1	0.38
2	0.76
3	1.14
4	1.52
5	1.90

For the ***worst-case scenario***

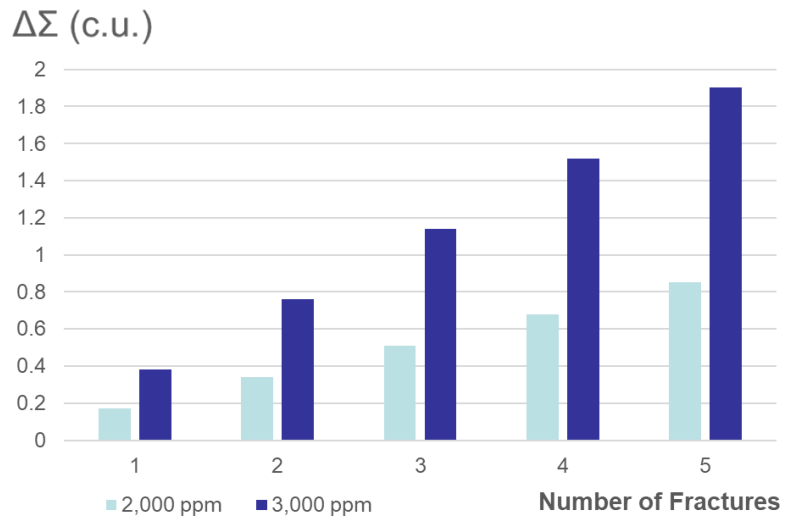


Figure 5-4 Σ change results for the worst-case scenario

The best-case scenario:

Considering dynamic fracture properties of 0.25 inch fracture width and 100% fracture porosity:

If there is only 1 fracture within the volume of investigation,

Using 2,000 ppm GdCl₃ tracer solution, the Σ change is:

$$\Delta\Sigma = C_f(\Phi\Sigma_{GdCl_3} - \Sigma_t) = \frac{0.25}{16} \times (100\% \times 224 - 40) = 2.875 \text{ c.u.} \quad (5.16)$$

Using 3,000 ppm GdCl₃, the Σ change is expected to be 4.625 c.u.

$$\Delta\Sigma = C_f(\Phi\Sigma_{GdCl_3} - \Sigma_t) = \frac{0.25}{16} \times (100\% \times 336 - 40) = 4.625 \text{ c.u.} \quad (5.17)$$

2,000 ppm GdCl ₃	
Fractures	$\Delta\Sigma$ (c.u.)
1	2.875
2	5.75
3	8.63
4	11.5
5	14.38

3,000 ppm GdCl ₃	
Fractures	$\Delta\Sigma$ (c.u.)
1	4.625
2	9.25
3	13.875
4	18.5
5	23.125

For the ***best-case scenario***

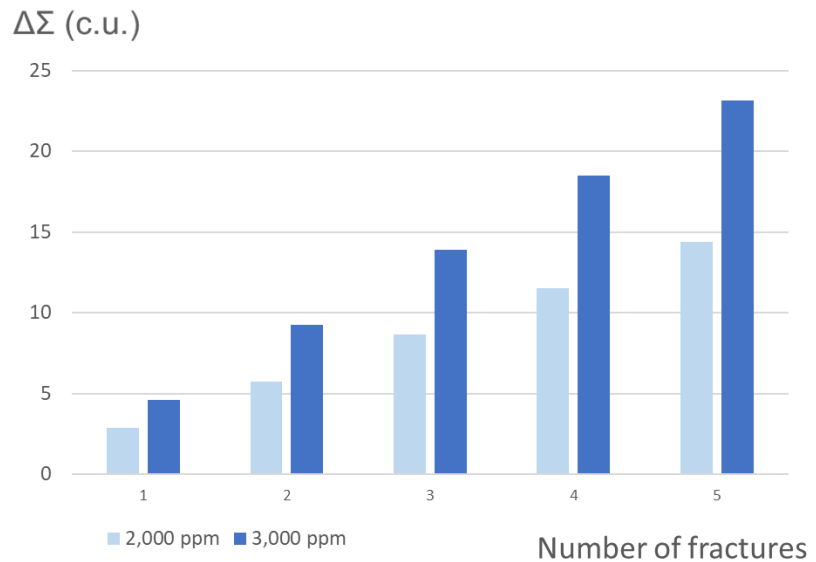


Figure 5-5 Σ change results for the best-case scenario

Assuming 10,000 bbl fracturing fluid is pumped for one stage, GdCl₃ tracer cost per stage is shown in Figure 5-6.

2,000 weight ppm GdCl ₃			3,000 weight ppm GdCl ₃		
Concentration	2.0	g/kg water	Concentration	3.0	g/kg water
	0.701	lb/bbl		1.0515	lb/bbl
Total Frac Fluid	10,000	bbl/stage	Total Frac Fluid	10,000	bbl/stage
Total GdCl ₃	7,010	lb/stage	Total GdCl ₃	10,515	lb/stage
GdCl ₃ Cost	\$7.03	USD/lb	GdCl ₃ Cost	\$7.03	USD/lb
Total Cost per stage	\$49,280	USD	Total Cost per stage	\$73,920	USD

Figure 5-6 GdCl₃ Tracer Cost Per Stage

5.4 Conclusions

Preliminary result shows that gadolinium-based compounds can be used as suitable fracture fluid tracer. They are conservative, chemically stable, and environmentally safe. The injection of gadolinium tracer will significantly enhance the macroscopic capture cross-section in the formation with induced fractures. A relatively low concentration can satisfy the detection requirements.

The pulsed neutron logging output will give a direct measurement of where fracture fluid has propagated to along the wellbore. This novel tracer method proposed can lead to completely new understanding of the conductive fractured region created by hydraulic fracturing.

However, like any other tracer technologies, limitations of utilizing gadolinium-based compounds exist. Compared to a variety of unique chemical fluid tracer, gadolinium tracer cannot be used for multi-stage diagnosis. Detection and monitoring technique

require logging tool intervention in the well. The pulsed neutron logging response is limited to the depth of investigation of the logging tool. Additionally, the cost of tracer materials should also be taken into account during the project planning. As shown in Figure 5-6, the cost of GdCl_3 tracer is relatively high compared to other available tracers.

CHAPTER 6

CONCLUSIONS

From this research, the following conclusions are drawn:

1. Tracers are effective diagnostic and measurement tools for oilfield development.

Numerous traditional tracer tests were conducted successfully across a wide range of applications in the broad context of reservoir characterization to improve oil and gas recovery. Knowing tracer properties and their chemical nature of a wide range of tracers helps identify the most ‘suitable’ tracers for specific research objectives and different categories of oilfield investigations. Environmental and safety considerations such as toxicity and disposal and any regulations or restrictions should also be taken into account associated with the usage of tracers.

2. Advanced oilfield tracer technologies to track both proppants and fluids in hydraulic fracture diagnosis have been developed over the years. Proppant tracer techniques allow for the detection of proppant location in both the near wellbore region and far-field from the wellbore. Chemical tracer technology has evolved to measured things previously thought to be impossible. With a large numbers of unique tracers available, higher tracer signature resolution and further granularity can be provided for production profiling and fracture communication in multi-stage hydraulic fracturing.

3. A novel fluid tracer approach is introduced to tag and locate fracture fluid. Gadolinium-based tracer is selected as an appropriate indicator of fracture fluid. It is capable of significantly increasing the macroscopic capture cross-section at even very low concentration. This new tracer method does not require collecting and analyzing flowback

samples. Instead, the gadolinium tracer is detected by running a pulsed neutron log. Comparison between the pre-fracture and post-fracture logs will be able to reflect the distribution of fracture fluid along the perforated interval.

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