

CALCIUM ACETATE: AN ALTERNATIVE TO GYPSUM FOR IMPROVING BRINE  
IMPACTED SOILS

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**Title**

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IMPROVING BRINE IMPACTED SOILS

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The Supervisory Committee certifies that this *disquisition* complies with North Dakota State University's regulations and meets the accepted standards for the degree of

**MASTER OF SCIENCE**

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## ABSTRACT

With North Dakota being ranked as a leading producer of oil and natural gas in the United States, the possibility of accidental produced water (aka “brine” or “salt water”) spills is a continuous concern. Brine water poses numerous threats to soil properties as it has the potential of causing soil dispersion by increased concentrations of sodium. The goal of this research was to compare the effectiveness of several calcium amendments: calcium acetate, flue gas desulphurization gypsum and pelletized gypsum, on improving the saturated hydraulic conductivity ( $K_s$ ) and removing sodium of three brine impacted soils. Ultimately, increasing rates of calcium acetate had the greatest effect on increasing the  $K_s$  but, in general, increasing rates of any amendment increased the  $K_s$  and removed sodium. A secondary goal was to produce a resource about the origin of brine water in the Williston basin for those affected by or interested in this topic.

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## GENERAL INTRODUCTION

As of 2022, North Dakota is ranked as the third largest producer of oil and natural gas in the United States after Texas and New Mexico (U.S. Energy Information Administration, 2022). In the 1980s, North Dakota adopted horizontal drilling techniques (Helms, 2008), but it wasn't until 2008 that horizontal drilling was used with the addition of fracking to further maximize productivity in North Dakota (Lin et al., 2018). Risks associated with oil and natural gas production include accidental spills of produced water (often referred to as brine or salt water) (Sublette et al., 2005; Guerra et al., 2011; Lauer et al., 2016; Green et al., 2019; Green et al., 2020) which is an especially abundant by-product (Guerra et al., 2011; Bluemle, 2016, p. 299) that's pumped to the surface as an emulsion with crude oil (Bluemle, 2016, p. 299; Thayee Al-Janabi et al., 2019).

Brine, in the Williston Basin, is primarily composed of sodium chloride (De Jong, 1982; Alberta Environment, 2001; Guerra et al., 2011; Pereira et al., 2015; Lauer et al., 2016; Derby et al., 2016; Green et al., 2019; Green et al., 2020) and is an unavoidable by-product of the oil and gas industry. When brine water is spilt across a landscape, it can have many detrimental effects on soil physical and chemical properties (Jury and Weeks, 1978; Barbour and Yang, 1993; Alberta Environment, 2001; Sublette et al., 2005; Lauer et al., 2016; Derby et al., 2016; Green et al., 2019; Green et al., 2020; Wang et al., 2021). Sodium from brine has the potential of causing soils to swell when wetted, which can then eventually lead to dispersion (Shainberg et al., 1982; De Jong, 1982; Barbour and Yang, 1993; Ashworth et al., 1999; Marchuk & Rengasamy, 2011; Rengasamy & Marchuk, 2011; He et al., 2013; Rath & Rousk, 2015; Derby et al., 2016; Wang et al., 2021).

There are multiple ex-situ and in-situ methods aimed to removed sodium from soil, but the purpose of this study was to investigate the effectiveness of several in-situ chemical

amendments on improving brine impacted soils. Gypsum has historically been the most common in-situ chemical amendment used for sodic and brine impacted soils (De Jong, 1982; Jury & Weeks, 1978; Alberta Environment, 2001; Keren & Miyamoto, 2013; Green et al., 2020). Gypsum, when applied with proper drainage equipment and irrigation, is an effective solution for improving brine impacted soils (Ashworth et al., 1999). When gypsum goes into solution it is able to supply enough calcium to displace sodium on soil exchange sites (Shainberg et al., 1982; De Jong, 1982; He et al., 2015; He et al., 2018; Green et al., 2020), but the effectiveness of gypsum as an amendment is limited by its solubility of 2.1-2.6 g L<sup>-1</sup> (Hulett & Allen, 1902; De Jong, 1982). Gypsum, either flue gas or pelletized, is readily accessible, effective under the right conditions and inexpensive, but can be difficult to use in semi-arid environments, like North Dakota, when irrigation is not possible.

Another calcium source that has been used as an amendment for brine impacted soils is calcium nitrate (De Jong, 1982; Ashworth et al., 1999; Franzen et al., 2019). Calcium nitrate has a solubility of nearly 1,300 g L<sup>-1</sup> (Hewlett et al., 2019), is readily accessible and has about the same amount of calcium as gypsum (24.4 g kg<sup>-1</sup> vs 23.2 g kg<sup>-1</sup>, respectively). However, the maximum contaminant level (MCL) of nitrate-N in North Dakota's ground water is 10 mg L<sup>-1</sup> (EPA, 2008). Calcium nitrate is a common fertilizer but the MCL of nitrate-N is a concern when using it as an amendment for brine impacted soils because the rates of application necessary to mobilize sodium are much higher than rates of calcium nitrate applied when it's used as a fertilizer (Hamdi et al., 2015).

With solubility being a concern when using gypsum and groundwater safety being a concern when using calcium nitrate, calcium acetate was hypothesized as a potential amendment for brine-impacted soils. Calcium acetate has a similar amount of calcium as gypsum (22.7 g kg<sup>-1</sup>

vs 23.3 g kg<sup>-1</sup>, respectively) and has a solubility of 347 g L<sup>-1</sup> (Macco Organiques, 2018).

Additionally, there is no literature documenting negative effects that the acetate complex would have on the environment, and, in fact, it is shown to stabilize proteins and act as an available carbon source (Stevenson & Katznelson, 1958; Ostendorf et al., 1993; Wander et al., 1996; Singh and Kishore, 2002). Calcium acetate is prevalent in food and drug production but is relatively expensive (greater than \$10 kg<sup>-1</sup> dependent on various circumstances, however) compared to other calcium sources.

This thesis is organized into three parts with the first chapter being a literature review covering oil production in North Dakota. This literature review gives context and background of the geological processes that lead to oil and natural gas accumulation in the Williston Basin and also dives into drilling operations, modes of transportation, how brine spills occur and the effects of brine on soil, plants and other soil organisms. Lastly, it reviews how brine spills are handled and discusses more in depth the pros and cons of several chemical amendments that are currently used to remediate brine spills and other potential alternative chemical amendments.

The second part of this thesis, chapter 2, is a laboratory study that compared the effectiveness of calcium acetate, flue gas desulphurization gypsum and pelletized gypsum on increasing the K<sub>s</sub> of three brine impacted soils. Residual sodium in post K<sub>s</sub> soils was also used to rank the effectiveness of these amendments on reclaiming brine impacted soils. The last part, an appendix, is written as an extension publication titled: *Origination of Produced Water (Brine) in the Williston Basin*. This work aims to educate readers of the geologic settings around 350 million years ago that led to the accumulation of organic matter in ancient oceans and the geologic processes that converted organic matter to crude oil and why brine water is an inevitable by-product of the oil and natural gas industry.

# **CHAPTER 1. LITERATURE REVIEW OF OIL AND GAS PRODUCTION AND RECLAMATION IN NORTH DAKOTA**

## **North Dakota Oil and Gas Production Context**

Oil and natural gas production in western North Dakota, within the Williston Basin, has become an important industry over the last 10-15 years in what is one of the largest unconventional oilfields in the United States (Lin et al., 2018). North Dakota is ranked as a leading producer of oil and natural gas and as of 2022, North Dakota was ranked as the third largest producer of crude oil only after Texas and New Mexico (U.S. Energy Information Administration, 2022). Production has increased in magnitude from hundreds-of-thousands of barrels of oil and natural gas per day to well over a million barrels of oil and natural gas per day (North Dakota Department of Mineral Resources, 2020; U.S. Energy Information Administration, 2022). The Bakken and Three Forks formations are the main rock units that serve as reservoirs for the oil and natural gas that North Dakota produces. In 2019, which was a peak year for oil and natural gas production, the Bakken formation alone produced an average of 1.4 million barrels of oil per day (U.S. Energy Information Administration, 2022). As oil and natural gas production continues to increase in North Dakota, the risk of accidental spills of produced water (brine) is a growing concern. In 2021, there were about 280 reports of brine related spills which was equivalent to over 50,000 barrels of brine (North Dakota Department of Environmental Quality, 2022). As of June 2022, there have been at least 140 reported brine related spills which equate to just over 16,000 barrels (North Dakota Department of Environmental Quality, 2022).

To begin investigating the impacts that oil and natural gas production has had on North Dakota, it may first be reasonable to discuss the origin of the rock units that hold most of North

Dakota's oil and natural gas. Additionally, it's important to discuss the formation of the oil and natural gas in these rocks. As stated above, the Bakken and Three Forks Formations are the two main rock units that serve as reservoirs for the oil and natural gas that North Dakota produces. The Three Forks Formation is a nearshore, marine deposit composed of interbedded shale, siltstone and dolomite and was deposited during the late Devonian period (Murphy et al., 2009). The Three Forks Formation, at its maximum, has been found to be as thick as 250 feet in McKenzie County, North Dakota (Bluemle, 2016, p. 293). The Bakken Formation directly overlies the Three Forks Formation and is an offshore marine deposit ranging in thickness from 75-150 feet (Bluemle, 2016, p. 293). The Bakken Formation is composed of interbedded shale and siltstone (Murphy et al., 2009) and was deposited in both the late Devonian and early Mississippian Periods (Murphy et al., 2009; Bluemle, 2016, p. 291). Even though the Bakken formation is the most productive of the two rock units, the Bakken and Three Forks Formations are often thought of as being one unit (Bluemle, 2016, p. 293). These two rock units formed as a result of the Kaskaskia transgression which is one of six major high sea level events in Earth's history (Gerhard et al., 1982). As rising sea levels began to invade continental interiors, an abundance of marine deposits, such as shales, limestones and siltstones, were deposited that distinctly mark these events.

The oil and natural gas that developed in the Bakken and Three Forks Formations is a result of the accumulation of decaying plant and animal debris (Hobson and Tiratsoo, 1975, p. 31; Bluemle, 2016, p. 294). The accumulation of this organic material was controlled by rates of sediment deposition in aquatic environments (Tissot and Welte, 1978, p. 55). As sedimentation occurred, dead plant and animal material was buried which prevented scavenging and promoted anaerobic decomposition (Hobson and Tiratsoo, 1975, p. 31). Phytoplankton and zooplankton,

examples being foraminifera and crustaceans, serve as the source for oil and natural gas (Tissot and Welte, 1978, p. 14; Bluemle, 2016, p. 294).

Nutrient rich, warm, shallow and sunny environments allowed both plants and animals to flourish in tropical mid-Paleozoic seas that were covering many parts of what's now the United States (Hobson and Tiratsoo, 1975, p. 14 & 31). As sedimentation continued, oxygen became depleted as pressures and temperatures rose. Under anoxic conditions coupled with the increased pressure and high temperatures, diagenesis of organic material occurred which transformed organic material into a substance called kerogen (Vandenbroucke and Largeau, 2007). Kerogen is an insoluble, sedimentary organic material and can be characterized by a variety of stages and compositions (Vandenbroucke and Largeau, 2007). The transformation of detritus into kerogen is the first step in altering organic material into fossil fuels (Hobson and Tiratsoo, 1975, p. 35 & Tissot and Welte, 1978, p. 123). As heat and pressure continued to build, kerogen then underwent a process called catagenesis, which is a thermal degradation process in which kerogen is converted into the hydrocarbons that are so valuable to us today (Tissot and Welte, 1978, p. 73; Vandenbroucke and Largeau, 2007). Catagenesis is the step before metamorphism of rocks or metagenesis of organic material. At pressures and temperatures in which metagenesis can occur, kerogen is then mineralized and would no longer be considered a petroleum source (Tissot and Welte, 1978, p. 71 & 123; Vandenbroucke and Largeau, 2007).

The Bakken and Three Forks Formations are generally classified as source rocks (Hobson and Tiratsoo, 1975, p. 2), not to be confused with reservoir rocks which are commonly sandstones or carbonates with a high porosity and permeability that are usually subject to vertical drilling operations (Hobson and Tiratsoo, 1975, p. 2-3; Bluemle, 2016, p. 288, 295-296). When oil can freely move within reservoir rocks and collect in concave up areas where rocks are less

permeable, such as the hinge zone of an anticline, horizontal drilling isn't always necessary (Tissot and Welte, 1978, p. 318-319; Hobson and Tiratsoo, 1975, p. 5; Bluemle, 2016, p. 293). For example, the Nesson and Cedar Creek anticlines are well known structures in western North Dakota and have accumulated oil and natural gas at their apices (Bluemle, 2016, p. 293). Source rocks, such as shales, have a relatively low permeability, meaning that the pore spaces in these rocks are poorly connected (Hobson and Tiratsoo, 1975, p. 3; Bluemle, 2016, p. 295). This characteristic traps oil and natural gas between rock layers and prevents them from accumulating elsewhere, making them accessible via horizontal drilling (Bluemle, 2016, p. 288). After horizontal drilling techniques were improved during the early 1980s, oil producers in North Dakota quickly adopted these methods and applied them throughout the state's oilfields (Helms, 2008). Even with horizontal drilling gaining popularity, it wasn't until 2008 that the first horizontal well used fracking to further maximize productivity by stimulating oil and gas flow through poorly connected reservoirs (Lin et al., 2018).

### **Consequences of Produced Water (Brine)**

A major concern associated with oil and natural gas production is the by-product of produced water, also known as brine (Sublette et al., 2005; Guerra et al., 2011; Lauer et al., 2016; Meehan et al., 2017; Green et al., 2019; Green et al., 2020). The most abundant constituent in brine within the Williston Basin is sodium chloride (De Jong, 1982; Alberta Environment, 2001; Guerra et al., 2011; Pereira et al., 2015; Lauer et al., 2016; Derby et al., 2016; Green et al., 2019; Green et al., 2020), but calcium and magnesium chlorides, sulphates and bicarbonates are also common in brine solutions (Guerra et al., 2011; Derby et al., 2016; Yassin et al., 2019). Sodium chloride is also the most abundant component of sea water (Tissot and Welte, 1987, p. 27), which then explains the high concentration of sodium chloride in brine solutions associated



with oil and natural gas production. Since oil and natural gas form in salty marine deposits, crude oil is pumped to the surface typically as an emulsion of oil and brine water (Bluemle, 2016, p. 299; Thayee Al-Janabi et al., 2019). Brine samples have total dissolved solid (TDS) measurements that often exceed  $300 \text{ g L}^{-1}$  (Lauer et al., 2016; Meehan et al., 2017) and electrical conductivity (EC) measurements that are commonly greater than  $200 \text{ dS m}^{-1}$  (Green et al., 2019; Green et al., 2020). Brine impacted soils have EC measurements that can reach  $120 \text{ dS m}^{-1}$  (Klaustermeier et al., 2016) and sodium adsorption ratios (SAR) that are often greater than 100 (De Jong, 1982).

Once oil is pumped to the surface, there are typically on-site and off-site operations that aim to separate the oil from brine and other soluble minerals through heating and washing processes; the entire process is called desalting. There are a couple reasons oil is separated from brine solutions, the first being that chloride from brine is highly corrosive on refinery and transportation equipment (Pereira et al., 2015; Thayee Al-Janabi et al., 2019; Yassin et al., 2019; Reneaa et al., 2021). Chloride can cause corrosion because it has the potential to form hydrochloric acid when chloride salts decompose under high temperatures (Pereira et al., 2015). Calcium and magnesium chlorides are known to hydrolyze readily to form hydrochloric acid (Egloff et al., 1937; Pereira et al., 2015; Yassin et al., 2019). Secondly, all salts in general can cause scale buildup and decrease heat transfer, which reduces the effectiveness of catalysts used during oil refining processes (Pereira et al., 2015; Yassin et al., 2019; Reneaa et al., 2021).

To remove brine from oil during on-site desalting processes, the initial emulsion of crude oil and brine water is first separated from natural gas in tanks near wells. Because natural gas has a lower density compared to oil or brine, separation of gas and liquid is achieved without the use of chemicals or heat. Next, fresh water is added to crude oil and brine which is then heated and

pressurized to reduce the viscosity of these materials. There are multiple combinations of these three additions to remove brine water from oil, but Egloff et al. (1937) determined that optimal conditions for removing brine water were achieved by adding 10% fresh water by volume of oil, heating to 200 °C and pressuring to 300 psi. Heating allows for water and minerals to more readily separate from oil due to density differences before more thorough desalting processes are conducted. When the residual crude oil is brought to off-site refineries, first, wash-water is added along with emulsifying agents. A mixing valve is used to ensure salts and other minerals go into solution when water and emulsifying agents are added. This mixture then goes into a desalter unit. At this step, chemical demulsifiers are used again to separate brine water from oil and to remove water, salts and minerals (Egloff et al., 1937 & Pereira et al., 2015). Once demulsifiers are added, oil and water either separate through gravity and density differences, otherwise, an electrostatic field produced between two electrodes helps to separate the smaller water droplets that remain trapped in oil; this is effective because water is a polar molecule (Pereira et al., 2015).

When brine is isolated from oil, it is then disposed of through deep injection at approved well sites and in North Dakota; it is most commonly pumped into the Dakota Formation (Bluemle, 2016, p. 299-300, Laurer et al., 2016). The Dakota Formation is a lower Cretaceous unit comprised of shale and sandstone (Murphy et al., 2009) and is around 200 ft thick and upwards of 4000 ft deep near Williston, North Dakota (Mohamed et al., 2017). When transporting crude or refined oil and its by-products, pipelines are the most common choice (Laurer et al., 2016; Allison & Mandler, 2018). Trucks are also used for transporting products and by-products short distances as they're more versatile than pipelines, yet not as energy efficient (Allison & Mandler, 2018). Transportation of oil via railways is also common and in

February of 2022, over 2 million barrels of oil were transported via rail (U.S. Energy Information Administration, 2022).

Accidental spills of produced water most often occur during desalting processes and transportation between facilities. Excess sodium and chloride from brine, when spilt across a landscape, can have negative impacts on plant and microbial communities and also on soil physical and chemical properties (Jury and Weeks, 1978; Barbour and Yang, 1993; Alberta Environment, 2001; Sublette et al., 2005; Lauer et al., 2016; Derby et al., 2016; Green et al., 2019; Green et al., 2020; Wang et al., 2021). The main effect of excess salts on plants is stunted growth and diminished productivity (Nieman, 1962 & Upadhyaya et al., 2013; Rath & Rousk, 2015; Uçarli, 2020; Wang et al., 2021). Brine is detrimental to plants because excess salts can induce drought like conditions by decreasing the osmotic potential between roots and the surrounding soil, which can slow germination rates and therefore inhibit plant establishment (Zhu et al., 1997; Upadhyaya et al., 2013; Derby et al., 2016; Meehan et al., 2017; Green et al., 2020; Uçarli, 2020). If osmotic stress on plants is too high, this prevents plants from taking up water and therefore, nutrient uptake is also reduced (Rath & Rousk, 2015). Excess salts can also cause osmotic stress upon microbial communities which decreases enzyme activity and protein synthesis (Rath & Rousk, 2015). High amounts of brine can also have toxic effects on plants when concentrations of solutes are significantly high (Upadhyaya et al., 2013; Derby et al., 2016). If osmotic stress is too high, and salt concentrations are great enough to create toxic conditions, this can induce oxidative stress upon plants which results from the accumulation of reactive oxygen species (ROS) in plant tissues (Upadhyaya et al., 2013). Oxidative stress can cause plants to exhibit stunted growth, wilting and necrosis and have less resilience to osmotic stress (Upadhyaya et al., 2013). Finally, excess salt from brine, especially sodium, can also cause

ionic stress upon plants (Rodríguez et al., 2005). Excess sodium ions in soil can cause ion concentrations in plants to be out of balance which can disrupt necessary plant functions (Rodríguez et al., 2005; Rath & Rousk, 2015).

Aside from the effects that salts from produced water, especially sodium, can have on plant and microbial communities, chloride is another major concern. Chloride, on top of causing damage to machinery, can have adverse effects on higher plants species (Geilfus, 2018). Chloride makes up 91% of anions in brine water produced in the western United States (Guerra et al., 2011) and has the potential of contaminating surface and groundwater systems if not properly disposed. As stated above, brine is usually disposed of through deep injection (Bluemle, 2016, p. 299-300), but accidental spills of brine can occur during transportation between refinery facilities and disposal. In North Dakota, chloride concentrations must not exceed  $1,000 \text{ mg L}^{-1}$  in surface waters or soils on well-pads (Green et al., 2020; Sam Croat, personal communication, 2022) and off well-pads, concentrations of chloride must not exceed  $250 \text{ mg L}^{-1}$  in surface and groundwater systems (North Dakota Department of Health, 2016; United States Environmental Protection Agency, 2022). Even though chloride is a micronutrient to higher plants species, at too high of concentrations, chloride can become toxic. Chloride toxicity initially causes leaf discoloration and lesions which can lead to necrosis and can result in yield reduction (Geilfus, 2018). There are no known negative effects that chloride has on consumer health, but high chloride concentrations can corrode lead pipes which can then lead to an increase in metals in drinking water (World Health Organization, 1996).

Finally, brine can also have especially adverse effects on soil chemical and physical properties. Sodium from brine, when introduced to soils, can cause clays to swell when wetted and can eventually lead to dispersion which may significantly decrease the saturated hydraulic

conductivity ( $K_s$ ) in soils (Shainberg et al., 1982; De Jong, 1982; Barbour and Yang, 1993; Ashworth et al., 1999; Marchuk & Rengasamy, 2011; Rengasamy & Marchuk, 2011; He et al., 2013; Rath & Rousk, 2015; Derby et al., 2016; Wang et al., 2021). Sodium makes up 81% of all cations in brine produced in the western United States which can lead to a significantly large influx of sodium to soil when spills occur (Guerra et al., 2011). Clay dispersion decreases macropore space and therefore decreases the number of preferential pathways that water would take when moving through a soil profile. This leads to water pooling at the soil surface or running off. Sodium itself doesn't decrease the  $K_s$  of a soil, it's the effect that sodium has on soil structure that decreases the  $K_s$  (Barbour & Yang, 1993). Once the macrostructure of a soil is destroyed and soil pores are clogged by dispersed particulates caused by the presence of sodium, the result is a significant decrease in  $K_s$  (Barbour & Yang, 1993). Depending on the clay type and other soil parameters, clays generally disperse when the ratio of the SAR to the EC is too high (Ashworth et al., 1999; Suarez et al., 2001; Marchuk & Rengasamy, 2011; Rengasamy & Marchuk, 2011; Nnadi et al., 2013; He et al., 2013; He et al., 2018; Green et al., 2020). In other words, dispersion will occur if the amount of adsorbed sodium exceeds the threshold of soluble salts required to maintain flocculation. The SAR:EC can reach high values if a sodium rich solution, such as brine, is introduced to a soil and other soluble salts in the soil are leached out with fresh water irrigation (Shainberg et al., 1982; Barbour & Yang, 1993; Derby et al., 2016).

Montmorillonite clays disperse when the EC falls below  $2 \text{ dS m}^{-1}$  and the SAR is 5 (He et al., 2013; He et al., 2015, He et al., 2018) and, as stated above, brine impacted soils were found to have SAR values over 300 (Guerra et al., 2011; Meehan et al., 2017; Green et al., 2020) and EC measurements of  $40 \text{ dS m}^{-1}$  and greater (De Jong, 1982). Smectite clays, such as montmorillonite and bentonite, are characteristic of arid and semi-arid regions (Regea et al.,

1997). Smectite, kaolinite and illite clays are the most common clay types found in North Dakota (Franzen & Bu, 2018). In the northwest oil producing counties in North Dakota, smectite clays dominate and in the southwestern oil producing counties, kaolinite clays dominate (Franzen & Bu, 2018). Smectite clays are more likely to disperse and are more sensitive to increasing SAR values compared to non-expanding clays such as kaolinite or illite (Klopp et al., 2020). Sodium is considered a dispersive cation as opposed to calcium, a cation that promotes flocculation, for the following three reasons: 1) sodium has an affinity to be hydrated (Tansel et al., 2005), 2) sodium has a relatively large ionic radius to its comparatively low charge (low ionic potential or charge density) (Marchuk & Rengasamy, 2011; Mähler and Persson, 2011) and 3) monovalent cations like sodium are less coordinated on soil exchange sites compared to other divalent cations such as calcium because bonds are weaker (Marchuk & Rengasamy, 2011; Rath & Rousk, 2015). In general, divalent cations flocculate soil particles and monovalent cations can lead to dispersion of soil particles. With this being said, sodium is a stronger dispersant than potassium and calcium and a stronger flocculant than magnesium (Rengasamy & Marchuk, 2011).

Sodium has a higher affinity to be hydrated than calcium for a few reasons, but to explain it most concisely, this relationship is caused by the charge and the ionic radius size of sodium compared to calcium. Cations such as magnesium and calcium have a +2 charge and relatively smaller ionic radii compared to potassium and sodium which have a +1 charge and comparatively larger ionic radii. For example, sodium has an ionic radius size ranging from 0.1011 – 0.117 nm and a +1 charge compared to calcium which has an ionic radius size ranging from 0.100 – 0.123 nm and a +2 charge (Tansel et al., 2005). The ionic potential of calcium is almost twice that of sodium meaning that calcium has a higher charge density which positively

influences soil particle flocculation (Marchuk & Rengasamy, 2011). The higher the charge density, the more tightly hydrated shells are held near the nucleus (Tansel et al., 2005). This means that the calcium complex swells when hydrated, but doesn't lead to clay dispersion because it simply cannot increase to the size required for clays to disperse when hydrated. Sodium, on the other hand, has a lower charge density and hydrated shells are held more weakly which allows for more water molecules to penetrate shell membranes therefore causing sodium to have a large, hydrated ionic radius (Tansel et al., 2005). Mähler and Persson (2011) concluded that “small, highly charged ions are structure makers while large ions with low charge density ... are definite structure breakers.”

### **Solutions for Brine Impacted Soils**

Since sodium is detrimental to soil physical and chemical properties, excess sodium from produced water needs be removed to improve and maintain soil health. There are currently multiple in-situ and ex-situ techniques used to remove excess sodium introduced by brine spills such as adding organic or chemical amendments, inverting soil, removing soil, using electro-kinetics, replacing impacted areas with new soil or cleaned soil, or by leaching salts out of the root zone aided with subsurface drainage etc. (Derby et al., 2016; Green et al., 2020). The most appropriate remediation method is chosen based on cost and site and soil characteristics (Green et al., 2020), but chemical amendment application with subsequent irrigation and washing is a popular, in-situ practice to remove brine from soil. To increase soil  $K_s$  and to prevent soil dispersion, a calcium amendment can be introduced to the soil to counter negative effects caused by excess sodium (De Jong, 1982; Ashworth et al., 1999; Suarez, 2001; He et al., 2013; Rath & Rousk, 2015; Derby et al., 2016; Green et al., 2020). Ideally, calcium would make up at least 60-80% of base cations (Robbins & Gavlak, 1989).

The most common amendment used for sodium-impacted soils is gypsum. Gypsum (a calcium sulfate) is relatively inexpensive and historically, has been the most common calcium amendment applied to sodic and brine-impacted soils (De Jong, 1982; Jury & Weeks, 1978; Alberta Environment, 2001; Green et al., 2020). Gypsum, when mass applied, supplies an adequate amount of calcium required to mobilize and replace sodium on soil exchange sites and is also able to maintain EC values to prevent dropping below the SAR:EC threshold that would cause dispersion of clay minerals in soil (Shainberg et al., 1982; De Jong, 1982; He et al., 2015; He et al., 2018; Green et al., 2020).

There are two types of gypsum that can be used for improving sodic or brine impacted soils with the first type being pelletized gypsum. Pelletized gypsum is a mined product (Kost et al., 2018) and can be found at any garden store or online. Many stores list 40-pound bags of pelletized gypsum at under \$10. Large scale fertilizers distributors such as USA Gypsum and Fertilizer Brokerage list pelletized gypsum at under \$400 ton<sup>-1</sup>. Large deposits of gypsum are found in ancient marine, playa and even eolian sediments (Drake et al., 2003), thus gypsum is mined refined globally. When making pelletized gypsum, raw gypsum is first crushed to a powder and binding agents are then introduced (Andrew Hoiberg, personal communication, 2022). Both the powder gypsum and binding agents are put into pelletizing pans which spin this mixture at specific angles and speeds, allowing pellets to form. Once pellets form to a certain size, centrifugal forces cause pellets to be expelled from spinning pans which are then screened for quality assurance before being packaged and sold (Andrew Hoiberg, personal communication, 2022).

A second type of gypsum is flue gas desulphurization gypsum, sometimes referred to as FGD gypsum, FGDG, or just flue gas gypsum. This type of gypsum is produced as a by-product



during the coal refinery process. As coal is heated, sulfur dioxide is produced (O'Brien et al., 1984; Dick et al., 2000, p. 506; Sparks, 2011, p. 51; Mao et al., 2008) and to prevent sulfur dioxide emissions, gases are routed through wet scrubbers and are then sprayed with a solution or slurry of calcium carbonate. Sulfur dioxide gas reacts with the calcium carbonate solution to form calcium sulfite (Sparks, 2011, p. 55-56). Calcium sulfite is a waste product and isn't of any use, so, depending on the engineering of the coal-fired plant, it is further force oxidized to form flue gas gypsum (O'Brien et al., 1984; Dick et al., 2000, p. 507; Sparks, 2011, p. 55-56). Most flue gas gypsum produced is used in drywall or concrete and also agriculture (O'Brien et al., 1984).

Even though gypsum is the most common amendment used for brine impacted soils, it has a relatively low solubility of 2.1-2.6 g L<sup>-1</sup> (Hulett & Allen, 1902; De Jong, 1982). Gypsum's low solubility is of utmost concern, especially in western North Dakota and other semi-arid regions where sodic or brine impacted soils are especially common. In most cases, calcium amendments like gypsum, are only effective when applied under conditions where irrigation and drainage are available (Ashworth et al., 1999). In other words, the soil water content needs to exceed the amendment's solubility in order to be of use (De Jong et al., 1982; Shainberg et al., 1982; Green et al., 2020). Irrigation is necessary in semi-arid environments to solubilize gypsum and to draw down other undesirable salts below the root zone (Derby et al., 2016; Green et al., 2020), as they typically accumulate near the surface in semi-arid climates (Mokni et al., 2010; Wang et al., 2021). To prevent salts from leaching into neighboring surface and groundwater systems, the addition of tile drainage may prevent unwanted downward or lateral movement of salts and makes collecting solutions high in sodium and chloride much easier. Tile drainage helps increase the depth of phreatic water from the soil surface which is important in areas with

high water tables and where evaporation exceeds precipitation. This helps to ensure that salts won't be deposited near the surface again and are instead collected and disposed of elsewhere. Not only does gypsum have a low solubility, the effect of gypsum in mobilizing sodium from clays is only successful to the depth at which gypsum is applied (De Jong, 1982; Sublette et al., 2005; Green et al., 2020). It has been found that incorporating gypsum into the soil instead of applying it at the surface is much more effective at mobilizing sodium from exchange sites (De Jong, 1982).

Gypsum can be difficult to use and requires more water than what may be realistic when reclaiming brine impacted areas. There have been other calcium sources used to remediate brine impacted soils, for example calcium chloride (Prather et al., 1987; De Jong, 1982; Ropp, 2013, p. 51). Calcium chloride is a calcium source that is much more soluble than gypsum as it has a solubility of around  $745 \text{ g L}^{-1}$  at room temperature (Ropp, 2013, p. 53). Calcium chloride is abundant and readily accessible as it has a variety of uses in food preservatives, de-icing agents and fertilizers (Ropp, 2013, p. 51) and can be manufactured easily through various methods (National Organic Standards Board Technical Advisory Panel Review, 2001). The price of calcium chloride differs between suppliers, but in general, prices range from about \$100-\$200  $\text{ton}^{-1}$  (prices shown are not for laboratory grade calcium chloride which would likely be more expensive). Calcium chloride is easily accessible, over 350 times more soluble than gypsum and relatively inexpensive and has even been found to be an effective tool in increasing  $K_s$  in soils with high SAR values (Prather et al., 1978; De Jong, 1982), however it can cause chloride contamination. As stated previously, off-well pad chloride concentrations cannot exceed  $250 \text{ mg L}^{-1}$  in surface and ground water systems (North Dakota Department of Health, 2016; United States Environmental Protection Agency, 2022) and chlorides are already highly abundant in

brine solutions (Guerra et al., 2011). Chloride concentrations in brine impacted areas can reach upwards of 1,000 to over 3,000 mg L<sup>-1</sup> (Sam Croat, personal communication, 2022). In short, applying calcium chloride to brine impacted soils isn't a realistic solution because the risk of ground water contamination far exceeds the benefits.

Another calcium source that is much more soluble than gypsum is calcium nitrate which has a solubility of nearly 1,300 g L<sup>-1</sup> (Hewlett et al., 2019). Calcium nitrate has been used as an amendment for brine impacted soils (De Jong, 1982; Ashworth et al., 1999; Franzen et al., 2019) and is even a recommended amendment for brine impacted areas (North Dakota Department of Health, 2016). Calcium nitrate is a common fertilizer and is easily accessible, but the cost of calcium nitrate is highly variable and is dependent on the cost of nitrogen. Recently, the price of nitrogen fertilizers has spiked as prices are directly correlated with the growing demand for natural gas (USDA, 2022). Another concern associated with calcium nitrate is nitrate contamination. According to the EPA (2019), nitrate-N must not exceed 10 mg L<sup>-1</sup>. Despite calcium nitrate being a common fertilizer, rates of application that are necessary for calcium nitrate to be an effective amendment for brine impacted areas far exceed typical application rates when calcium nitrate is used as a fertilizer.

Aside from pure calcium nitrate, there are many other products sold for the purpose of brine remediation that contain some form of nitrogen. Many of these products don't disclose exact chemical compositions and only list "active components". In many cases, if they don't contain nitrate, they often contain ammonium. There are multiple examples of products with both active calcium and ammonium that aim to reduce sodium but they still pose a risk of nitrate contamination. Something to consider when using products with active ammonium is that nitrate

contamination is still a risk because through nitrification, ammonium can be converted into nitrate.

Another soil amendment is the mineraloid leonardite. Leonardite is produced as lignite weathers (Akimbekov et al., 2020) and is essentially an oxidized form of lignite coal (Qian et al., 2015; Akimbekov et al., 2020; Wang et al., 2021). Leonardite is a soft, friable material that is waxy in texture and contains 30-80% humic acid (Qian et al., 2015; Akimbekov et al., 2020). Due to leonardite's waxy consistency, it is only able to go into solution when exposed to alkaline conditions (Akimbekov et al., 2020). Leonardite is applied to soils for many reasons, but is applied primarily because it serves as a soil conditioner and assists in making nutrients more available to plants (Akimbekov et al., 2020). Leonardite is also used as a plant stimulant and can improve chemical and biological properties of soil (Akimbekov et al., 2020; Wang et al., 2021) and is often compared to biochar because of its high carbon content but it's significantly less expensive, about \$30 ton<sup>-1</sup>, than biochar (Wang et al., 2021). One of leonardite's uses has been as an amendment for sodic soils and can indirectly supply enough calcium to displace sodium on soil exchange sites (Wang et al., 2021). Due to leonardite's high acid and organic carbon content, excess calcium is only available when leonardite is applied to alkaline soils. Under alkaline conditions, leonardite can go into solution and react with carbonate salts. Similar conditions could be created if leonardite were to be applied to a neutral pH soil along with the addition of lime which could increase soil pH and also serve as a calcium source. Soils with higher pH values tend to have excess calcium carbonate which then, given the presence of water, can react with carbon dioxide produced by the mineralization of leonardite, which yields excess calcium and bicarbonate anionic complexes (Wang et al., 2021). Leonardite is highly abundant, economical, but the effectiveness of leonardite at supplying calcium for sodic or brine impacted

soils is highly dependent on soil pH and water availability, which may make leonardite more difficult to use when reclaiming brine impacted soils.

To summarize the list of in-situ chemical amendments that can be used for brine impacted soils, gypsum is available, but highly insoluble. There is also calcium chloride, calcium nitrate and other nitrogen containing amendments, but groundwater contamination is a concern when working with these materials. Lastly, there is leonardite, but leonardite is not a direct source of calcium and the effectiveness of leonardite is highly dependent on soil pH. The pros and cons of current in-situ chemical amendments for brine spill remediation prompted the idea of using calcium acetate as an amendment for brine impacted soils. Calcium acetate is readily soluble, around  $347 \text{ g L}^{-1}$  (Macco Organiques, 2018), and contains about the same amount of calcium, by weight, as gypsum does ( $22.7 \text{ g kg}^{-1}$  vs.  $23.2 \text{ g kg}^{-1}$ ). There are no known negative effects of acetate on groundwater safety. Additionally, acetate is a preferential carbon source in aerobic environments and microorganisms will metabolize more quickly when acetate is available (Stevenson & Katznelson, 1958; Ostendorf et al., 1993; Wander et al., 1996). The calcium acetate product used for laboratory experiments discussed in later parts of this thesis is from The Lab Depot (62-54-4, Dawsonville, GA) and retails for about \$44 and \$181  $\text{kg}^{-1}$  but, depending on the manufacturer and mass ordered, costs can be decreased to less than \$10  $\text{kg}^{-1}$ . Despite the cost, less water and less time is needed for calcium acetate to go into solution, potentially making it an effective amendment for improving brine impacted soils.

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## **CHAPTER 2. EFFECTS OF CALCIUM AMENDMENTS ON HYDRAULIC CONDUCTIVITY AND SODIUM CONTENT OF BRINE IMPACTED SOILS**

### **Abstract**

As oil and natural gas production continues in the Williston Basin, risks of accidental spills of produced water (brine) are a growing concern. Brine, when spilt across a landscape, has the potential of causing decreased biological activity and soil dispersion. A common treatment for brine impacted soils is to remove sodium from soil exchange sites and replace it with other cations that promote soil flocculation such as calcium. The purpose of this study was to investigate the effects of several calcium amendments, including 1) calcium acetate, 2) flue gas desulphurization gypsum (FGD gypsum or flue gas gypsum) and 3) pelletized gypsum, on increasing the saturated hydraulic conductivity ( $K_s$ ) and on removing sodium of three brine impacted. Increasing rates of calcium acetate, up to  $44.8 \text{ Mg ha}^{-1}$ , were the most effective at increasing  $K_s$  rates in brine impacted soils from initial  $K_s$  rates near  $0 \text{ cm hr}^{-1}$  to  $0.4 \text{ cm hr}^{-1}$  in high smectite soils and from rates near  $0 \text{ cm hr}^{-1}$  to  $1.2 \text{ cm hr}^{-1}$  in high illite soils. Increasing rates of flue gas gypsum, up to  $44.8 \text{ Mg ha}^{-1}$ , were somewhat effective at increasing  $K_s$  from rates near  $0 \text{ cm hr}^{-1}$  to  $0.15 \text{ cm hr}^{-1}$  in high smectite soils and from rates near  $0 \text{ cm hr}^{-1}$  to  $0.5 \text{ cm hr}^{-1}$  in high illite soils. It was concluded that a saturated calcium acetate solution, which has an electrical conductivity of  $34 \text{ dS m}^{-1}$ , contributed a greater ionic strength leading to stronger flocculation and therefor higher  $K_s$  rates compared to a saturated solution of gypsum, which has an electrical conductivity of  $2 \text{ dS m}^{-1}$ . Rates as low as  $2.2 \text{ Mg ha}^{-1}$  of flue gas gypsum were just as effective as rates of up to  $22.4 \text{ Mg ha}^{-1}$  and  $44.8 \text{ Mg ha}^{-1}$  of calcium acetate at displacing sodium from upwards of  $25 \text{ cmol}(+) \text{ kg}^{-1}$  to  $0 \text{ cmol}(+) \text{ kg}^{-1}$ . All rates of pelletized gypsum did

not significantly affect rates of  $K_s$ , while increasing rates up to  $44.8 \text{ Mg ha}^{-1}$  were only occasionally effective at removing sodium.

## **Introduction**

Brine, or produced water, is an unavoidable by-product of the oil and gas industry and has the potential of disrupting soil physical, biological and chemical properties if not managed properly. Brine is found co-located with crude oil deposits because as sedimentation occurred in marine environments, trapped organic material was eventually transformed into fossil fuels (Hobson and Tiratsoo, 1975, p. 31; Ourisson et. al., 1984; Bluemle, 2016, p. 294; Yassin et al., 2019) and salts from surrounding ocean water were also concentrated in these sediments (Tissot and Welte, 1978, p. 69). There are a variety of salts in brine solutions (Guerra et al., 2011; Pereira et al., 2015; Derby et al., 2016; Yassin et al., 2019), the most common being sodium chloride (De Jong, 1982; Guerra et al., 2011; Pereira et al., 2015; Lauer et al., 2016; Derby et al., 2016; Konkel, 2016). In crude oil reservoirs, oil and natural gas float above brine water due to density differences (Abel et al., 2015) but, drilling and pumping operations disrupt this heterogeneity so when crude oil is pumped to the surface it's typically as an emulsion of oil and brine water (Thayee Al-Janabi et al., 2019; Yassim et al., 2019).

There are several on and off-site separation efforts that aim to separate brine from the crude oil emulsions before further transportation because of the hazards that salts pose on the integrity of refinery and transportation equipment (Pereira et al., 2015; Thayee Al-Janabi et al., 2019; Reneaa et al., 2021). Brine is especially abundant and can sometimes exceed the amount of oil that's pumped to the surface (Tissot and Welte, 1978, p. 69; Bluemle, 2016, p. 299; Yassin et al., 2019), so many desalting efforts occur soon after crude oil is brought to the surface at on-site facilities. There are many different types and combinations of desalting processes (Guerra et al.,

2011) but most commonly, desalting processes involve heating crude oil to allow oil and water to more easily separate due to density differences with the aid of demulsifying agents, mixing elements and electrical currents (Pereira et al., 2015; Yassin et al., 2019).

Once brine is removed from oil, it's then discarded by injecting into disposal wells (Bluemle, 2016, p. 299-300, Laurer et al., 2016; Konkel, 2016). Before brine is disposed of, it's most commonly transported through pipelines and tanker trucks (Konkel, 2016; Laurer et al., 2016; Allison & Mandler, 2018), which are the routes for many accidental spills (Konkel, 2016). Brine, when released across a landscape has the potential of disrupting typical plant and microbial functions and productivity (Nieman, 1962; Zhu et al., 1997; Rodríguez et al., 2005; Upadhyaya et al., 2013; Rath & Rousk, 2015; Meehan et al., 2017; Wang et al., 2021). In addition, brine has the potential of causing soil dispersion (Shainberg et al., 1982; De Jong, 1982; Sumner and Naidu, 1998, p. 78-94; Barbour and Yang, 1993; Ashworth et al., 1999; Marchuk & Rengasamy, 2011; Rengasamy & Marchuk, 2011; He et al., 2013; Rath & Rousk, 2015; Derby et al., 2016; Wang et al., 2021)

In order to reclaim brine impacted soils and prevent soil dispersion, excess sodium needs to be removed while maintaining a low SAR to EC ratio (Ashworth et al., 1999; Suarez et al., 2001; Marchuk & Rengasamy, 2011; Rengasamy & Marchuk, 2011; Nnadi et al., 2013; He et al., 2018; Green et al., 2020). Depending on soil parameters clays will disperse, when wetted, if the ratio between the SAR and the EC exceeds 6 (He et al., 2013). There are multiple in-situ and ex-situ methods that aim to remove sodium from brine impacted soils but historically, the most common in-situ chemical amendment used to remediate brine impacted soils is gypsum (De Jong, 1982; Jury & Weeks, 1978; Alberta Environment, 2001; Green et al., 2020).

Gypsum, when mass applied to a brine impacted soil, supplies enough calcium required to mobilize sodium and is also able to maintain low SAR to EC values which prevent soil dispersion (Shainberg et al., 1982; De Jong, 1982; Suarez and Wood, 2008; He et al., 2015; He et al., 2018; Green et al., 2020). There are two general sources of gypsum: mined, pelletized gypsum and byproduct flue gas gypsum. Pelletized gypsum is usually a mined product (Kost et al., 2018), is inexpensive (less than \$0.50 kg<sup>-1</sup>) and can be commonly found where commercial fertilizers are sold. Flue gas gypsum is also inexpensive (less than \$0.10 kg<sup>-1</sup>) and readily accessible where coal combustion facilities choose to produce it. The only difference is that flue gas gypsum is manufactured most commonly in a powder form, allowing for a higher surface area than pelletized gypsum. Both sources of gypsum are commonly used as amendments for sodic and brine impacted soils, yet the effectiveness of gypsum is limited by its solubility (2.1-2.6 g L<sup>-1</sup>), which is an important consideration since North Dakota's brine impacted areas are in semi-arid climates (Hulett & Allen, 1902; De Jong, 1982). There are other, more soluble calcium amendments but there are often risks associated with nitrate (Ca(NO<sub>3</sub>)<sub>2</sub>) and chloride (CaCl<sub>2</sub>) concentrations.

Calcium acetate has about the same amount of calcium as gypsum by weight (22.7 g kg<sup>-1</sup> vs. 23.2 g kg<sup>-1</sup> respectively) and more importantly, has a solubility of up to 374 g L<sup>-1</sup> (Macco Organiques, 2018). Not only is calcium acetate more soluble and able to supply an adequate amount of calcium capable of mobilizing sodium in brine impacted soils, there are no known negative effects of acetate on the environment. Furthermore, it's hypothesized that the acetate will actually serve as an available carbon source for soil microbes (Stevenson & Katznelson, 1958; Ostendorf et al., 1993; Wander et al., 1996). However, calcium acetate is significantly

more expensive than gypsum because most available products are sold in smaller quantities and are either food or lab grade quality.

Given the need to better assess the effectiveness of calcium acetate as an amendment for brine-impacted soils, the objectives of this study were to evaluate if calcium acetate is more effective at 1) increasing water flow and 2) reducing sodium in brine impacted soils compared to gypsum. The first hypothesis of this study is that calcium acetate will be the most effective amendment, compared to flue gas gypsum and pelletized gypsum, at increasing water flow and removing sodium due to its high solubility. The second hypothesis is that flue gas gypsum will have intermediate effects at increasing water flow and removing sodium because despite flue gas gypsum and pelletized gypsum both having a low solubility of  $2.1 - 2.6 \text{ g L}^{-1}$ , flue gas gypsum has a much higher surface area than pelletized gypsum allowing it to react more readily. The last hypothesis is that pelletized gypsum is going to have the least effect at increasing water flow or removing sodium from brine impacted soils because not only is it limited by its low solubility, but also by its low surface area.

## **Materials and Methods**

### *Soil Description*

From the Williston Basin, three brine-impacted soils were collected, air-dried and ground to pass through a 2 mm sieve. The first soil, termed as Glenburn, was collected near a well pad in a barley (*Hordeum vulgare*) field located in Glenburn, North Dakota. The second soil, Williston, was collected within 30 km of Williston, North Dakota. The third soil, Bainville, was collected within 15 km of Bainville, Montana.

The Glenburn and Bainville soils were both surface soils while the Williston sample is a subsoil. Other soil information including particle size distribution and soil chemical properties

are provided in Table 1. The particle size distribution was measured by using the hydrometer method and soil chemical properties were determined by Agvise Laboratories (Northwood, North Dakota). Based on the particle size distribution, the Glenburn and Bainville soils are loams and the Williston soil is a sandy loam. Additionally, Table 2 provides the mineral identification and clay speciation (Code E9 XRD, Activation Laboratories Ltd) of each soil. The Williston and Bainville soils were dominated by smectite, while the Glenburn soil was dominated by illite.

TABLE 1. Particle size distribution and soil chemical properties of soils used for this study.

	Glenburn	Williston	Bainville
Particle size distribution (% by weight)			
Sand	45.7	52.2	44.5
Silt	28.6	28.7	29.1
Clay	25.7	19.1	26.5
Soil chemical properties			
EC <sub>1:1</sub> (mS cm <sup>-1</sup> )	22.8	17.9	24.6
CEC (cmol(+) kg <sup>-1</sup> )	12.3	17.1	20.9
pH	7.12	7.15	6.89
OM (%)	1.9	1	1
Ca (mg L <sup>-1</sup> )	4030	5080	4370
Mg (mg L <sup>-1</sup> )	1910	1140	870
Na (mg L <sup>-1</sup> )	7360	5780	10400
K (mg L <sup>-1</sup> )	579	372	275
%Na	46	41.2	60.3

TABLE 2. Mineralogy of soils used for this study.

	Glenburn	Williston	Bainville
Mineral fraction (% by weight)			
Quartz	41	47.2	34.5
Plagioclase	9.2	5.8	9
K feldspar	3.9	3.4	5.7
Amphibole	1.2	1.2	1.1
Muscovite/Illite	3.6	4.9	4.3
Chlorite	0.9	1.1	1.9
Kaolinite	0.6	0.7	1
Smectite	0.4	15	6
Calcite	2.2	4.9	4
Dolomite	5.6	9.1	11.5
Gypsum	0.5	n.d.	n.d.
Clay fraction (% by weight)			
Smectite	7	71	61
Illite	68	20	28
Kaolinite	10	4	6
Chlorite	15	5	5

#### *K<sub>s</sub> Laboratory Methods*

Each soil was mixed with differing rates of calcium acetate, pelletized gypsum and flue gas gypsum. The pelletized gypsum was purchased from Calcium Products (SuperCal SO<sub>4</sub>, Fort Dodge, IA). Pellets ranging from 2-4 mm were used while larger and smaller pellets were excluded. The flue gas gypsum was sourced from central North Dakota and had a powder like consistency. The calcium acetate purchased (62-54-4, The Lab Depot, Dawsonville, GA) for this experiment also had a powder like consistency. These three amendments were mixed into the three soils at five rates: 0, 2.2, 11.2, 22.4 and 44.8 Mg ha<sup>-1</sup> which correlate to rates of 0, 1, 5, 10 and 20 tons ac<sup>-1</sup>. To achieve an application rate of 2.2 Mg ha<sup>-1</sup>, 2.6 g of each amendment was added to 500 g soil and to achieve rates of 11.2, 22.4 and 44.8 Mg ha<sup>-1</sup>, the amendments were added at rates of 13.5 g, 27.8 g and 58.8 g, respectively, to 500 g of soil.



Once soils were homogenized, methods similar to those of Sommerfeldt et al. (1984) were used to measure the  $K_s$  of the three soils with their corresponding rates of each amendment. Each soil and amendment combination were packed into tempe cells (model 1400/1405, Soilmoisture Equipment Corp., Goleta, Ca), which are comprised of seven main parts (Figure 1). First, a cylindrical copper core with a volume of  $68.2 \text{ cm}^3$  (3 cm in height) held the soil within the tempe cell. This core was capped on the top and bottom with Whatman grade 202 filter paper that had been cut to the outside diameter of the copper core to retain soil particulates. Two screens were put on the outside of the filter paper to aid in evenly distributing water across the entire surface of the soil. To hold these five parts together, top and base plexiglass caps were tightened around the inner components using wingnuts to fasten bolts that were connected to the base cap and positioned through the top cap.

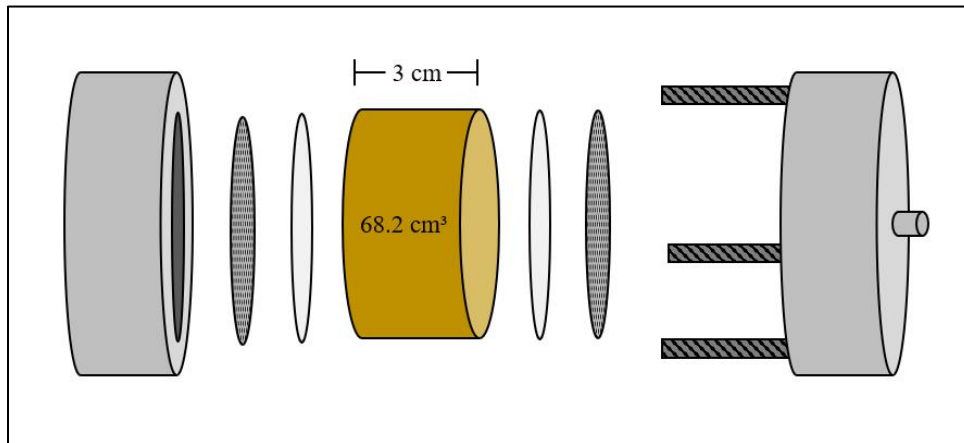


FIGURE 1. Tempe cell showing the bottom cap on the right side of the figure and the top cap at the left side of the picture. Not shown are the washers and wing nuts used to fasten all pieces of the tempe cell together after bolts are placed through top cap. Gaskets in the top and bottom caps, used to prevent water from leaking, are also not shown.

First, the bottom cap, screen, filter paper and copper core were assembled. Then, the soil with its amendment, was put into the copper core in about one cm increments. A small, plastic funnel was used to aid in this step. The edge of the tempe cell was tapped between each cm application with a wooden dowel to allow the soil to settle and compact slightly. This was done

while firmly holding the copper core to the base cap to prevent soil from escaping through the bottom edge of the copper core. After tapping the tempe cell, the surface of the soil was disturbed to prevent any artificial boundary from forming between soil layers added to the tempe cell. The weight of each tempe cell and the soils inside were recorded throughout the assembly process.

Once all of the tempe cells were assembled, they were placed on an elevated wooden stand in a random order. Typically, nine tempe cells were packed at a time including: two of the three amendments were chosen at four corresponding rates with the addition of a control. For each soil, there were three amendments, with four rates that were replicated four times. There were also four replicates of a control, which represents a rate of  $0 \text{ Mg ha}^{-1}$ . In total, there were 52  $K_s$  runs per soil. Once each cell was placed on the wooden stand, the bottom caps of the tempe cells were connected to a Mariotte bottle containing degassed distilled water using a manifold made up of silicon tubes, connectors, joints and shutoff valves. The Mariotte bottle was adjusted visually to have a near 0 cm head compared to the tempe cells. Valves on the manifold were opened to allow soils to saturate from below a day before experiments were conducted.

After saturating soils overnight, tempe cells were weighed to determine porosity and were then placed back onto the wooden stand with the top of the cell then connected to the Mariotte bottle with a 20 cm head whereas Sommerfeldt et al. (1984) used a 3 cm head. The same silicon tubing used for the manifold was then connected to the bottom of each tempe cell to direct water moving through cells into centrifuge tubes to collect leachate samples in measured increments. Most runs were completed within a period of 2 - 8 hours but some were allowed more time for sufficient sample collection and to establish a steady flow rate.

### *Equations and Calculations*

The  $K_s$ , in  $\text{cm hr}^{-1}$ , was determined based on the amount of water that moved through each tempe cell after a given amount of time as:

$$K_s = \frac{\text{flux}}{h} = \frac{\text{flux}}{\frac{23}{3}}$$

where “h” is the hydraulic head in cm and “l” is the length of the copper core in cm. The height of the hydraulic head and the length of the copper core, in this laboratory experiment, were always 20 cm and 3 cm respectively, thus the total hydraulic head is 23 cm. The flux was calculated as:

$$\text{flux} = \frac{\frac{L}{\left(\frac{V}{l}\right)}}{(\text{time } 2 - \text{time } 1) * 24} = \frac{\frac{L}{\left(\frac{68.2 \text{ cm}^3}{3 \text{ cm}}\right)}}{(\text{time } 2 - \text{time } 1) * 24}$$

and is also reported in  $\text{cm hr}^{-1}$ . The flux is a measurement of the water moving through each tempe cell where “L” the volume of leachate collected in mL, “V” is the volume of the inner copper core in  $\text{cm}^3$ , and “l” is the length of the copper core. The value (time 2 – time 1) represented the difference in time between leachate sample collection and the coefficient of 24, which converts the units of flux from  $\text{cm day}^{-1}$  to  $\text{cm hr}^{-1}$ . Once laboratory experiments were completed, rates of  $K_s$  were calculated and soils, post  $K_s$  runs, were air-dried, ground to pass a 2 mm sieve, and Agvise Laboratories Inc. determined the %Na in each soil. Data for  $K_s$  and residual sodium, quantified as %Na, were compiled with soil type, rate and amendment type being considered as factors in further data analysis.

### *Statistical Analysis*

All statistical analyses were conducted using R 4.2.0 software (R Core Team, 2022). The response variables,  $K_s$  and residual sodium, were calculated separately using a two-way analysis

of variance (ANOVA) with fixed factors including soil, amendment and rate, at  $\alpha = 0.05$ . A two-way ANOVA for soil \* amendment, soil \* rate and amendment \* rate was also calculated. When main effects were significant ( $p < 0.05$ ), Fisher's Least Significant Difference (LSD) test was applied to determine significant pairwise comparisons at  $\alpha = 0.05$  level (package 'agricolae'; de Mendiburu, 2021).

## **Results and Discussion**

In general, increased rates of any amendment had a significant effect on increasing the  $K_s$  and on decreasing residual sodium of the three brine impacted soils chosen for this experiment (Table 3). This is supported by De Jong (1982) who found, through a laboratory experiment, that with increased rates of several different amendments (from about  $0 \text{ Mg ha}^{-1}$  –  $145 \text{ Mg ha}^{-1}$ ), there was generally an increase in water flow in sodic soils. Sodic soils without any amendment showed little to no accumulation of water moving through them after about a 2-day period whereas sodic soils mixed with up to  $145 \text{ Mg ha}^{-1}$  of gypsum had 120 times more accumulated leachate during that same time (De Jong, 1982). Mao et al. (2016) also found, through field experiments, that with increased rates of an amendment (up to  $60 \text{ Mg ha}^{-1}$  of gypsum), there was a decrease of nearly 70% in sodium from sodic soils after a 6-month period.

TABLE 3. Mean values (with standard deviation) for  $K_s$  ( $\text{cm hr}^{-1}$ ) and residual sodium ( $\text{cmol}(+) \text{kg}^{-1}$ ) from saturated hydraulic conductivity experiments for treatments within each main effect and their interactions.

<b>Effect</b>	<b>Mean <math>K_s</math></b>	<b>Mean Residual Na</b>
	<b><math>\text{cm hr}^{-1}</math></b>	<b><math>\text{cmol}(+) \text{L}^{-1}</math></b>
<b>Soil</b>		
Glenburn	0.343 a	0.986 c
Williston	0.089 b	7.07 b
Bainville	0.071 b	12.9 a
<i>p</i>	***	***
<b>Amendment</b>		
Calcium Acetate	0.280 a	6.14 b
Flue Gas Gypsum	0.172 b	3.81 b
Pelletized Gypsum	0.050 c	10.9 a
<i>p</i>	***	***
<b>Rate (<math>\text{Mg ha}^{-1}</math>)</b>		
44.8	0.341 a	2.46 c
22.4	0.225 b	3.75 c
11.2	0.168 c	4.49 c
2.2	0.074 d	9.10 b
0	0.029 d	15.0 a
<i>p</i>	***	***
<b>Soil · Amendment</b>	***	**
<b>Soil · Rate</b>	***	**
<b>Amendment · Rate</b>	***	ns

*Note:* Different letters in each main effect indicate significant difference identified by Fisher's LSD test at  $\alpha = 0.05$ . When *p* values were not significant, they were labeled with ns; \* $p < 0.05$ . \*\* $p < 0.01$ . \*\*\* $p < 0.001$ .

Of the three amendments, calcium acetate had the most significant effect at increasing  $K_s$  rates compared to flue gas gypsum, which had intermediate effects, and pelletized gypsum, which had the least effect at increasing  $K_s$  rates across soils (Table 3). There are no studies comparing calcium acetate to gypsum for improving water flow in sodic or brine impacted soils but, Mao et al. (2018) reported that finer gypsum is more effective at improving soil structure and therefore improving water flow in shorter amounts of time due to it having a greater surface area, allowing it to solubilize and react more readily. Chawla and Abrol (1982) also found that finer gypsum ( $< 0.125 \text{ mm}$ ) caused initial  $K_s$  rates to be nearly 12% higher than  $K_s$  rates of soils

mixed with coarser gypsum (1.0-2.0 mm). Additionally, Chawla and Abrol (1982) found that  $K_s$  rates of soil with finer gypsum slowed over time whereas  $K_s$  rates of soils with coarser gypsum increased with time and concluded that a combination of both amendments are best for long term success. Lastly, Abdel-Fattah et al. (2015) also found that  $K_s$  rates increased by almost 75% when soils were mixed with finer gypsum (<0.5 mm) compared to coarser gypsum (1.0-2.0 mm).

Both calcium acetate and flue gas gypsum were effective at displacing sodium while pelletized gypsum was the least effective at displacing sodium (Table 3). Again, there are no studies comparing calcium acetate to gypsum for displacing sodium in sodic or brine impacted soils, but Kost et al. (2018) found that 50% more sodium leached from sodic soils when they were mixed with flue gas gypsum compared to pelletized. Based on this outcome, Kost et al. (2018) concluded that the high surface area of flue gas gypsum allowed it to solubilize more readily than pelletized gypsum. Abdel-Fattah et al. (2015) also found that the EC of soils mixed with finer gypsum (<0.5 mm) was 43% less than that of the control, while the EC of soils mixed with coarser gypsum (1.0-2.0 mm) was only 17% less compared to the control. Even though flue gas gypsum is able to react more readily than pelletized, any type of gypsum, when in solution, is effective at displacing sodium in sodic or brine impacted soils (Shainberg et al., 1982; Jury and Weeks, 1978; Robbins, 1986; Ashworth, 1999; Suarez, 2001; Green et al., 2022).

The effect of each soil on  $K_s$  rates and residual sodium was significantly different even though all three soils were similar textures (Table 3). This effect is likely due to a difference in clay mineralogy and initial chemical properties (Barbour and Yang, 1993; Suarez and Wood, 2008; He et al., 2015). The Glenburn soil had a small amount of smectite and was dominated by illite clay compared to the Williston and Bainville soils which were dominated by smectite clays (Table 2), similar to many North Dakota soils (Derby et al., 2016; Franzen and Bu, 2018). The

interaction between the soil \* amendment and soil \* rate also had significant effects on the final  $K_s$  and residual sodium content. This is also likely due to difference in clay mineralogy and initial soil chemical metrics.

The interaction between the amendment \* rate significantly affected final  $K_s$  rates meaning that increased rates of each amendment resulted in different effects from one another (Table 3). As stated previously, this was also observed by De Jong (1982) who found, that increasing rates of gypsum (from 0 Mg ha<sup>-1</sup> up to 145 Mg ha<sup>-1</sup>) improved water flow of sodic soils over a 2-day period more so than increased rates of calcium nitrate (also from 0 Mg ha<sup>-1</sup> to 145 Mg ha<sup>-1</sup>) by over 250%. There was, however, no significant effect from the interaction between the amendment \* rate on residual sodium meaning the amendment type affected the residual sodium in similar way that increasing rates also did (Table 3). Although this outcome was unexpected, there was a high level of variability in residual sodium data which may have led to this result.

For the Glenburn soil, increased rates of calcium acetate caused  $K_s$  rates to continuously increase and these rate differences are statistically significant (Figure 2a). With increased rates of flue gas gypsum,  $K_s$  rates did not continue to increase, but any rate of flue gas gypsum resulted in  $K_s$  rates that did differ from the control. Rates of flue gas gypsum as low as 2.2 Mg ha<sup>-1</sup> resulted in rates of  $K_s$  that did not statistically differ from  $K_s$  rates of soils mixed with up to 44.8 Mg ha<sup>-1</sup> of flue gas gypsum. Finally, any rate of pelletized gypsum did not differ from the control. Based on these results, it's likely that the effectiveness of flue gas gypsum at increasing  $K_s$  was limited by its low solubility and effectiveness of pelletized gypsum was limited by its low solubility in addition to its low surface area, which resulted in decreased reactivity.

Rates of calcium acetate as low as 2.2 Mg ha<sup>-1</sup> removed amounts of sodium statistically similar to that of rates of up to 44.8 Mg ha<sup>-1</sup> and did not statistically differ from each other, although trends may suggest otherwise in that increased rates of calcium acetate gradually displaced more sodium (Figure 2b). Additionally, the lowest rate of flue gas gypsum also removed similar concentrations of sodium as the highest rates of flue gas gypsum. Like calcium acetate, any rate of flue gas gypsum removed similar amounts of sodium and did not statistically differ from each other. Lastly, increased rates of pelletized gypsum removed sodium gradually but ultimately, the highest rates of pelletized gypsum removed similar amounts of sodium as the highest rates of flue gas gypsum and calcium acetate and these amounts did not statistically differ from each other.



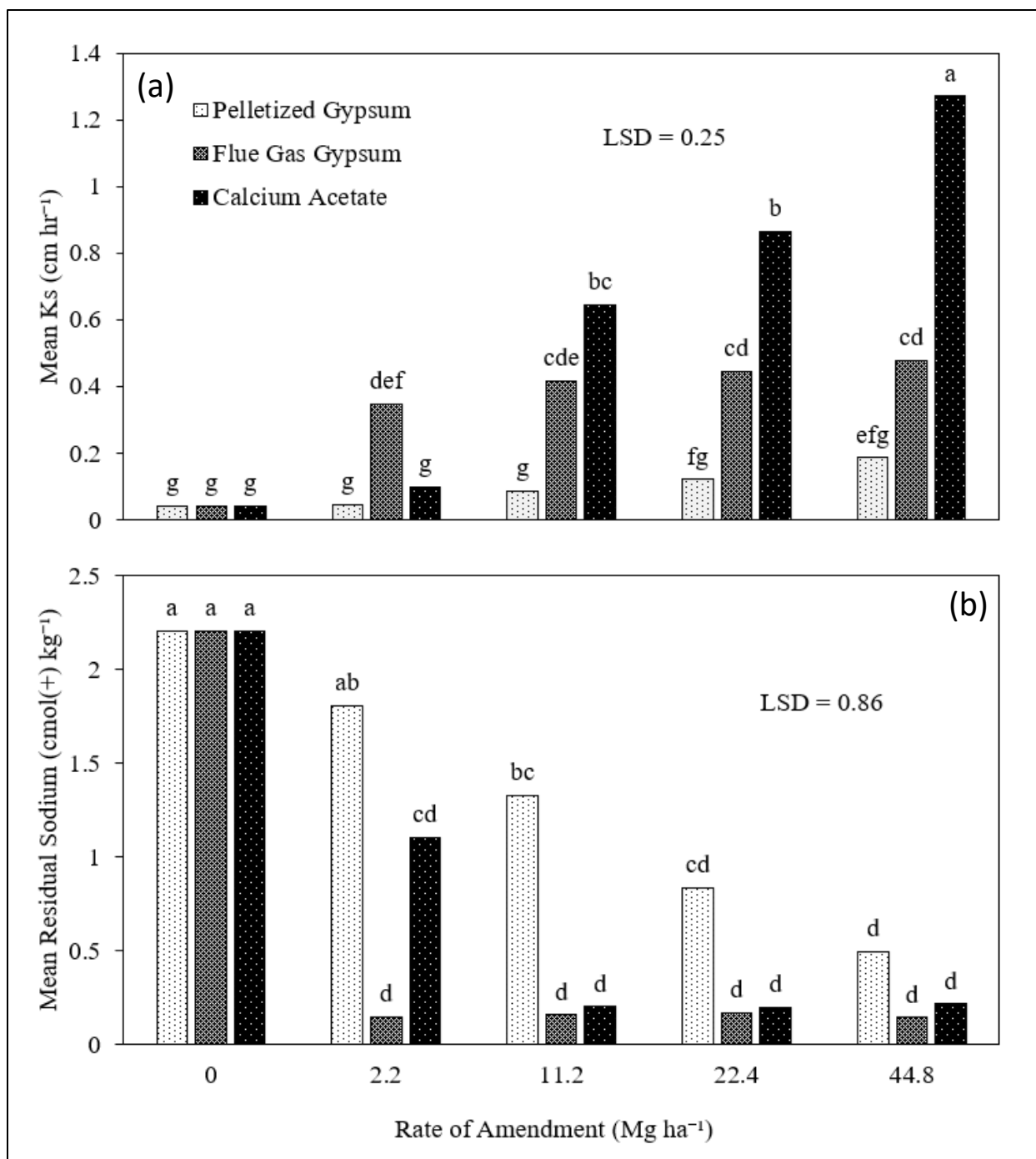


FIGURE 2. (a) Mean  $K_s$  ( $\text{cm hr}^{-1}$ ) and (b) average concentration of residual sodium ( $\text{cmol}(+) \text{kg}^{-1}$ ) for the Glenburn soil as a function of amendment and rate of application. Different letters indicate significant difference identified by Fisher's LSD test at  $\alpha = 0.05$ .

The Williston soil was similar to the Glenburn soil in that increased rates of calcium acetate increased  $K_s$  rates and the rate difference were statistically significant (Figure 3a). With increased rates of flue gas gypsum,  $K_s$  rates continued to increase but only slightly compared to calcium acetate. This is different than what was seen in Figure 2a in that increased rates of flue gas gypsum continuously increased  $K_s$ . Lastly, similar to Figure 2a, increased rates of pelletized gypsum did not increase rates of  $K_s$ . The final  $K_s$  with the highest rate of 44.8 Mg ha<sup>-1</sup> of pelletized gypsum did not differ from  $K_s$  rates of the control.

Increased rates of calcium acetate continuously reduced concentrations of sodium from the Williston soil (Figure 3b). Additionally, the lowest rate of flue gas gypsum removed similar amounts of sodium as the highest rates of flue gas gypsum, similar to what is shown in Figure 2b. Any rate of flue gas gypsum removed almost the same amount of sodium and the amounts did not statistically differ from each other. Increased rates of pelletized gypsum displaced sodium more slowly compared to flue gas gypsum or calcium acetate but ultimately, the highest rates of pelletized gypsum removed similar amounts of sodium as the highest rates of flue gas gypsum and calcium acetate and these amounts did not statistically differ from each other.

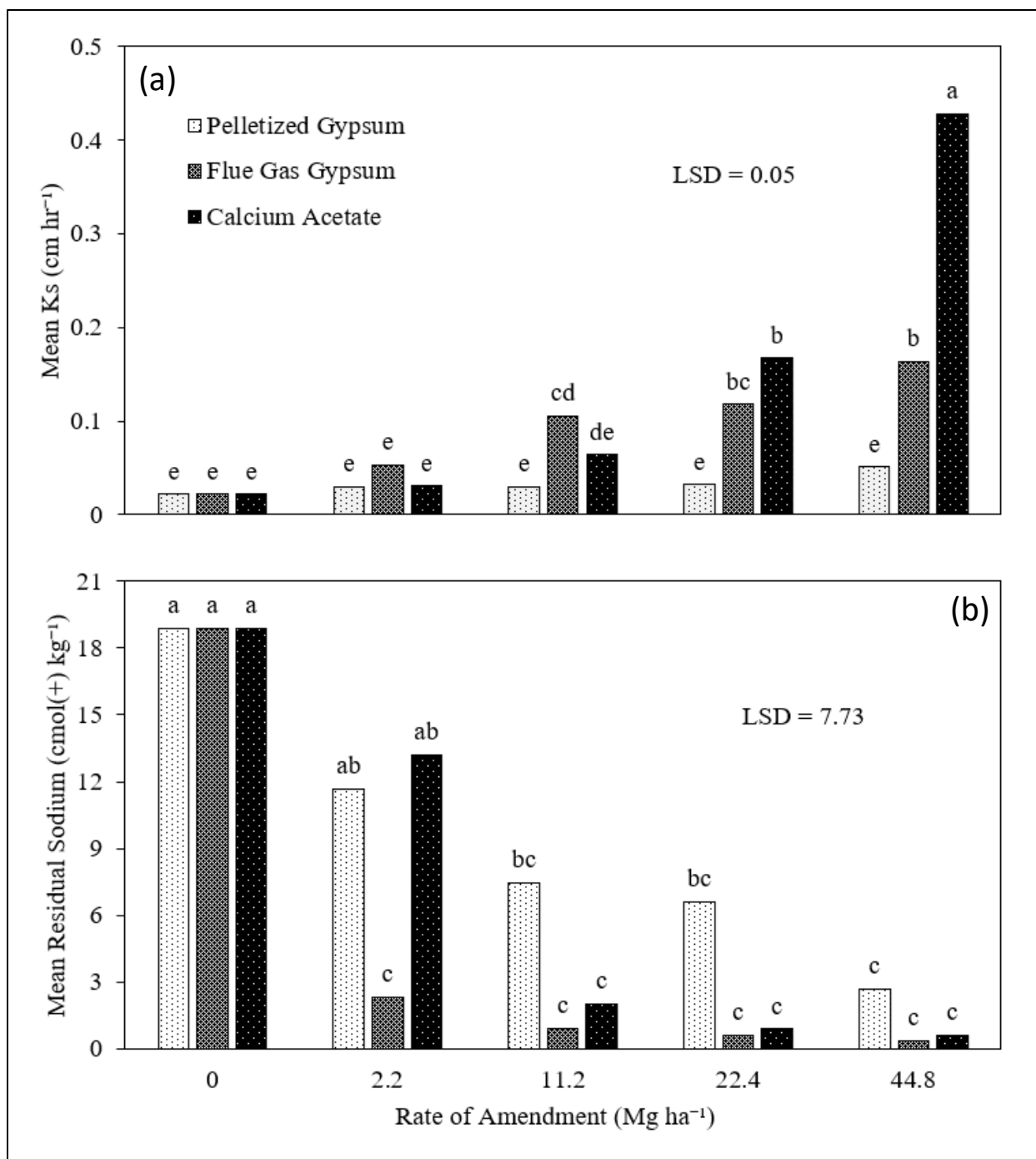


FIGURE 3. (a) Mean  $K_s$  ( $\text{cm hr}^{-1}$ ) and (b) average amount of residual sodium ( $\text{cmol}(+) \text{kg}^{-1}$ ) for the Williston soil as a function of amendment and rate of application. Different letters indicate significant difference identified by Fisher's LSD test at  $\alpha = 0.05$ .

Increased rates of calcium acetate led to increased  $K_s$  rates in the Bainville soil (Figure 4a) similar to what was seen in both Figure 2a and Figure 3a. The effect of increased rates of calcium acetate on the  $K_s$  is delayed compared to Figure 2a and Figure 3a, but this was likely due to the significantly higher concentration of sodium the Bainville soil initially had compared to the Glenburn or Williston soil. Next, like Figure 2a but unlike Figure 3a, with increased rates of flue gas gypsum,  $K_s$  rates did not continue to increase. Both lower and higher rates of flue gas gypsum influenced  $K_s$  rates similarly and did not statistically differ from each other. Lastly, as previously shown in Figure 2a and Figure 3a, increased rates of pelletized gypsum did not increase rates of  $K_s$ . The final  $K_s$  with the highest rate of 44.8 Mg ha<sup>-1</sup> of pelletized gypsum did not differ from  $K_s$  rates of the control.

With increased rates of calcium acetate, sodium is removed gradually from the Bainville soil (Figure 4b) and is similar to what is seen in both Figure 2b and Figure 3b. Also similar to Figures 2b and 3b, the lowest rate of flue gas gypsum removed similar concentrations of sodium as the highest rates of flue gas gypsum. Any rate of flue gas gypsum removed similar amounts of sodium that did not statistically differ from each other. Lastly, increased rates of pelletized gypsum removed sodium slowly but ultimately, the highest rates of pelletized gypsum removed statistically similar amounts of sodium as the highest rates of flue gas gypsum and calcium acetate while also not differing from the control. Despite the clear difference between the amount of residual sodium of soils mixed with 44.8 Mg ha<sup>-1</sup> of pelletized gypsum compared to soils mixed with 44.8 Mg ha<sup>-1</sup> flue gas gypsum or calcium acetate, there was a lot of variability in residual sodium data for the Bainville soil which lead to a larger LSD value. Trends still show similar patterns to previous graphs.

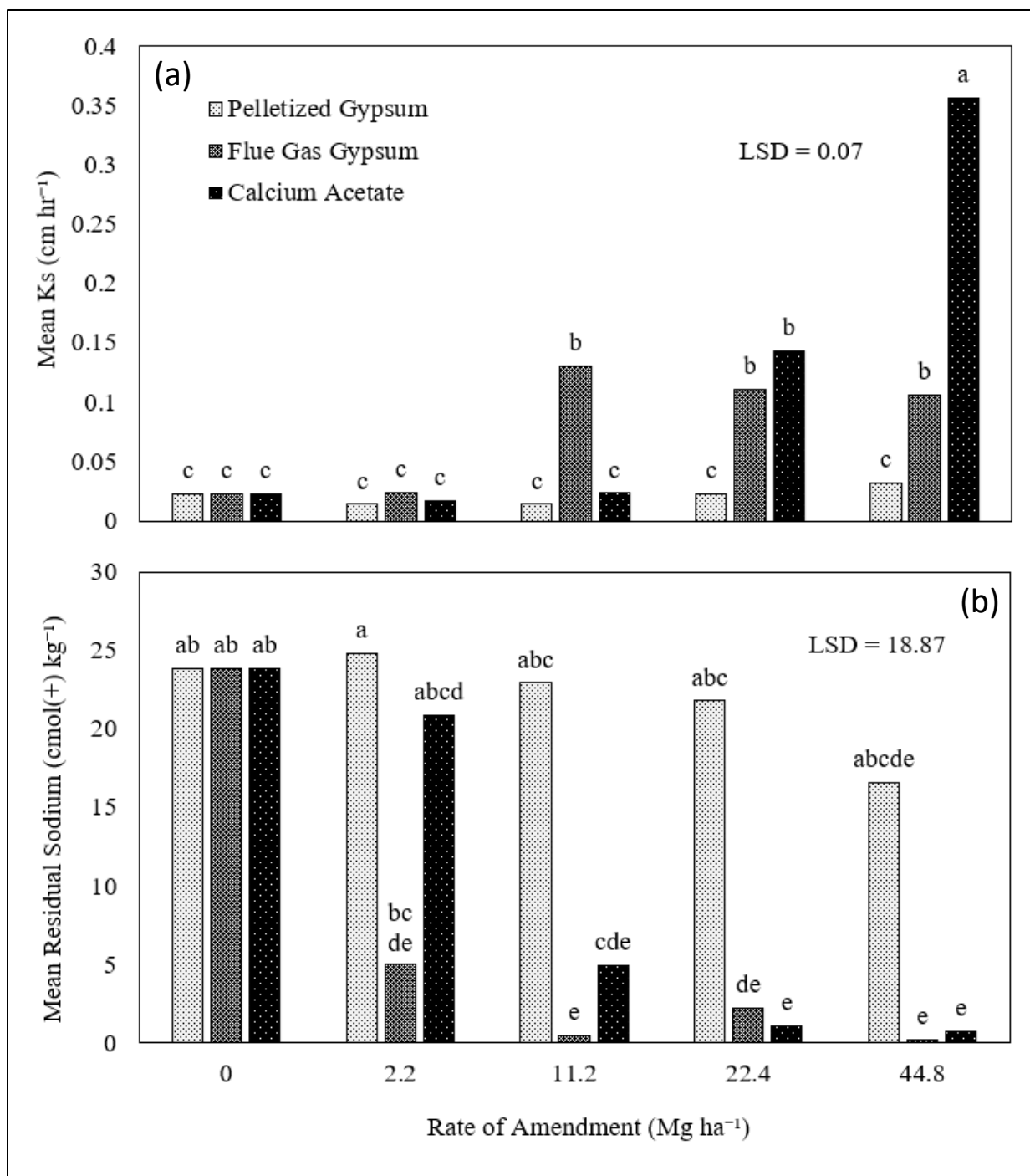


FIGURE 4. (a) Mean  $K_s$  ( $\text{cm hr}^{-1}$ ) and (b) average amount of residual sodium ( $\text{cmol}(+) \text{kg}^{-1}$ ) for the Bainville soil as a function of amendment and rate of application. Different letters indicate significant difference identified by Fisher's LSD test at  $\alpha = 0.05$ .

## Conclusion

When brine spills occur, it's necessary to remove sodium to prevent the risk of soil dispersion from occurring and to replace it with calcium to promote soil flocculation. Ultimately, increased rates of calcium acetate had the greatest effect on increasing  $K_s$  compared to flue gas gypsum or pelletized gypsum in each soil. Calcium acetate has an electrical conductivity of 34 dS m<sup>-1</sup> which likely lead to stronger flocculation and higher  $K_s$  rates, but the cost of calcium acetate is high (greater than \$10 kg<sup>-1</sup>) compared to either type of gypsum. Calcium acetate is produced primarily for food and drug purposes at either a food grade or lab grade quality which likely correlates to its high price. If large quantities of cheaper, non-lab or non-food grade calcium acetate were available, calcium acetate could be a viable solution to improving water flow in brine impacted soils. Calcium acetate, however, was not always as effective as flue gas gypsum at decreasing sodium. Only at higher rates was calcium acetate consistently able to increase water flow and displace sodium.

Pelletized gypsum is the most widely accessible of the three amendments and is available at most stores in large quantities. Despite being easily obtainable, pelletized gypsum was the least successful at increasing  $K_s$  rates and at displacing sodium. Pelletized gypsum is limited not only by its solubility, but also by its low surface area, which decreases its reactivity making pelletized gypsum an ineffective solution for improving water flow in brine-impacted soils, especially those found in semi-arid regions where water may be an additional limiting factor. Since pelletized gypsum is reasonably priced and available just about anywhere, this makes pelletized gypsum a favorable option despite its shortcomings as an effective amendment.

Flue gas gypsum is a somewhat effective amendment for brine impacted soils when water isn't a limited resource. Increased rates of flue gas gypsum had intermediate success at

increasing  $K_s$  rates while the lowest rates of application flue gas gypsum were the most successful at displacing sodium from each soil. Flue gas gypsum did supply enough calcium to displace sodium effectively, but a saturated solution of gypsum, with an electrical conductivity of  $2 \text{ dS m}^{-1}$ , likely did not contribute an ionic strength necessary for stronger flocculation that would promote higher  $K_s$  rates. Additionally, flue gas gypsum is that it's the cheapest of the three amendments (less than  $\$0.10 \text{ kg}^{-1}$ ) but is only readily available if coal refineries are equipped with proper engineering capable of producing calcium sulfate from calcium sulfite, the initial waste product produced during the coal refining process.

This study was conducted because there was lack of research assessing calcium acetate as an alternative to gypsum for improving brine impacted soils. The outcomes of this laboratory experiment supported initial hypotheses in that increased rates of calcium acetate lead to an increase in water flow and were effective at reducing sodium in brine impacted soils. The next step in this research would be to investigate if the acetate complex is a beneficial carbon source for soil microbes in brine impacted soils. Additionally, it was hypothesized that calcium acetate could be a more effective amendment than gypsum, especially in semi-arid environments where water is a limited resource. An experiment evaluating different saturation levels to simulate semi-arid conditions seen in North Dakota could be useful before designing a field experiment. Eventually, a field experimental design could follow this laboratory experiment to determine if calcium acetate is an effective amendment for brine impacted soils at a spill site within the Williston Basin.

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## APPENDIX

### ORIGINATION OF PRODUCED WATER (BRINE) IN THE WILLISTON BASIN

#### Williston Basin Context

The Williston Basin is a sedimentary basin found in southern Saskatchewan, southern Manitoba, eastern Montana, northwestern South Dakota, and in North Dakota with a large portion of North Dakota underlain by the Williston Basin. The Williston Basin is one of the most complete sequence of sediments found worldwide. The geographical extent of this 110,000 mi<sup>2</sup> basin is shown in Figure A1.

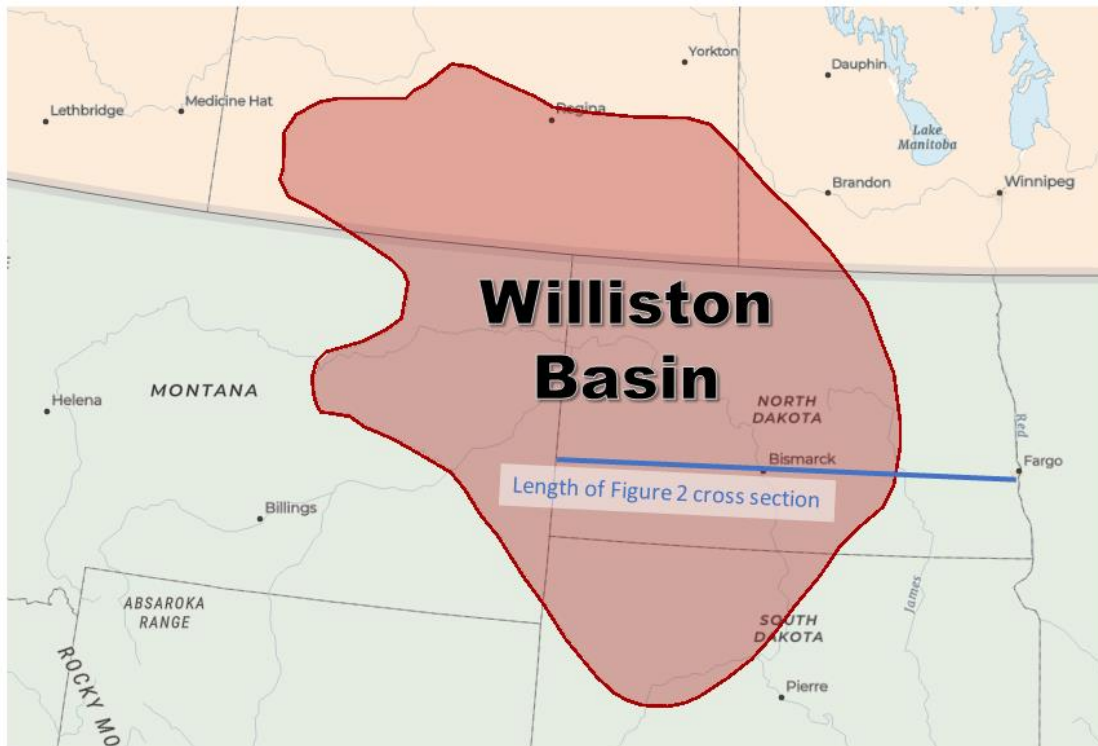


FIGURE A1. Geographical boundary of the Williston Basin. The blue transect line represent the cross section shown in figure 2.

Sediments were deposited in the Williston Basin first in the early Cambrian period (over 500 million years ago (Ma)) and were almost continuously deposited up until the Quaternary period (~2.5 Ma). Exceptions to this include four brief moments in time not recorded with the rest of the geologic history represented within the Williston Basin. There are a wide variety of

rocks that make up the Williston Basin that were deposited in terrestrial, fluvial and most abundantly, marine settings. The depth and relative thicknesses of rocks that make up the Williston Basin, in North Dakota are shown in Figure A2.

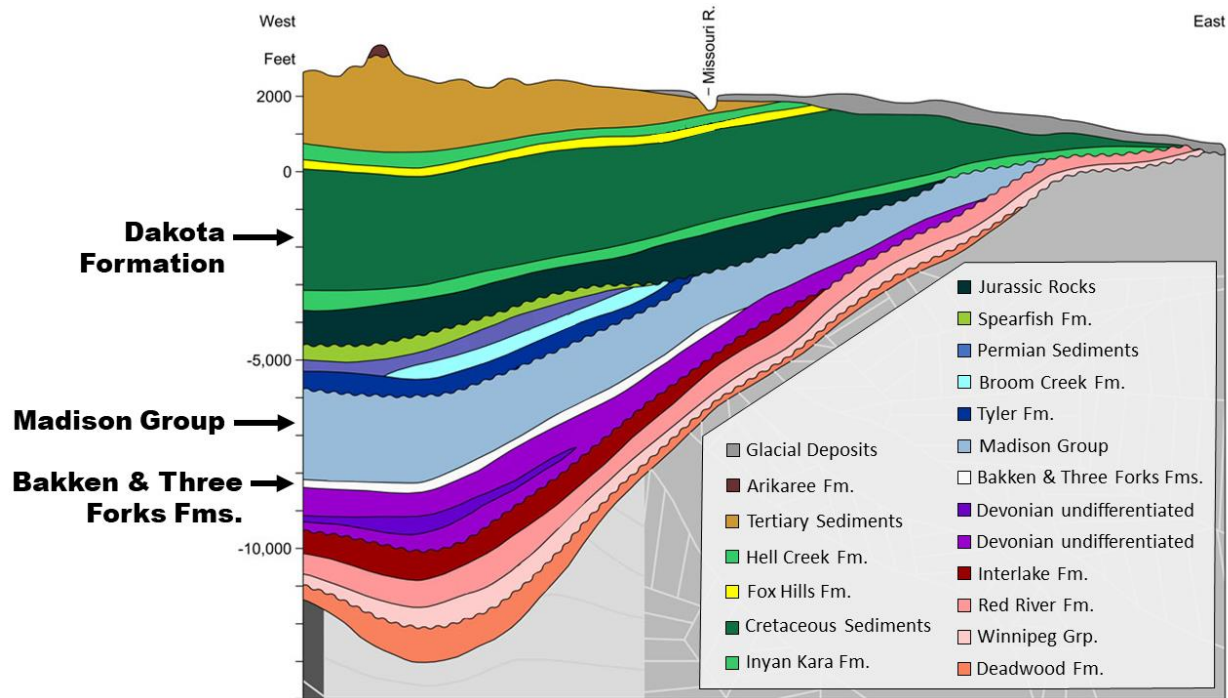


FIGURE A2. Cross section of the Williston Basin in North Dakota adapted from the North Dakota Geological Survey. Cross section is not drawn to scale.

### History of Oil and Gas Exploration

Some of the most notable rock units within the Williston Basin are the Bakken and Three Forks Formations as they currently hold most of the oil and natural gas that North Dakota produces today. Historically, the Madison Group (consisting of the Mission Canyon and Charles Formations) produced most of the oil and natural gas during the mid to late 1900s when conventional production techniques dominated this area (Figure A3). In the early 2000s, oil production from the Bakken and Three Forks Formations began to exceed production from the Madison Group due to advances in unconventional drilling (Figure A3).

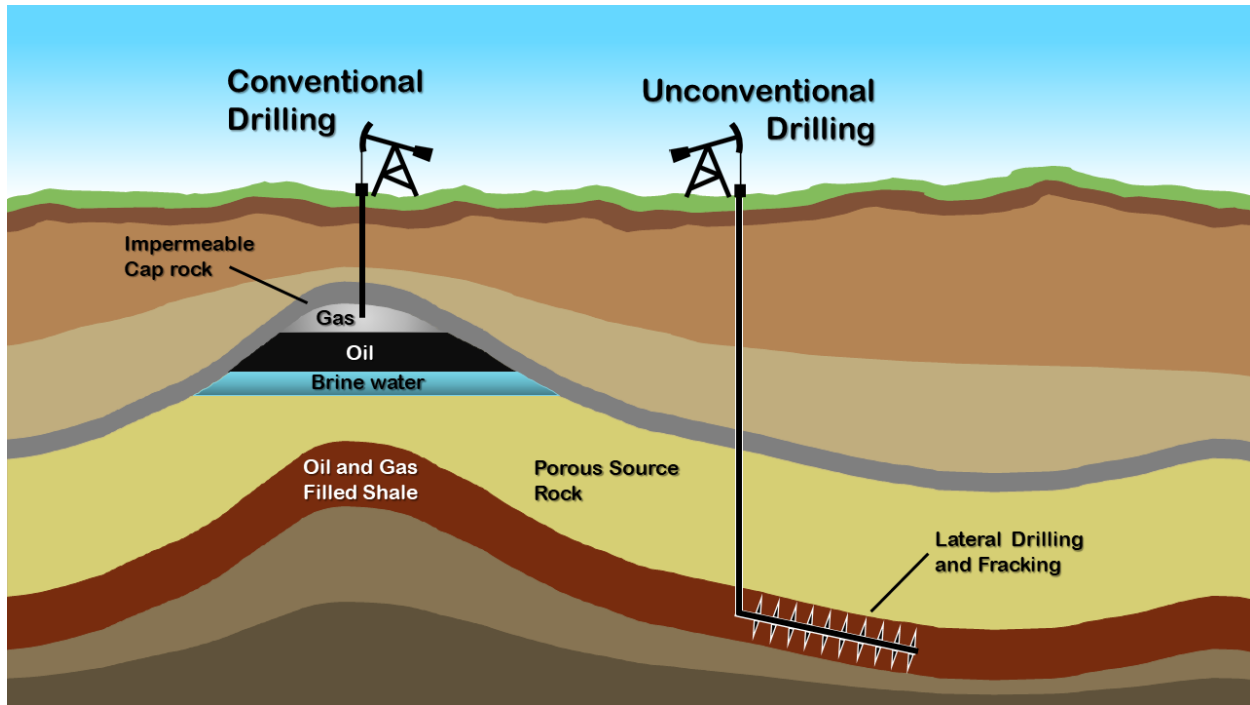


FIGURE A3. Schematic showing the difference between conventional oil extraction compared to unconventional oil extraction.

Unconventional drilling involves drilling down vertically to a kickoff point (KOP) where drilling then continues horizontally through rock units. Once drilling is complete, hydraulic fracturing, also known as “fracking” is used to further increase production in rocks with poorly connected voids. Conventional drilling, on the other hand, only involves drilling down vertically into large reservoirs of oil and natural gas. There is no need for fracking or horizontal drilling when conventional methods are used. Although unconventional drilling is more labor intensive and time consuming, its use allows access to immense amounts of untapped reserves of oil and natural gas within the Bakken and Three Forks Formations that far surpass reserves found within the Madison Group and other conventional reservoirs in the Williston Basin.

### **Geology and Formation of Oil and Gas Holding Rocks**

The Bakken Formation is an offshore, marine deposit composed of both shale and siltstone and ranges in thickness from 75 – 150 ft. The Three Forks Formation directly underlies



the Bakken Formation and is a nearshore, marine deposit composed of shale, siltstone and dolomite. The Three Forks Formation reaches 250 ft thick near west-central North Dakota.

The Bakken Formation was deposited during both the late Devonian and early Mississippian Periods (~360 Ma) and the Three Forks Formation was deposited during the late Devonian Period (385-359 Ma). Despite being two separate rock formations, the Bakken and Three Forks are often thought of as being one unit. The Bakken and Three Forks Formations range from 8,500 -10,000 ft in depth below ground surface in the western part of North Dakota.

Much time and a variety of geologic processes are required to transform marine sands and silts into rocks that contain oil, natural gas and the by-product of brine water. Oil and natural gas form as a result of the accumulation of plant and animal debris, sometimes referred to as organic material, that was altered by high temperatures and pressures in anaerobic (without oxygen) conditions. The amount of organic material that was deposited over 350 Ma was dependent on rates of deposition and sedimentation. All sediments are eroded from high points like hills or mountain tops and deposited in depressional areas like basins, lakes or oceans (Figure A4). This is the reason there is a continuous accumulation of sediments in marine basins.

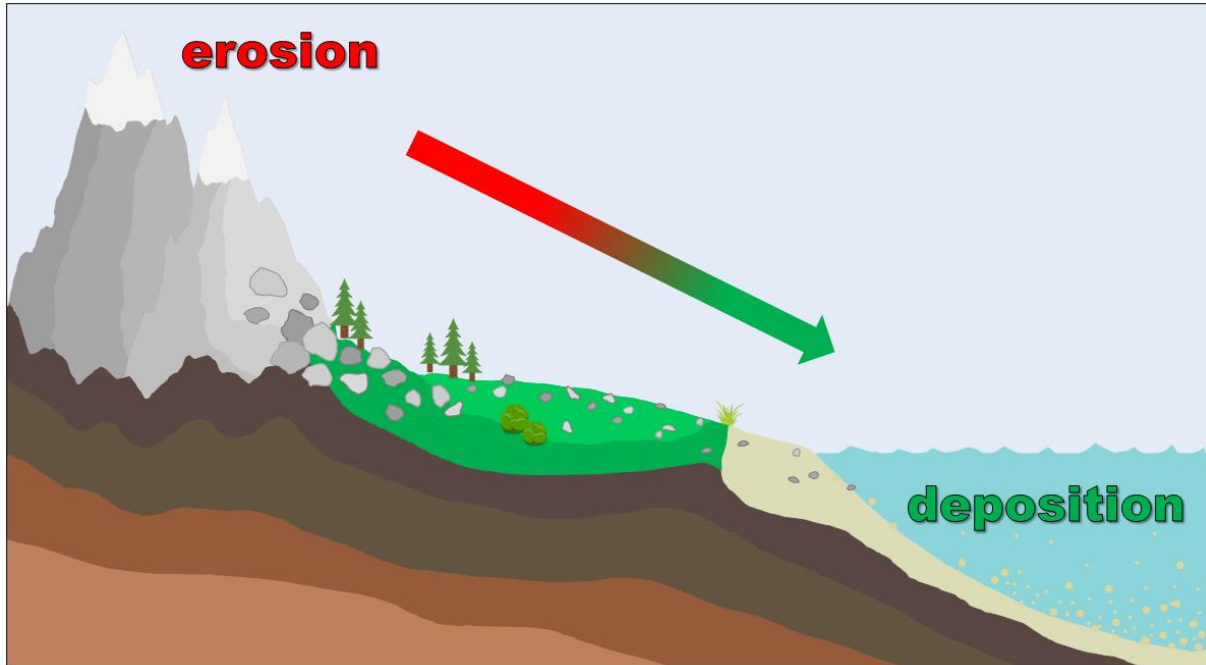


FIGURE A4. Schematic showing erosion occurring at higher elevations and deposition occurring at lower elevations.

Conditions leading to the formation of oil and natural gas need to be ideal. This means that there needs to be favorable climate conditions to support appropriate plant and animal communities necessary for forming oil and natural gas. Low energy, depositional environments are also necessary to bury organic material and promote anaerobic degradation before this organic material can be scavenged upon. Beach environments, for example, are less than ideal for organic matter accumulation because as waves crash upon the shore, water is aerated and the contact between bacteria and organic material is accelerated leading to decomposition rather than accumulation.

As sedimentation occurs in marine environments, organic material is buried by sediments that are loosely compacted and, during a majority of the Paleozoic era (540 -248 Ma) in North Dakota, saturated with sea water. As deposition and sedimentation continues, organic material and salts (primarily NaCl) from sea water are concentrated as water is squeezed out from between pore spaces due to increasing pressures building above (Figure A5).

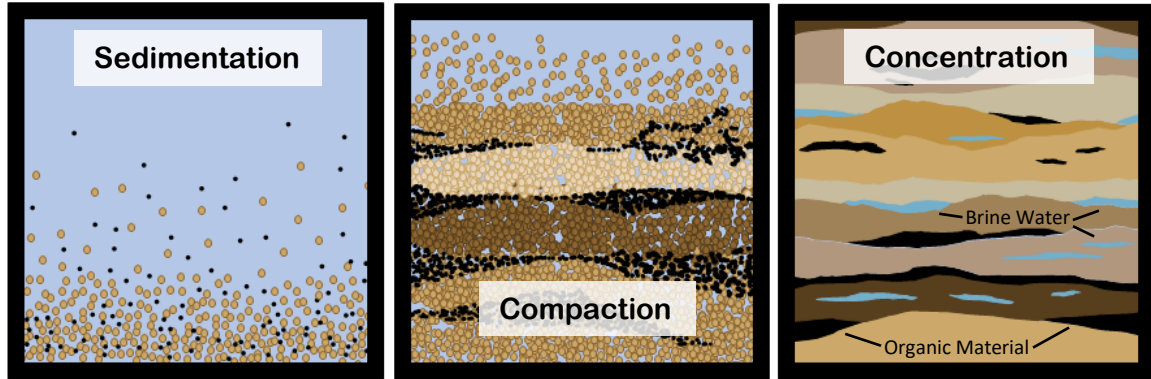


FIGURE A5: Schematic showing sedimentation and compaction of marine sediments and organic material and concentration of ocean water and organic material composed of plant and animal debris.

### Formation and Occurrence of Oil, Gas and Brine

Pressures and temperatures build as sedimentation continues and at depths of about 0.6-1.2 miles (1-2 km) below ground surface and at temperatures of about 120 °F, accumulated plant and animal debris is converted into a substance known as kerogen through a process called diagenesis. Kerogen is a waxy, insoluble, sedimentary organic material. The formation of kerogen from plant and animal material is the first step in altering organic material into fossil fuels (Figure A6).

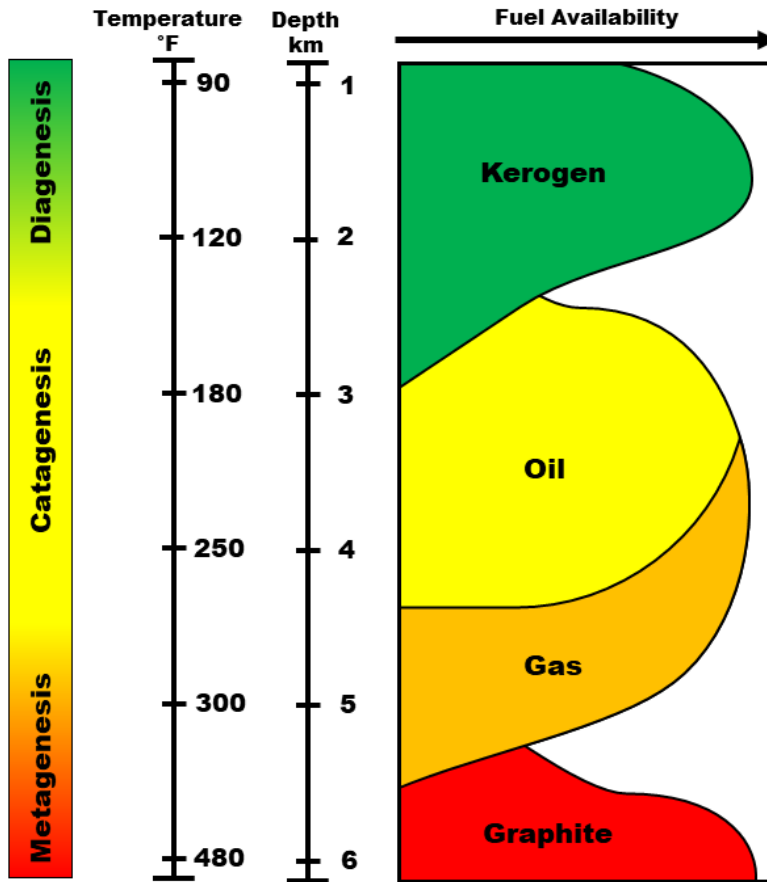


FIGURE A6. Chart showing fuel availability and thermal degradation processes given different pressure and temperature regimes.

At depths reaching 1.8-3.0 miles (3-5 km) below ground surface and temperatures ranging from 180-250 °F, kerogen is converted into oil through a process called catagenesis which is a type of thermal degradation. The formation of natural gas comes later only if temperatures continue to increase to between 250-300 °F. If temperatures continue to rise to near 400 °F, however, oil and natural gas will go through a process called metagenesis. Metagenesis will mineralize oil and gas, turning them into graphite, as they combust under high temperatures and thus they will no longer be a fossil fuel.

Oil and natural gas tend to move through connected pore spaces in rock and accumulate in areas where porosity in rocks is low and permeability is no longer feasible. Concentrated ocean water, also known as brine, brine water, or produced water also travels through rocks and

accumulates with oil and natural gas. In these pockets, due to density differences, oil floats on brine and gas floats on oil (Figure A7).

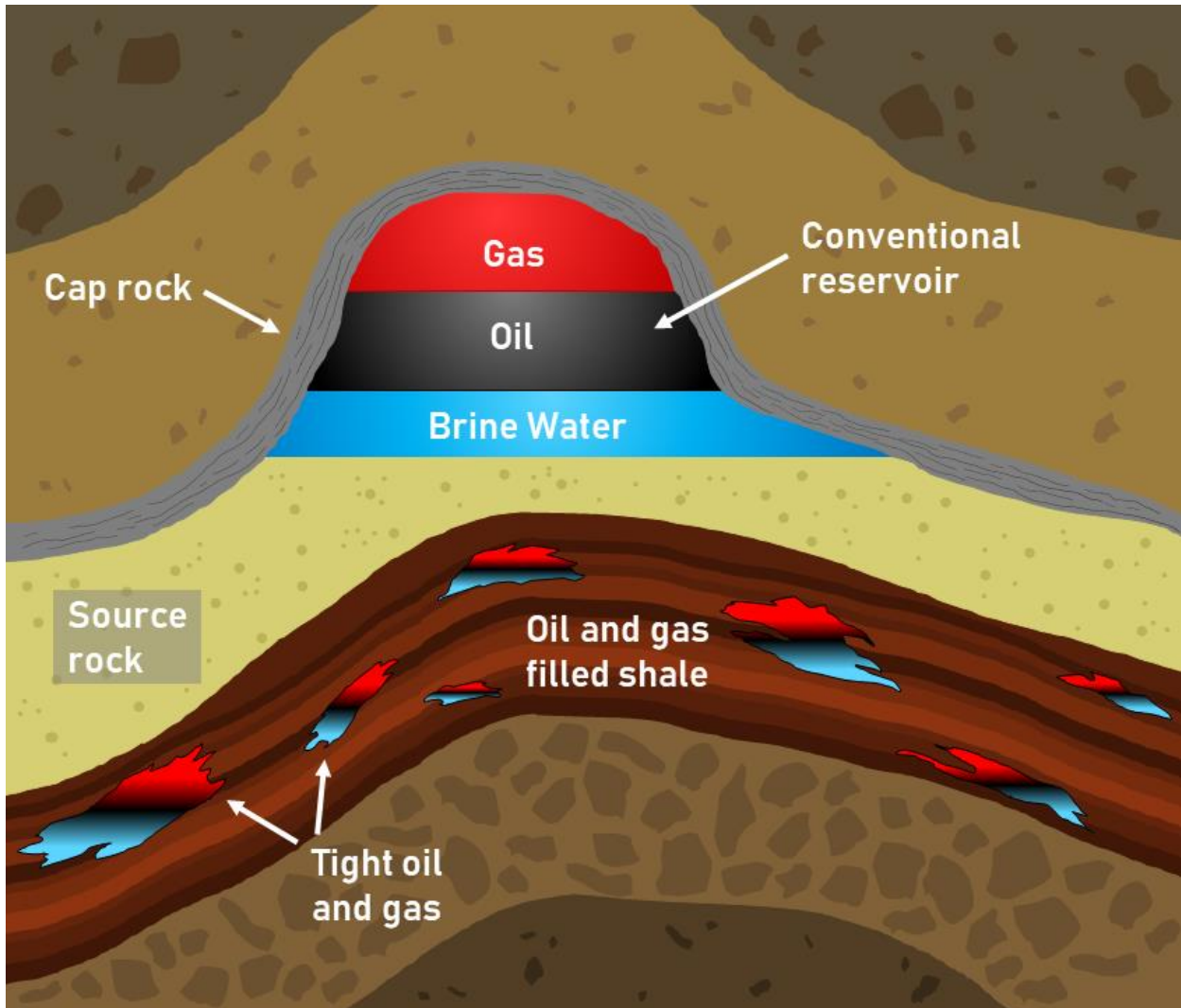


FIGURE A7. Schematic showing three sources of oil and natural gas: a conventional oil and gas reservoir, a tight oil and gas reservoir and an oil and gas filled shale.

### **Production and Separation of Oil, Gas and Brine**

This heterogeneity (distinct separation) of brine, oil and gas is disrupted by drilling and fracking processes. Disturbances caused by high intensity fracking and pumping cause oil, gas and brine to be brought to the surface as an emulsion (a homogenous mixture) (Figure A8). The amount of brine produced in the Williston Basin alongside oil and gas varies through time.

Newer wells typically produce about a 2:1 to 4:1 ratio of oil to brine whereas older wells produce ratios ranging from 1:2 to 1:100 of oil to brine.

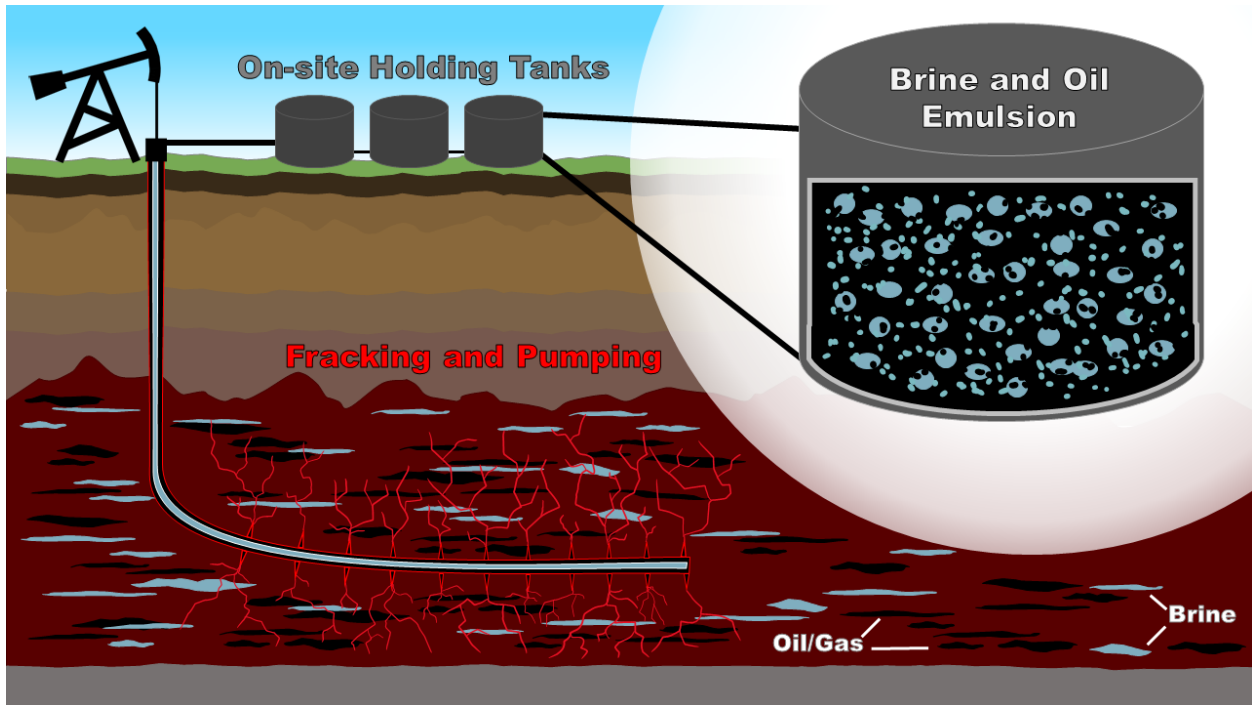


FIGURE A8. Fracking into an oil shale to access poorly connected reservoirs of oil, gas and consequently, brine water. High energy fracking causes oil and water to emulsify.

There are onsite and offsite processes that aim to separate brine from oil and gas because of the negative impacts that brine can have on machinery, refinery equipment and on the environment. Once at the surface, gas readily separates from oil and brine through density differences in onsite tanks leaving oil and brine behind. In these same tanks, some brine separates from oil without assistance but typically, additional heat, pressure, separation agents and mixing elements are necessary to remove as much brine from oil as possible before further, offsite, refinery processes can take place.

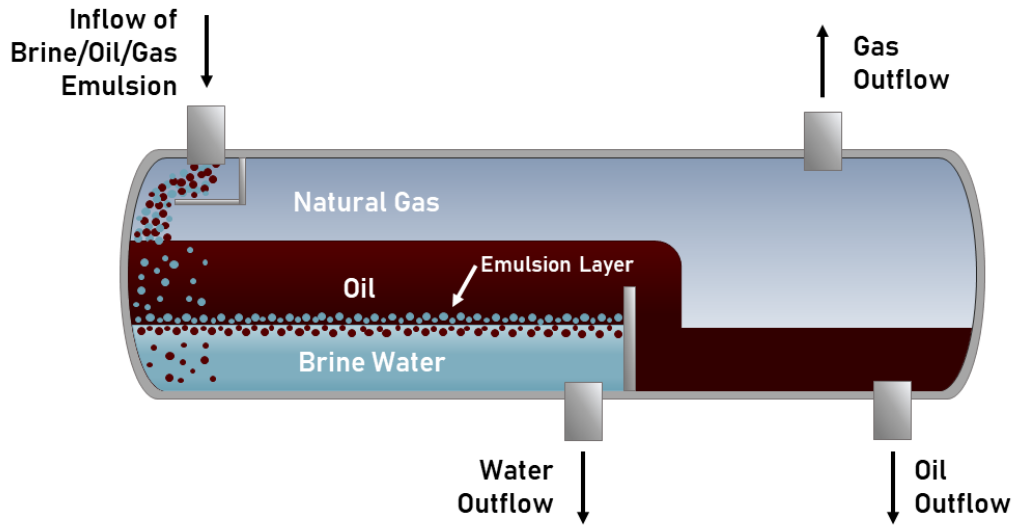


FIGURE A9. Simplified on-site tank used for the purpose of demulsifying brine, oil and gas.

Although Figure A9 shows a simplified version of how brine, oil and gas are separated from each other, it is an idealized schematic. As oil and gas flow out of on-site demulsifying tanks, temperatures can drop by over 100 °F. This can sometimes lead to further separation of brine from oil and gas causing there to be large pockets of brine in oil and gas pipelines. These pipelines are not constructed to handle brine and can eventually corrode, which leads to leaks.

### **Potential Risks of Disposal and Transportation**

Once brine is separated from oil and gas, it then needs to be safely disposed of. Disposal is typically done through deep well injection into the Dakota Formation (Figure A2) which is a Cretaceous (108-94 Ma) age rock unit nearly 2,000 ft below ground surface in western North Dakota. Pipelines are the most common mode of transporting brine to injection site (Figure A10a). Trucks are also used to transport brine because they're versatile for shorter distances (Figure A10b).





FIGURE A10. (a) Pipelines on a well pad (Harold Rhodes) and (b) an example of a tanker truck used to transport both fresh water and brine water (Sam Croat).

Most brine spills occur during the transportation of brine to an injection well site. In many cases, these spills can go initially undetected especially when pipelines fail underground. Brine spills can range from a few hundred gallons to upwards of a few million gallons. Brine impacted areas often exhibit sparse vegetation (Figure A11a) and an accumulation of salts at the surface (Figure A11b).



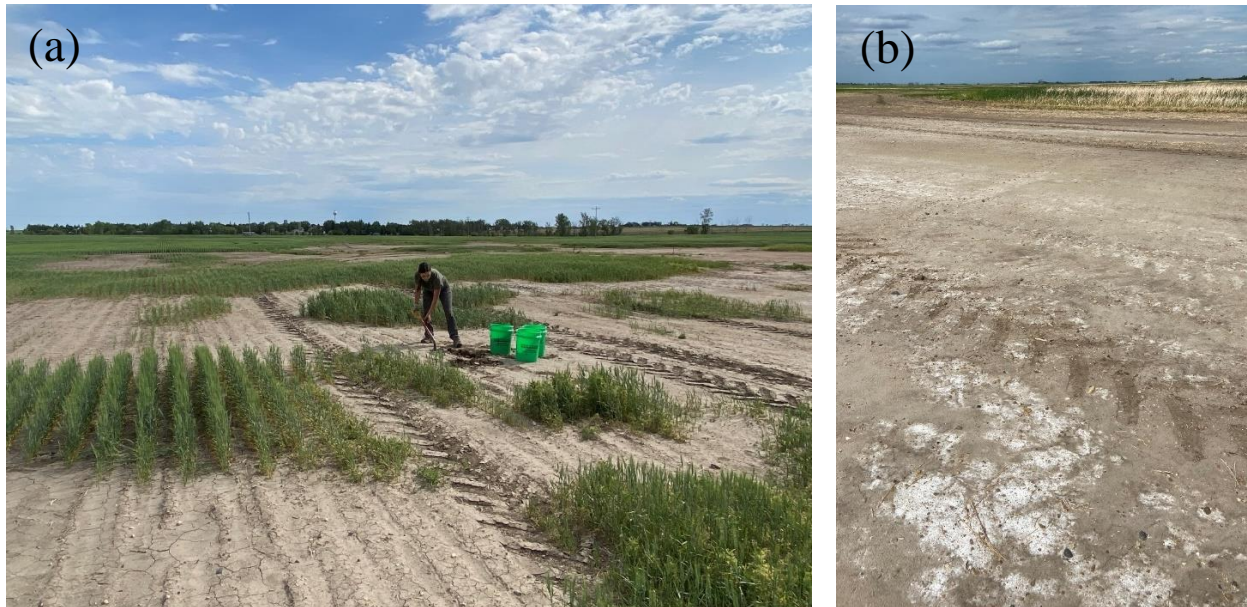


FIGURE A11. (a) Sparse Vegetation near a well-pad in Glenburn, ND and (b) salt crust that has accumulated at the surface near a well-pad in Glenburn, ND.

The log of these spills can be found on the North Dakota Department of Environmental Quality website: [https://deq.nd.gov/wq/4\\_spill\\_investigations/reports.aspx](https://deq.nd.gov/wq/4_spill_investigations/reports.aspx). Additionally, reporting a spill can also be done through the state of North Dakota website: <https://www.spill.nd.gov/>. Brine is an unavoidable by-product of the oil and gas industry. Close monitoring and quick mitigation of pipelines and leaks are especially important to prevent large, accidental spills from occurring and impacting large areas or volumes of soil and subsoil.

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