

**A GUIDE FOR REMEDIATION
OF
SALT/HYDROCARBON
IMPACTED SOIL**

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Remediation Philosophy

Goal: Return the site to a state consistent with original land-use.

- Based on practical, accurate, and reproducible procedures.
- Use of select analyses, measurement of key indicators, recommended treatment, and a follow-up program.
- Remediation process presented is continually being evaluated and improved.
- Depending on various factors, plan on 3-4 year remediation duration.

“Remediation requires patience.”

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Disclaimer

This remediation guide is published to be used as an aid to the petroleum industry to remediate soil contaminated with salt water or petroleum hydrocarbons.

The author and contributors to the publication are not responsible for any consequences or results that occur upon implementing any recommendation stated in this guide or stated in any oral presentation of this guide.

Tips For Use of the Field Guide:

1. Read and understand the various steps in the remediation guide before using the field guide.
2. Establish a record keeping system. Record all data, observations, and processes as soon as possible.
3. Maintain consistency in all tests and observations. Remember you are comparing data points to the control sample and to samples over time.
4. Always take the control sample first.
5. Accuracy and consistency will increase the rate of success.
6. The procedures used in this guide are designed to remediate a site over a 3 to 4 year period.

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INTRODUCTION

The goal of this Remediation Guide is to assist field personnel in restoring impacted soil to a state consistent with the original land use. Sections I through IX of the guide are intended as a field reference for remediation of salt and/or hydrocarbon impacted soils. Documentation of basic soil science used to develop the field guide is included as appendices E (Soil Properties) and F (Soil Chemistry).

This remediation guide is based on practical, reproducible, and field-friendly procedures. The remediation method requires a limited amount of analytical data to formulate a remediation procedure. The analytical methods can be conducted in the field by a trained technician or in a local laboratory. A nominal investment of time and equipment are required to perform these analyses and obtain accurate data. Steps detailing these analyses are outlined in the guide.

When the impact of a produced water or hydrocarbon discharge is examined, a number of critical factors can indicate the immediate and long-term impacts on soil structure and fertility. The use of and response to these factors are key to a successful remediation.

Field experience has demonstrated a success rate greater than 80% when the methods in this guide are properly followed. The remediation is based on a 3 to 4 year duration, with the exception of difficult problem sites, where only partial remediation may be obtained. In these cases, additional remedial actions may be warranted.

The remediation method in this guide utilizes naturally occurring soil amendments, basic soil chemistry, and time

to achieve success. Gypsum, the major remediation amendment, is a naturally occurring product in the earth's crust. Additionally, HumexTM, (also known as leonardite) is a secondary amendment that is also naturally-derived.

Cost of the remediation process is an important part of the remediation plan; however, cost may vary significantly from area to area. Therefore, costs are not included in this guide.

Record keeping can be tailored to the unique needs of each operator. There is an example of a record keeping form in Appendix D to help organize and archive site and remediation information. The record keeper may prefer to develop their own format and strategies for documentation depending on company requirements and data needs. The use of a GPS unit, a computer, and appropriate software will increase accuracy and reduce time spent on documentation.

I. IMPACT OF SALT/HYDROCARBONS ON SOIL

A. Impact of Salt on Soil

There are three major impacts on soil and plants when salt water spills occur.

- Soil particles are dispersed which destroys aggregation
- Osmotic potential reduces the plants ability to up take water
- Ionic balance of the soil solution is impacted reducing nutrient absorption

1. Impact of sodium on soil and plants

The Na^+ ion of sodium chloride causes the dispersion of the soil. Due to the large number of Na^+ ions available, the Na^+ ions are able to exchange with a sufficient number of the Ca^{++} and Mg^{++} ions. The Na^+ ion is a large ion therefore weakening the normal soil aggregate stability. The major impact of a salt water spill is the destruction of the soil aggregates by dispersion. Dispersion will occur when more than 15% of the cation exchange capacity sites on clays are occupied by sodium ions and when the total EC in the soil solution is low. The potential dispersion of a soil can be determined by the exchangeable sodium percentage (ESP).

Soil dispersion results in:

- Loss of soil structure
- Loss of pore structure
- Reduced air and water movement
- Reduced bioactivity
- Reduced nutrient transfer

- Increased water run off and erosion of soil

Due to the major impact of the Na^+ ion in the soil root zone, the remediation process is focused on restoring the soil aggregation. When the soil aggregation is restored the secondary impact due to osmotic pressure will also be reduced.

In the remediation process it is very important to treat the soil as soon as possible. Rain on the spill site before gypsum is added will increase the rate of soil dispersion.

As the salt (NaCl) concentration in the water solution increases, the change in osmotic potential makes the roots work harder to take in water. The amount of water intake by a plant will directly affect plant growth. As rain fall events occur salt in the water solution will be diluted. In most cases the first year rain fall (12-14 inches of rain) will significantly reduce the salt concentration in the soil solution.

2. Impact of chloride on soil and plants

Depending on the chloride concentration in the spill event, direct chloride toxicity can occur at high levels of Cl^- ions. Sensitivity to the Cl^- ion will depend on the plant species. The Cl^- ion in the soil water solution is usually flushed below the root zone by the first year of rain fall.

The Cl^- ion, due to its negative charge, moves rapidly out of the root zone through the negatively charged soil aggregates. Chloride concentration does not have a direct impact on soil structure except for being one of the ions which increases the osmotic potential in the soil solution.

B. Impact of Hydrocarbon on Soil

When a hydrocarbon spill occurs, in most cases, salt water is also involved. These spills can be considered an emulsion spill. The impact from both sodium chloride and hydrocarbon affects soil structure and plant growth.

1. Impact of hydrocarbon on soil structure

When hydrocarbons are spilled on soil, the light hydrocarbons will evaporate according to the type of hydrocarbon, temperature, and wind conditions. It is not uncommon to see 20 to 30% of the hydrocarbon evaporate. As might be expected, the higher the API gravity of the crude, the higher the evaporation rate.

The hydrocarbons which do not evaporate will move through the soil. Soil texture and moisture content will determine how fast and how far the hydrocarbons will migrate into the soil profile.

Hydrocarbons move rapidly in moist soil conditions. When soils are saturated (pores filled with water), hydrocarbon movement is reduced. Similarly, in dry soil conditions hydrocarbon movement through the soil will also be reduced. In general, hydrocarbon moves as a contact front through the soil matrix. As the soil wets, the hydrocarbon front moves forward. Hydrocarbon movement through soil is not homogeneous.

Hydrocarbon spills impact soil by:

- Affecting soil physical structure by coating soil aggregates
- Affecting soil water holding capacity
- Reducing and diverting water infiltration into the soil

- Obstructing air and water movement in the soil matrix
- Reducing cation/anion ion exchange on soil aggregates

At low hydrocarbon concentrations, the impact on plants is due to the physical impact on soil structure. Soils contaminated with 1 to 2% hydrocarbon can be remediated with the normal salt spill remediation process. At hydrocarbon concentrations of 4% or greater, some direct toxicity to plants occurs. At hydrocarbon concentrations of 7%, direct toxicity to plants occurs. These actual hydrocarbon concentrations will vary depending on the type of hydrocarbon, type of soil and the species of plants. At hydrocarbon concentrations greater than 2%, additional remediation steps are required which are described in the remediation amendments section.

2. Impact of fresh water on salt water spills

During clean up of hydrocarbons, water or hot water is often used to assist the hydrocarbon removal. DO NOT USE FRESH WATER TO CLEAN UP HYDROCARBONS WITHOUT A CALCIUM AMENDMENT. The most efficient method is to add “BioCal” to the wash water. BioCal primarily contains calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and can be diluted with fresh water at a ratio of one part BioCal to 50 parts of fresh water. If a large amount of washing is required the mix ratio can be increased to 1 to 100.

The calcium amendment can also be over sprayed with a 1 to 20 BioCal to fresh water solution before and periodically during the hydrocarbon clean up. If Bio Cal is not available, gypsum can be added at 5 tons/acre before hydrocarbon washing is initiated.

NOTE: WASHING EMULSION SPILLS OR RECEIVING RAIN PRIOR TO ADDITION OF A CALCIUM AMENDMENT CAN INCREASE THE RATE OF SOIL DISPERSION. THIS WILL ALSO MAKE REMEDIATION MORE DIFFICULT BY INCREASING AMENDMENT CONCENTRATION AND INCREASING REMEDIATION TIME.

Since BioCal is predominantly $\text{Ca}(\text{NO}_3)_2$, the use of BioCal is restricted in environmentally sensitive areas. Do not use BioCal near ponds or water ways. The nitrates in the BioCal mixture are highly soluble.

C. Process of Remediation

The primary goal of remediation is to reduce the amount of soil dispersion caused by the Na^+ ion. This is accomplished by adding calcium ions. Gypsum is a good source of Ca^{++} ions in the form of calcium sulfate (CaSO_4).

As stated earlier, it is important to add gypsum before washing or rainfall occurs on the site.

The first step is to prepare a suitable soil surface to receive the remediation amendments. Under normal conditions, work the top 4 inches of soil similar to a “seed bed.” In some areas a layer of hard soil, “hard pan”, will be encountered at 6-8 inches into the soil profile. When core tests indicate an impermeable “hard pan,” the area should be tilled to 10-12 inches. It is important to have an area below the “active root zone” for flushing of the soluble salts out of the active root zone. For remediation purposes, this is considered below 6-8 inches.

Following the selection of remediation amendments, the amendment material is worked into the soil. In most cases, it is recommended to blend the amendments into the soil by

working the top 2 inches of soil. Rototilling or disking are both acceptable methods for this process.

The most critical variable in the remediation process is rainfall. In most remediation processes it takes 12-14 inches of moisture to remediate 10,000 uS/cm of electrical conductivity (EC). This is of particular concern in North Dakota where the annual rainfall is a limiting factor. Ionic exchange can occur during winter months; however, the rate of remediation appears to be slower. This could be a function of temperature reducing reaction rates or the limited water movement under frozen conditions.

It generally requires 3-4 years to complete remediation of a 30,000 uS/cm EC soil. This of course is a general estimate of the time required for remediation. Patience is required for a successful remediation.

1. First year remediation

In the first year of remediation, repair to dispersed soil is beginning but may not yet be visually evident. The remediation rate during this first year is slow but accelerates as aggregation of the soil is restored. Close evaluation of the soil will reveal some restoration of the aggregate soil particles and weeds may be present. Soil sampling and testing is generally not required in the first year of remediation.

2. Second year of remediation

In the second year of remediation, aggregation repair is evident and weeds will begin to appear. It may be possible to control weeds by mulching in mid summer to late summer. Weeds should be cut or mulched before seeds are formed.

Late in the second year the site should be sampled and EC and pH analyses conducted. In addition, aggregation and bio-activity should be evaluated. A 40 to 50% remediation improvement at the end of the second year should be expected. If good results are obtained, dormant seeding is recommended. Plant growth on the impacted site will aid the remediation process.

3. Third year of remediation

At the end of the third year the site should be re-sampled and tested for EC, pH, percent aggregation, and bio-activity. A 70 to 90% remediation improvement should be observed. Depending on the site location, the landowner can be allowed to work or plant the site. If the site does not reach 70% of remediation and a cover crop was not planted in year 2, a dormant seeding is recommended. The decision to plant a cover crop and the type of cover crop planted should be approved by the state agencies and the land owner.

4. Fourth year of remediation

By the end of the fourth year, the remediation process should be complete. If the remediation is not complete, additional amendments must be added. Determine the percentage of remediation not accomplished (subtract the current EC reading from the initial EC reading) and reapply this amount of amendment plus 10% to the site. If the EC remediation percentage is not determined, repeat the original amendment at 50% of the original concentration. If the remediation results are not successful it may be beneficial to review the history of the site and the original evaluation data.

II. SITE EVALUATION

Proper protocol must be followed to identify and report spill occurrences involving salt water and/or hydrocarbon. The area supervisor or environmental technician must follow the prescribed procedure and rules to document the event. Each government agency and operator will have specific reporting procedures. Comprehensive and accurate record keeping is imperative during the remediation procedure.

Several examples of forms used in the remediation processes are provided in the appendices. These forms are provided as templates and can be modified as necessary.

A. Measurement of the Site

The process of remediation should begin as soon as possible following an incident. Any precipitation at the site prior to placement of amendments will increase the difficulty of an effective remediation. A thorough evaluation and accurate record-keeping are critical to remediation success. Measurement of the site should include the following steps:

- Determine the size of impact area by measuring the perimeter. The recommended method utilizes a global positioning system (GPS) unit. If a GPS unit is unavailable, a surface wheel will suffice.
- Rule of thumb: When measuring the perimeter, take the perimeter measurement 2 feet out from the impacted area to streamline irregularities in its shape.
- Calculate the square footage of the impact area.

- One acre = 208.71 ft x 208.71 ft = 43,560 sq ft.
- Secure area if necessary (fencing or flags).
- Document the initial site with pictures if possible.

B. Type of Impact

Generally speaking, oil and gas environmental impacts can be viewed as either current or historical. With the exception of initial response, the approach to their respective remediation procedures is similar. However, in many cases, the historical site may be more difficult to remediate due to age of the impacted site.

Oil and gas environmental impacts are listed below by type. Some cases may require special remediation procedures:

- Salt water (brine)
- Hydrocarbons
- Salt water and hydrocarbons (emulsion)
- Erosion
- Weed control chemicals
- Old pits
- Decommissioning of site – removal of base construction material

C. Area Topography

Site grade and direction should be recorded in both the permanent record and site sketch. Special attention should be devoted to topography adjacent to the impacted site at potentially sensitive areas.

Determine site grade and direction:

- Flat < 1%
- Slight 1 – 2%
- Moderate 2 – 5%
- Steep >5%

Examine the surrounding topography; record hills, valleys, bodies of water, and other significant land features.

Note how to access the impact area.

Communicate with the landowner regarding your remediation plans and address any landowner concerns.

Identify any erosion problems.

- Repair major erosion trails.
- Determine erosion causes and establish erosion prevention program if required.
- In most cases (accidental spills), it may not be possible to repair erosion trails before amendments are placed. Repair erosion problem during remediation.
- In historical remediations, site erosion and lease cover material should be addressed before amendments are applied.

D. Soil surface

Identify the general land use such as crop, summer fallow, pasture, etc., and the type and amount of plant growth.

Identify predominant soil types:

- Sand
- Silt
- Clay

Note whether scoria, gravel, or heavy clay removal is required. Will vary by location.

Before a decision is made to remove soils due to salt or hydrocarbon contamination, the following factors should be considered:

- Soil test results and depth of salt penetration – if contained in top 1 – 2 inches removal may be the best option.
- Soil removal (and replacement) is generally recommended for soil conductivities exceeding 35,000 uS/cm.
- Consider sensitivity of area and time required to remediate.
- Hydrocarbon contamination depth and concentration.
- Replacement soil should have an electrical conductivity below 1,000 uS/cm.

Note uniformity of site. This information will be useful in determining sampling procedure.

E. Record Keeping

Samples of record keeping forms are located in the Appendices.

Note: Accurate record keeping is critical to remediation success.

III. Soil Sampling

Three major factors must be considered when developing a sampling procedure for an impact site: number of samples, uniformity of soil surface, and method of obtaining samples.

A. Number and Location of Samples

1. Number of samples

- 1/3 acre, 14,520 sq ft = 3 site samples, one control
- 2/3 acre, 29,040 sq ft = 4 site samples, one control
- 1 acre, 43,560 sq ft = 5 site samples, one control

Obtain the control sample first, approximately 150 ft from the area of impact. The control sample should represent the area soil. If in question, take an extra control sample and average the EC readings.

2. Site uniformity

Adjust sample number according to site uniformity. Non-uniform features may include heavy clay, sand, heavy scoria, vegetated vs. non-vegetated areas, grade, and other areas significantly different from control:

- More than three non-uniform features - add one sample point.
- Less than three non-uniform features - reduce one sample point in sites greater than two thirds acre.

B. Procedure for Taking Soil Samples

The technique for taking soil samples must be standardized from sample to sample and site to site. A standard procedure will enable accurate comparison of accumulated data.

- One inch diameter coring tube cut is the most useful soil sample. Sample depth is 6 inches (0 – 6 inch sample).
- If coring tube is not used, cut an 8 inch deep face with a tilling spade and use a spatula or garden trowel to obtain sample. The sample should be 6 inches deep, 1/2 inch wide and 3/8 inch thick.
- Select sample points to best represent the soil surface of the impact area. Mark location with flags or GPS. Mark location on site map. Sample the non-uniform area if it represents 1/4 of the site area.
- Place the soil sample in a pre-labeled plastic bag. Label bags with pertinent identifying information including:

Site

Date

Sample ID number

Technician's initials

- Roll the bag, eliminating any air trapped within. Do not leave samples in the sun.
- Conduct EC and pH tests within 72 hours if possible. Record results as you complete each analysis.

IV. Procedure for Conducting Physical Evaluation of Soil

Four physical evaluations of the soil will aid in determining the impact of the incident. In addition, these evaluations will aid in determining the proper remediation procedure and in monitoring remediation progress.

A. Percent Aggregation

Determine the amount of aggregation by using the top 1-2 inches of the soil profile.

- Poor – no aggregation.
- Fair – small clumping but majority of loose particles.
- Good – Moderate aggregation throughout soil sample.
- Excellent – Consistent throughout sample – garden quality soil.

B. Biological Activity

Determine, by the sense of smell, the presence and amount of biological activity in the top 1-2 inches of soil. The relative amount of “earthy” odor will quantify the amount of biological activity.

- None – No earthy odor.
- Fair – Faint earthy odor.
- Good – Obvious earthy odor.
- Excellent – Heavy earthy odor.

C. Clay Content of Soil

The clay content of the soil can be determined by the “ribbon test,” whereby a small amount of soil is squeezed

and rolled between the thumb and forefingers to determine the relative clay content of the soil. Soil that remains intact but curls upon itself is considered to contain greater than 50% clay. Although the type of clay will impact the soil quality, clay type is not considered in the test matrix.

- < 35% - normal productive soil
- 35 – 50% - clay soil
- >50% - predominantly clay

Note: If it is determined that the soil contains >50% clay, a 20% increase in gypsum should be considered.

D. Depth of Topsoil

Depth of top soil can be determined by measuring the soil profile from the core sample or from the sidewall cut. A thicker topsoil layer is ideal for supporting plant growth.

- Shallow: 1-2 inches
- Moderate: 2-4 inches
- Productive: 4-6 inches

Adjustments:

- Top soil 1-2 inches – increase Humex™ concentration by 30%.
- Top soil 2-4 inches – increase Humex™ concentration by 20%.
- Top soil 4-6 inches – no increase required.

V. Soil Analytical Tests

A. Analytical Procedure to Determine the Electrical Conductivity (EC) of Soil:

- Soil sample preparation
 - a) Mix soil sample from 0-6 inch analysis.
 - b) If soil is “wet,” reduce soil moisture content by air drying.
 - c) If soil is “damp,” proceed with analysis.
- Measure a level tablespoon of soil into 60 ml of distilled water. This will result in a 1 to 5 dilution of soil, one part soil into four parts distilled water. The volume of one level tablespoon is 15 ml.
- Shake mixture for 2 minutes. After mixing, allow sample to stand for additional 2 minutes.
- Prepare the syringe with the millipore filter adaptor and draw the fluid sample (0.5 to 1 ml) into syringe.
- Place the fluid sample onto the instrument sensor and discard the first sample load. Repeat this “flushing” procedure, then test and record the third load.
- Calculate the EC by multiplying the EC reading on the meter by five.

Instrument EC reading x 5 = soil EC

- Wash the instrument sensor using a dedicated “wash syringe” and distilled water.

- Record results of the test and other information and disable and discard the syringe.
- Repeat procedure for additional depths, if necessary.

Note: Use the same fluid sample to measure the pH. No additional calculations are needed; pH is measured directly by the meter.

Note: Most EC units read as microsiemens per centimeter (uS/cm). In addition, high EC readings may read as millisiemens per centimeter (mS/cm). It should be noted one millisiemen (mS/cm) is equal to 1,000 microsiemens (uS/cm). Either unit may be used, but to compare data, choose one unit for all analyses, and convert all readings to the chosen unit. This remediation guide uses uS/cm.

A siemen is an inverse ohm (conductance = $1/\text{resistance}$). The original siemen was measured though a distance of one meter. Most of the field equipment measure one centimeter unit (cm). Although not precise, one millimhos/cm is equal to one millisiemen/cm. For remediation purposes the field guide uses mS/cm or uS/cm.

B. Ribbon Test

- Take a sample of soil, add water, and make a ball (size of a golf ball).
- Work soil like putty.
- Squeeze out a ribbon between the thumb and forefinger.
- Sand will feel gritty, silt is smooth and silky, and clay is sticky and forms a ribbon.
- Ribbon of 2 in. or longer -- heavy clay -- 50% plus clay content.

VI. Selection of Remediation Amendments

A. Generic Amendments

Quantity of required amendments can be selected from the generic table provided. The main criterion used in this table is electrical conductivity (EC) of the soil. The generic table is applicable for soils in most of the oil producing counties of North Dakota. Nevertheless, for some counties, the best results may require minor adjustments to amendment quantities.

To tailor chemical amendments most accurately, a set of guidelines are provided below. If the guidelines are not followed, total remediation time may be longer.

Using the EC values from the soil analysis, select the amount of gypsum and HumexTM required. The quantity of amendments is given as pounds/1000 sq ft or tons/acre. Note: there are 43,560 sq ft in one acre. EC values are obtained by calculating the average EC of samples in the impacted area.

The remediation procedure is designed to be completed in 3-4 years.

GENERIC AMENDMENTS TABLE

Electrical Conductivity	Gypsum		Humex	
	lbs/1000 sq ft	tons/acre	lbs/1000 sq ft	tons/acre
0 - 5,000	180	4	100	2
5 - 7,000	227	5	136	3
7 - 10,000	272	6	180	4
10 - 13,000	318	7	250	5.5
13 - 16,000	364	8	318	7
16 - 20,000	450	10	364	8
20 - 25,000	450	10	364	8
25 - 30,000	450	10	364	8

B. Site Preparation

Depending on the impact on the site, soil preparations prior to the addition of amendments may be necessary. On historical sites, removal of scoria or heavy clay cover is often necessary. In some cases, repair of erosion trails and soil replacement may be required. In discharges of hydrocarbon, salt water, or emulsion, the first priority is fluid containment, recovery, and cleanup.

1. Initial site preparation

- Conduct accidental discharge impact assessment and reporting procedure as required.
- Protect sensitive environments with berms and dikes.

- Initiate cleanup as soon as possible.
- Remove scoria if necessary. Remove heavy clay where used as cap material.
- Apply BioCal or gypsum stabilization amendments as soon as possible (if delay in remediation process seems likely).
- Spray with $\text{Ca}(\text{NO}_3)_2$ solution (BioCal diluted with fresh water 30:1). Application rate of BioCal is 2 barrels of $\text{Ca}(\text{NO}_3)_2$ per acre or treat area with gypsum at rate of 300 lbs/1000 sq ft or 4 tons/acre.
- Work top 2 inches of soil when possible.

Note: The success of any remediation will be significantly reduced if rain or other heavy precipitation occurs on site prior to the application of appropriate amendments and will increase the time and effort required to adequately restore a site to its original condition.

C. Addition of Amendments

1. Work soil to prepare for remediation amendments.
 - Work soil 4-6 inches.
 - Use disc or rototill equipment.
 - In some cases deeper spiking of the soil may be required to break down “hard pan” area of the soil profile.
2. Select amendment treatments from the generic table.
 - Gypsum, agricultural grade if possible.
 - HumexTM.
 - Fertilizer 10/20/10/10 or equivalent in area. (nitrogen, phosphorous, potassium, sulfur)
 - Sulfur if required.

3. Work soil to incorporate the amendment material to 2 inches.

D. Remediation Amendments

Except for commercial fertilizer, all amendments are naturally occurring products. The amendments, in addition to remediating the salt or hydrocarbon contamination, will improve the overall fertility of the soil. The generic amendment recommendation may not meet the requirement of every site and may require adjustments for a more tailored fit. Past experience has shown generic amendments were greater than 80% successful.

1. Gypsum

There are several different grades of gypsum. If possible use agricultural grade gypsum which is more economical but not readily available in North Dakota. Agricultural grade gypsum contains particles ranging from very small dust to 3/8 of an inch. Solubility of gypsum depends on particle size and moisture content of the soil and plays a role in remediation time.

When wallboard gypsum is used, the particle size is uniformly small. Solubility will be more uniform as well. Wallboard grade gypsum will place more calcium in solution per unit of time at a constant moisture level; however, this grade of gypsum is more expensive.

2. HumexTM

HumexTM is the trade name for leonardite, a naturally occurring mineral closely related to soil humus. Humus is an important element of soil fertility. In

addition to improving soil fertility, Humex™ can be used to reduce weed killer chemical toxicity. Add Humex™ according to the Generic Amendment table presented previously.

3. Fertilizer

Fertilizer stimulates microbial growth and increases rate of hydrocarbon biodegradation.

Fertilizer should initially be applied at a rate of 5 lbs/1000 sq ft or 220 lbs/acre.

Use 10/20/10/10 or equivalent (nitrogen, phosphate, potassium, sulfur). If hydrocarbon contamination is above 1%, increase fertilizer to 20 lbs/1000 sq ft or 880 lbs/acre.

If hydrocarbon is visible in the second year of remediation, reapply fertilizer at 10 lbs/1000 sq ft. Work soil to aerate and mix in fertilizer to 4 inches.

4. Sulfur

A small amount of sulfur is included with regular fertilizer but more can be added to reduce pH.

2,200 lbs/acre of sulfur is required to reduce pH by one unit (50 lbs/1000 sq ft).

If pH is greater than 8.7, additional sulfur is needed.

Reduction in pH will increase solubility of gypsum and increase remediation rate.

Note: If sulfur is not used in cases where pH is high (>8.6), remediation time will be extended.

E. Adjustments of Amendments

- Clay content
Clay heavy and content greater than 50% - increase gypsum concentration by 20%.
- Depth of top soil
Shallow (1-2 inches), increase HumexTM concentration by 30%.
Moderate (2-4 inches), increase HumexTM by 20%.
Productive (4-6 inches), no increase required.
- pH > 8.7
Increase gypsum by 25 lbs/1000 sq ft (1,100 lbs/acre).

F. Winter Remediation

The objective of remediation of produced fluid spills during the winter is containment and recovery. Very little useful remediation can be accomplished when the soil is frozen. The standard remediation process can commence when the soil is no longer frozen and the soil is dry enough to work with tools.

- Contain and recover as much spilled fluid as possible.
- **NEVER WASH A SPILL WITH FRESHWATER.** Doing so will set sodium (salt) on the clay particles and cause dispersion of the soil and will prolong the total remediation process. To increase hydrocarbon recovery, wash area with a 50:1 solution of fresh water and $\text{Ca}(\text{NO}_3)_2$ (Bio Cal).
- In cases where additional hydrocarbon recovery is not feasible, overspray with a 30:1 solution of

freshwater and $\text{Ca}(\text{NO}_3)_2$ (Bio Cal) at a rate of one 55 gal drum/acre.

- As soon as possible, after the soil has thawed, test the soil. If average soil EC is greater than 20,000 uS/cm, overspray with 20:1 freshwater and $\text{Ca}(\text{NO}_3)_2$ (Bio Cal) at a rate of one 55 gallon drum/acre.
- When the area is dry and workable, conduct the regular generic remediation.
- Over spraying with Bio Cal can reduce the gypsum requirement by 30%.

G. Hydrocarbon/Salt Water Spill Remediation

- Conduct initial containment, recovery, and cleanup as required.
- If hydrocarbon concentrations are less than 1%, no additional treatment is required.
- If hydrocarbons are greater than 1%, follow generic amendment table with the following adjustments:
 - Increase HumexTM by 30%.
 - Increase fertilizer by 20%.
 - Work area to 4 inches two to three times per year until remediation is complete.
 - Evaluate once per year. If required, repeat the HumexTM and fertilizer treatment and work soil two times per year.
 - When hydrocarbon contamination is >5% the remediation should be on a case by case basis.

VII. ALTERNATIVE REMEDIATION OPTIONS

A. Soil Removal

- When the average EC of the 0-6 inch samples is greater than 35,000 uS/cm, soil removal and replacement may be more economical than treatment.

Additional EC measurements are required to determine precisely where the salt contamination is located within the soil profile. Use the same soil analysis procedures as presented previously; the only difference is that specific soil profile intervals are being tested.

Test EC at 0-1 inch

Test EC at 1-2 inches

Test EC at 2-3 inches

Test EC at 6-7 inches

If the EC tests indicate the majority of the salt is concentrated in the top of the soil profile, removal and replacement is the remediation of choice.

- When removal and replacement remediation is used, the quality of the soil replacement is important. Electrical conductivity of replacement soil should be 1,000 uS/cm or less. Test the replacement soil at the source before the soil arrives at the site.

Note: Landowner's consent is required for soil replacement.

B. Manure Amendments

Manure can be successfully applied as an amendment if a supply of 6 to 8 year old manure is available. Three inches of manure is equal to approximately 6 tons per acre of gypsum.

- Add 3 inches of manure and work material into top 4 inches of soil.
- Need landowners consent to use manure. In most cases, the manure has to come from the landowner's property.
- Manure can carry numerous weed seed species – the number of live weed seeds is reduced by the aging process.
- Manure has a high nitrate content. Do not use manure near ponds, streams, water supplies, and residences.
- Work soil two times in the second and once in the third year to stimulate remediation and bacterial growth.
- Control weeds by mulching or mowing before weed seeds mature.
- Remediation time may be extended by one year if manure is used.

VIII. Remediation Monitoring and Closure

During the remediation process, some monitoring should be conducted to determine the progress of the remediation. In the more difficult remediation sites, some adjustment may be necessary. Note, the remediation process normally requires 3 to 4 years to complete.

A. Monitoring

First year: monitoring is not required. In some cases, weed control may be required. Mow weeds before seeds drop.

Second year: conduct EC analysis, percent aggregation, and bioactivity at the original sample points. A 40-50% remediation improvement should be observed. Make any adjustments if required. Weed control is usually required; possibly 2 – 3 times per year. In some cases, cover crop should be seeded as dormant seeding.

Third year: conduct EC analysis, percent aggregation, and bioactivity at the original sample points. A 70-100% remediation improvement should be observed. Record plant type and growth. Make any adjustments required.

Fourth Year: remediation should be complete and all goals of the remediation process achieved. If remediation is not completed, the site requires re-evaluation and causes other than salt contamination should be considered. Additional treatments may be required. Repeat the original amendments at 50% concentration.

1. Incident factors affecting remediation
 - Concentration of salt.
 - Concentration of hydrocarbons.
 - Remediation is not a linear relationship to contamination concentration.
2. Environmental factors affecting remediation
 - Moisture (minimum requirement of 12 – 14 inches rain per year)
 - Soil type
 - Soil texture
 - Past usage
 - Grade/slope

- Drainage
- Temperature

B. Site Closure

1. Who determines site closure:
 - a) NDIC representative
 - b) Operator: Environmental Technician, Foremen, and Environmental Coordinator
 - c) Landowner
2. Closure Criteria
 Evaluation and consensus determine when the remediation has been completed. Criteria used to determine completion of remediation include:
 - Plant growth
 - Aggregation of soil
 - Bioactivity of soil
 - Electrical Conductivity (EC)

EC guideline: 80% of control EC + control EC

Example:	Control EC	600 uS/cm
	80% control	480 uS/cm
	Endpoint	1080 uS/cm

Endpoint should be achieved in 4 years remediation.

IX. SUMMARY OF REMEDIATION GUIDE

Site Evaluation

Measurement of site

Type of impact

Area topography and soil surface

Soil Sampling

Number of samples

1/3 acre – 3 site samples plus one control

2/3 acre – 4 site samples plus one control

1 acre – 5 site samples plus one control

Site non uniformity – more than three, add one sample point

Take Soil Samples

Coring tube or tilling spade

0-6" deep sample

Place soil in pre-labeled plastic bag

Roll bag to eliminate air, do not leave bag in sun

If soil is wet air dry

Conduct Physical Evaluation of Soil

Percent Aggregation

Poor – no aggregation

Fair – few small clumps (25%)

Good – 60% aggregation

Excellent – garden quality soil

Biological Activity

None – no earthy smell

Fair – faint earthy smell

Good – obvious earthy smell

Excellent – heavy earthy smell

Clay Content (ribbon test)

< 35 % – normal productive soil

35 – 50 % – clay soil

50 % – predominantly clay

Depth of Top Soil

1 –2 inches – shallow

2- 4 inches – moderate

4 – 6 inches – productive

Soil EC Analysis

One tablespoon of soil into 60 ml distilled water

Shake mixture for 2 minutes

Draw fluid through filter into syringe

Place fluid into instrument and test third load

Calculate the EC by multiplying by 5

Soil pH Analysis

Use same fluid as for EC test to measure pH

The pH measurement is a direct reading

X. GLOSSARY

Acid soil: A soil with a preponderance of hydrogen ions, and probably aluminum, in proportion to hydroxyl ions. Specifically, soil with a pH value of less than 7.0; for most practical purposes, a soil with a pH value of less than 6.6.

Adsorption: The attachment of compounds or ionic parts of salts to a surface or another phase. Nutrients in solution (ions) carrying a positive charge become attached to (adsorbed by) negatively charged soil particles.

Aggregate, soil: Many fine particles held in a single mass or cluster. Natural soil aggregates, such as granules, blocks, or prisms, are called peds. Clods are aggregates produced by tillage.

Alkali soil: (1) A soil with a high degree of alkalinity (pH of 8.5 or higher) or with a high exchangeable sodium content (15% or more of the exchange capacity), or both. (2) A soil that contains sufficient alkali (sodium) to interfere with the growth of most crop plants.

Alkaline soil: Any soil whose pH is greater than 7.0.

Capillary water: The water held in the capillary, or small pores, of a soil, usually with a tension greater than 60 cm of water.

Cation exchange capacity (CEC): The total amount of exchangeable cations that can be held by the soil, expressed in terms of milliequivalents per 100 grams of soil at neutrality (pH 7.0) or at some other stated pH value. Soil clays and organic matter have a relatively large number of negative charge sites which retain cations in dynamic equilibrium with the soil solution. The number of cation

positive charges retained by 100 grams of soil is called the cation exchange capacity.

CEC: See cation exchange capacity.

Clay: As a soil separate, the mineral soil particles less than 0.002 mm in diameter. As a soil textural class, soil material that is 40% or more clay, less than 45% sand, and less than 40% silt.

Colloid soil: “Colloid” refers to organic or inorganic matter with very small particle size and a correspondingly large surface area per unit of mass. Most colloidal particles are too small to be seen with the ordinary compound microscope. Soil colloids do not go into true solution as sugar or salt do, but they may be dispersed into a relatively stable suspension, and thus, be carried in moving water. By treatment with salts and other chemicals, colloids may be flocculated, or aggregated, into small crumbs or granules that settle out of water. (Such small crumbs of aggregated colloids can be moved by rapidly moving water or air just as other particles can be.) Many mineral soil colloids are really tiny crystals, and the minerals can be identified with X-rays and in other ways.

Disperse: (1) To break up compound particles, such as aggregates, into the individual component particles. (2) To distribute or suspend fine particles, such as clay, in or throughout a dispersion medium, such as water. Dispersion is an electro-chemically induced process which results in physical movement of clay particles. Dispersion in soil is the reverse process to aggregation. When freshwater is applied after a saltwater spill, it dilutes and leaches the total salt concentration in the soil solution leaving mostly sodium cations to balance electrically the cation exchange sites. This condition of dilute total salts consisting of predominantly sodium cations causes clay particles to repel

from each other and migrate into pore spaces thereby clogging pores.

Dispersed soil: Soil in which the clay has dispersed. A dispersed soil consists of discrete soil particles which are not segregated into aggregates or structural peds. The soil macropores become clogged with particles and greatly restrict water and air movement into and through the soil.

EC: See electrical conductivity.

Electrical conductivity (EC): Conductivity measured directly in reciprocal units of resistance and reported in mmhos/cm. EC is an indirect measure of total dissolved solids (TDS).

ESP: See exchangeable sodium percentage.

Exchangeable sodium percentage (ESP): The extent to which the adsorption complex of a soil is occupied by sodium. Amount of exchangeable sodium expressed as a percentage of total exchangeable cations. Refer to discussion under exchangeable cation percentage. It is expressed as follows:

$$\text{ESP} = \frac{\text{Exchangeable sodium (meq/100g soil)}}{\text{Cation exchange capacity (meq/100g soil)}} \times 100$$

Field capacity: Water content of a soil after it has been saturated and allowed to drain freely, usually expressed as a percentage of its oven-dry weight or volume.

Gravitational water: Water that moves into, through, or out of the soil under the influence of gravity.

Hardpan: A hardened or cemented soil layer in the B or lower A soil horizon.

Humus: The well decomposed, more or less stable part of the organic matter in mineral soils.

Lime, agricultural: A soil amendment consisting principally of calcium carbonate, but including magnesium carbonate; used to furnish calcium and magnesium and to neutralize soil acidity.

Loamy: Intermediate in texture and properties between fine-textured and coarse-textured soils. Includes all textural classes with the word loam or loamy as a part of the class name, such as clay loam or loamy sand.

Osmotic: A type of pressure exerted in living bodies as a result of unequal concentration of salts in both sides of a cell wall or membrane. Water will move from the area that has the lesser salt concentration through the membrane into the area that has the greater salt concentration; it therefore, exerts additional pressure on its side of the membrane.

Pans: Horizons or layers in the soils that are strongly compacted, indurated, or very high in clay content.

pH, soil: The negative logarithm of the hydrogen-ion activity of a soil. The degree of acidity (or alkalinity) of a soil as determined by means of a glass electrode or indicator at a specified moisture content of soil-water ratio and expressed in terms of the pH scale (see reaction, soil).

Pore space: The total space not occupied by soil particles in a bulk volume of soil.

Porosity: The volume percentage of the total bulk not occupied by solid particles.

Saline-sodic: (1) A soil containing sufficient exchangeable sodium to interfere with the growth of most crop plants and also containing appreciable quantities of soluble salts. (2) A soil in which the exchangeable sodium percentage (ESP) is greater than 15% and the conductivity of the saturation extract (EC) is greater than 4 mmhos/cm.

Saline soil: A nonsodic soil containing sufficient soluble salts to impair its productivity. The conductivity of the saturation extract is greater than 4 mmhos/cm (at 25°C) and the pH is usually less than 8.3.

Salinity: A term describing water solutions containing dissolved mineral solids. The U.S. Geological Survey has assigned terms for degrees of salinity for waters with the following dissolved-solids concentration ranges:

Slightly saline	1,000 to 3,000 mg/L
Moderately saline	3,000 to 10,000 mg/L
Very saline	10,000 to 35,000 mg/L
Briny	over 35,000 mg/L

Sand: (1) A soil particle between 0.05 and 2.0 mm in diameter. (2) Any one of five soil separates, namely: very coarse sand, coarse sand, medium sand, fine sand, and very fine sand. (3) A soil textural class.

SAR: See sodium adsorption ratio.

Silt: As a soil separate, individual mineral particles that range in diameter from the upper limit of clay (0.002 mm) to the lower limit of very fine sand (0.05 mm). As a soil textural class, soil that is 80% or more silt and less than 12% clay.

Sodium adsorption ratio (SAR): The empirical mathematical expression developed as an index of the

sodium hazard in soils. The concentrations of sodium, calcium, and magnesium are expressed in meq/L:

$$\text{SAR} = \frac{[\text{Na}]}{\sqrt{\frac{[\text{Ca}] + [\text{Mg}]}{2}}}$$

Soil separates: Mineral particles less than 2 mm in equivalent diameter and ranging between specified size limits. The names and sizes (in mm) of separates recognized in the U.S. are as follows:

Very coarse sand	2.0 to 1.0 mm
Coarse sand	1.0 to 0.5 mm
Medium sand	0.5 to 0.25 mm
Fine sand	0.25 to 0.10 mm
Very fine sand	0.10 to 0.05 mm
Silt	0.05 to 0.002 mm
Clay	less than 0.002 mm

Soil solution: The aqueous liquid phase of the soil and its solutes that consists of ions dissociated from the surface of the soil particles and of other materials.

Structure, soil: The arrangement of primary soil particles into compound particles or aggregates. The principal forms of soil structure are as follows: *platy* (laminated), *prismatic* (vertical axis of aggregates longer than horizontal), *columnar* (prisms with rounded tops), *blocky* (angular or subangular), and *granular*. *Structureless* soils are either *single grained* (each grain by itself, as in dune sand) or *massive* (the particles adhering without any regular cleavage, as in many hardpans).

Texture, soil: The relative proportions of sand, silt, and clay particles in a mass of soil. The basic textural classes, in order of increasing proportion of fine particles, are *sand*,

loamy sand, sandy loam, loam, silt loam, silt, sandy clay loam, clay loam, silty clay loam, sandy clay, silty clay, and clay. The sand, loamy sand, and sandy loam classes may be further divided by specifying “coarse,” “fine,” or “very fine.”

Note: definition of the terms included in this glossary were excerpted from API publication 4663, Remediation of Salt-Affected Soils at Oil and Gas Production Facilities.

XI. APPENDICES

APPENDIX A

Environmental Equipment List

EC and pH meters

Filter

Spatulas

Measuring wheel

Hand-coring tool

Plastic, stacking sample cups (for mixing soil/distilled water)

Whirl-pak sampling bags – or Ziploc type plastic bags

pH buffer standards

Wash bottles (distilled water)

Hand garden trowel

Box to store smaller equipment

GPS

Vest

Logbook/composition book

Digital camera

Indelible pen (permanent marker or ink pen)

Site evaluation and investigation forms

APPENDIX B

Analytical Equipment and Amendment Suppliers

<u>Product & Product Information</u>	<u>Approx. Price</u>	<u>Suppliers</u>
<u>EC and pH Meters</u>		
Cary Twin EC Meter #2205	\$294.00	Spectrum Technologies, Inc. 23839 W Andrew Rd Plainfield, IL 50644 1-800-323-4340 www.specmeters.com
Cary Twin pH Meter #2103	\$249.00	
pH Pro Meter #2100A	\$169.00	
<u>Filters</u>		
National Scientific 25 mm Nylon Filters Part # F2500-50 Pore size – 5.0 um Qty/box – 50	\$133.00	National Scientific 1790 Satellite Blvd Bldg 180 Duluth, GA 30097 1-800-332-3331 www.nationalscientific.com
<u>Soil Sampler Tube</u>		
Cole-Parmer 10-inch, hand soil sampler Page 1744 #U – 99027-00	\$ 21.00	Cole-Parmer 625 East Bunker Court Vernon Hills, IL 60061 1-800-323-4340 www.coleparmer.com

LSS Lab Supplies
17-inch hand soil sampler
Page 802 #4BC - 106078

\$ 33.40

LSS Lab Supplies
PO Box 1368
Janesville, WI 53547
1-800-356-0783
www.lss.com

pH Buffer Standards

Pint size
pH 7.0
pH 10.00

\$ 9.00

Cole-Parmer,
National Scientific, or
LSS

Wash Bottles

250 ml

\$ 20.00

Any supplier listed
above

Miscellaneous

Tilling spade
Hand garden trowel—6 inch blade, narrow and sharp
Box to store smaller equipment
Plastic containers for mixing soil and distilled water
Distilled water
Spatulas
Measuring wheel
HumexTM

GeoResources, Inc.
P.O. Box 1505
Williston, ND 58802
(701) 572-2020
www.georesources.net

APPENDIX C

References and Additional Resources

1. Plaster, Ed. S. 1992. Soil Science and Management, 3rd Edition. Delmar Publishers.
2. Brady, N.C. and Weil, R.R. 2002. The Nature and Properties of Soil, 13th Edition. Prentice Hall.
3. Bohn, H.L. et al. 2001. Soil Chemistry. 3rd Edition. John Wiley and Sons, Inc.
4. American Petroleum Institute- Remediation of Salt-Affected Soil At Oil and Gas Production Facilities.

APPENDIX D

Record Keeping Form Example

Date_____Site Name_____

Location Information_____

Field_____County_____

Volume of Fluid_____

Oil/Water Ratio_____

Hydrocarbon present over one percent: yes / no

Area Impacted (sq. ft.)_____

Area H. C. penetrated soil over 10 inches (sq. ft.)_____

Immediate Spill Response_____

Type of release_____

Environmental Impact_____

Crop kind_____Range land_____Surface water_____

Special Environmental Endangerment_____

Remediation

Date_____Soil Work_____

Gypsum(lbs)_____HumexTM(lbs)_____Fertilizer(lbs)_____

Organic Material_____

Final Soil Work_____

Soil and Weather Conditions_____

Soil Work History_____

Form Completed

by:_____Date_____

APPENDIX E

Soil Properties

A. Physical Components of Soil.

Soil has four physical components; inorganic solids, organic matter, air and water. The typical proportions of these components in a healthy soil are:

- 45% inorganic solids
- 5% organic matter
- 25% air
- 25% water

Depending on the environment, the percentage of air and water in the pore spaces can change in a relatively short time period. In contrast, inorganic solids and organic matter remain somewhat constant but can change over long periods of time.

Although soil appears to be a simple media, it is the most complex ecosystem on our planet. As the world population grows, we are experiencing a high demand on our soils for agriculture use as well as for non-farm use. In addition, our soil quality is deteriorating due to poor agriculture practices.

Soil is a renewable resource but the process is very slow. Due to many factors, agricultural soil is impacted, rearranged, lost, and even destroyed as a functional agricultural media.

Soil fertility is the result of a relationship between physical, chemical, and biological components of soil in an interactive balance. The ratio of one element to another is more important in soil fertility than the level of total

nutrients. The key to soil fertility and plant growth is ionic balance among the four physical components in the soil solution.

1. Inorganic Solids

The inorganic parts of soil are made up of three components: sand, silt, and clay. These solids occur as a mixture of variously sized particles, known as “soil separates,” and contain various types of chemical charges. Soils types are classically differentiated by particle size.

	Particle Size (mm)	Particle Texture	Chemical Activity	Approx. surface Area (sq ft/g)
Sand	2 – 0.05	Gritty	Inactive	0.05
Silt	0.05 – 0.002	Silky	Inactive	5
Clay	< 0.002	Waxy	Active	5,000

The various amounts of each soil separate (sand, silt, and clay) will determine the properties and fertility of soil. Clays and organic matter are chemically active (are negatively charged) whereas sand and silt are not. Organic matter should also be considered a soil separate even though it is not included in particle size classification. Nevertheless, organic matter in soil constitutes a major role in soil fertility and plant growth. It is common for fertile soil to contain 5% organic matter.

Soils also contain large-size particles (> 2 mm) like gravel and stones. These larger sized particles are not a major concern unless they occupy large volumes of space in the soil.

The sand and silt particles commonly consist of quartz, mica, and feldspar minerals. These particles are not chemically active and function as a media for plant roots and associated chemical reactions which occur in the water interface of the soil.

Clay particles in soils are negatively charged and chemically reactive. Clays are the focal point of a majority of the chemical reactions in soil chemistry. This is due primarily to the volume of clay as compared to the volume of organic matter in the soil.

A wide variety of clay particles with very different characteristics are found in the soil. The differences in clay type will affect the characteristics of the soil quality.

2. Soil Triangle

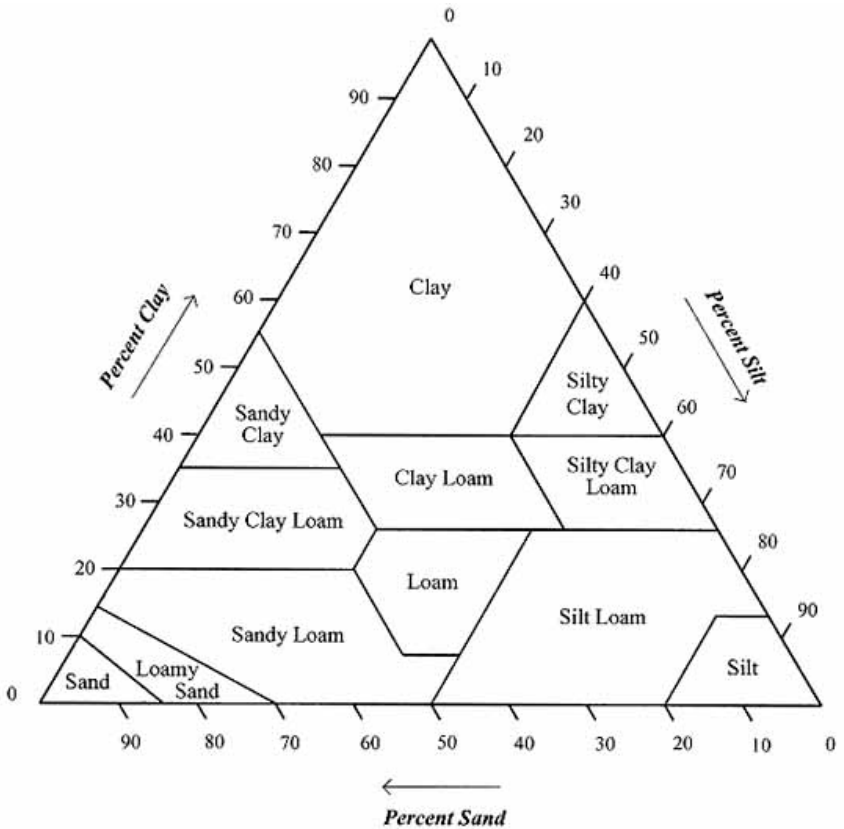


Figure 4 - Textural triangle illustrating the twelve USDA soil classifications.

- Soil with 40% clay it is classified as a clay soil.
- Soil with 50% sand is classified as a sandy soil.
- Soil with equal parts of sand and silt and 20% clay is considered a loam type soil.
- Each soil separate has a broad range.
- Soil texture combinations include: loam, sandy loam, silty loam, and clay loam.

3. Soil Clays

There are many different clay types and various charge properties. In this remediation guide, clay content is not broken down by clay type and is considered as “total clay.”

It is possible to estimate the total cation (-) charges in the soil by determining cation exchange capacity (CEC). The CEC is related to the clay “activity” in soil but its use in soil remediation is questionable. Moreover, since there are no simple in-the-field methods to determine CEC, analyses must be conducted in a laboratory which can take considerable time to obtain. Nonetheless, CEC data has indirect applicability when developing a remediation strategy: in most soils, as clay content increases, the CEC will correspondingly increase. Therefore, for the purposes of this guide, amendment volumes are adjusted relative to soil clay content.

4. Organic Content of Soil

Mineral soils like those typically found in North Dakota commonly contain 4 to 5% organic matter. Similar to clays, organic matter is chemically active and normally carries a dominant negative charge. Organic matter can exceed 40% of the total CEC of the soil. Proportionately, organic material accounts for only 5% of the soil volume yet contributes at least 40% of the CEC.

Organic matter is the single most important material responsible for the stability and formation of soil aggregation. In turn, soil aggregation is central to soil fertility. A majority of the nutrients are supplied, stored, or in part produced by the complex organic matter. This material also aids the storage of moisture. Organic matter and humus are considered to be the same material.

The source of a majority of the organic matter found in soil comes from the decomposition of plant tissue. A complex group of microorganisms biodegrade plant tissue to form humus. In addition, certain forms of animal life like earthworms, ants, and centipedes also are involved in the formation of organic matter. Humus is highly colloidal and is amorphous in nature.

The large variety of compounds found in humus is due primarily to the various rates of biodegradation of organic compounds. In the process of forming soil humus, all the nutrients and elements are made available for healthy plant growth. Chemical elements in this process are carbon, hydrogen, oxygen, nitrogen, phosphorous, potassium, sulfur, calcium, magnesium, and a variety of trace elements. Various mineralization cycles continue to drive the process.

The formation of humus (organic matter), although an exceedingly complex biochemical process, is reduced to relatively simple terms. Factors which stimulate the production of humus also increase soil fertility.

An increase in salt concentration in soil will reduce biological activity and reduce the production of humus. To reduce this impact, HumexTM is added to the soil following a salt water spill event. The HumexTM amendment will increase the microbiological activity which will stimulate the production of humus. In addition, the addition of HumexTM will help restore the formation of aggregation in the soil. HumexTM will also assist the transportation and adsorption of water in the soil.

HumexTM can also be used to increase the biodegradation rate of chemicals commonly used for lease weed control.

5. Sand and Silt

Although sand and silt particles are not chemically active, they do play an important role in the total fertility of soil. In the soil triangle classification, when clay content of soil is 20-30% and sand and silt are 30-40%, an “ideal” loam soil is obtained. Organic matter, although not part of the particle classification, should be 5% of the total soil composition.

Sand and silt together form the bulk of the soil media. Pore spaces between the sand and silt particles allow the exchange and infusion of air and water into the soil root area. A pore space of 50% is considered optimum.

In an ideal mixture of sand and silt, pore spaces provide for easy penetration of roots and unimpeded mixing and exchange of air, water, and nutrients in the rhizosphere (plant root zone).

Determination of the relative proportions of silt, sand, and clay in soil can easily be conducted in the field using the classic “ribbon test,” whereby a small amount of soil is squeezed between the thumb and forefingers to determine the relative clay content of the soil. Soil that remains intact but curls upon itself is considered to contain greater than 50% clay. Although the soil content of sand and silt is not directly related to determining amendment concentration, small adjustments may reduce the time required to remediate the site.

Sand particles will feel gritty in a water/soil paste mixture. In contrast, a silt component of soil will feel silky and smooth but will not have structure like the clay particles. Clay will have a waxy feel with the structural strength related to clay content.

An “ideal” soil solids mix consists of:

Silt	40%
Sand	30%
Clay	25%
Organics	5% “plus”

B. Soil Profile

Soil is divided into several horizons depending on the depth from the soil surface. The majority of the remediation will be focused in the top A horizon which is usually 10 inches in depth. The soil profile may also include the top 1 to 2 inches which in prairie, forest, and continuous cropping environments is described as the loose non-organized O horizon. In cropped and cultivated environments, the O horizon is unrecognizable.

In a majority of cases, we are concerned with remediation of the top 6 – 8 inches of soil (i.e., the root or plow zone). The major impact of a spill occurs in this “top soil” area where a majority of the plant’s roots are active. Roots can penetrate below the 10 inch A horizon. However, the top 6-8 inches of soil will contain the majority of salt and/or hydrocarbon in a spill event. This area also contains the majority of the plant roots and a majority of the biochemical soil interaction. Therefore, remediation will focus on removing the contaminants from the A horizon and restoring the soil to its original productivity.

SOIL PROFILE

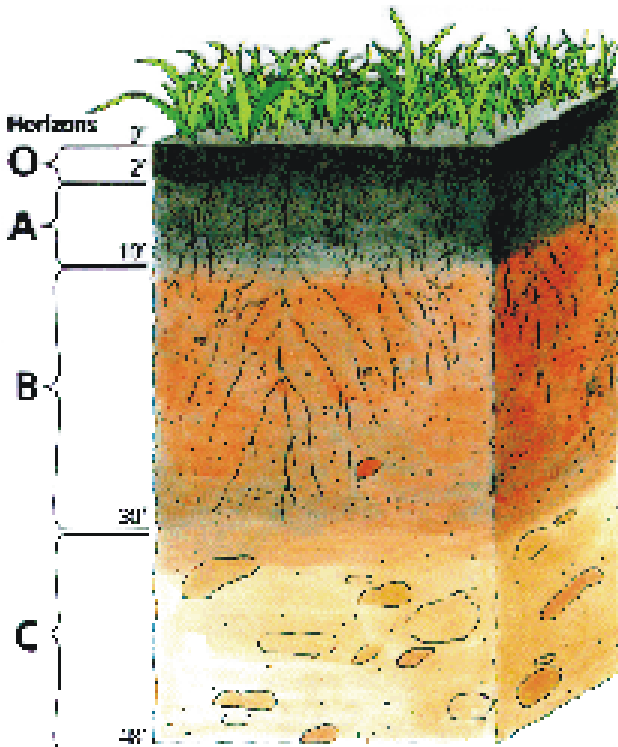


Photo © <http://www.mo15.nrcs.usda.gov/.../images/horizons.gif>

Profiles vary from site to site. Remediation involves the top 6 to 8 inches of soil. Soil horizon types and depth influence contamination and thus, the remediation process; however, we will consider this parameter only in spills of significant impact.

C. Soil Aggregation

One of the most important properties of soil structure is aggregates. The aggregate structures are produced naturally in soil under normal conditions. Aggregates are the bases of soil fertility and plant growth and are formed from a mixture of sand, silt, clay, humus, minerals and bacterial interactivity. The amount of aggregates can be enumerated by visual inspection.

Soil aggregation:

- Provides pore spaces for proper nutrient exchange.
- Allows moisture to enter and be stored in the root zone.
- Promotes gas exchange in the root area.
- Provides a stable media for root development.
- Promotes bacterial activity for mineralization cycles.
- Provides a medium for maximum plant development and nutrient uptake.
- Provides an environment where plants can survive adverse conditions.

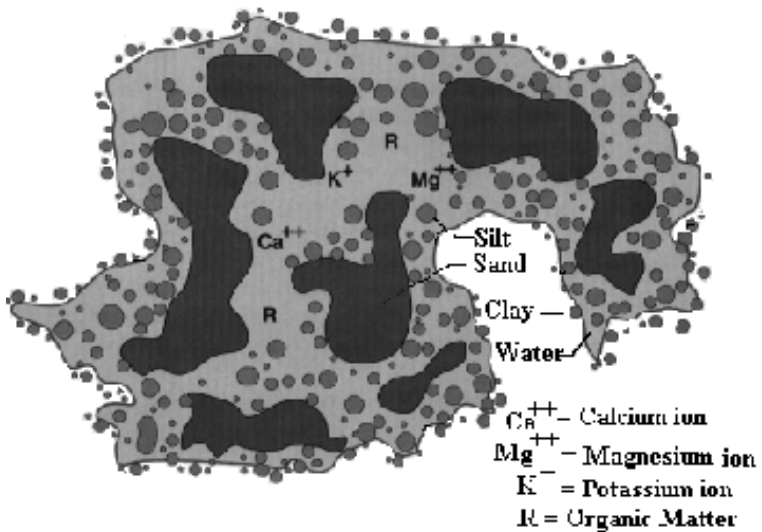
Aggregation of soil is destroyed by an introduction of high amounts of sodium ions. The high sodium concentrations cause an imbalance in the cation exchange capacity and promote a state of dispersion. When aggregation is destroyed by sodium, dispersion of soil particles occurs. In addition, osmotic stress on the plant root occurs. The osmotic stress reduces the plants ability to obtain water from the soil.

Soil dispersion causes:

- Loss of aggregate structure.
- Loss of pore structure.

- Reduction of air and water movement in soil.
- Reduction of biological activity.
- Reduction of nutrient storage and transfer.
- Increased water run off and erosion.

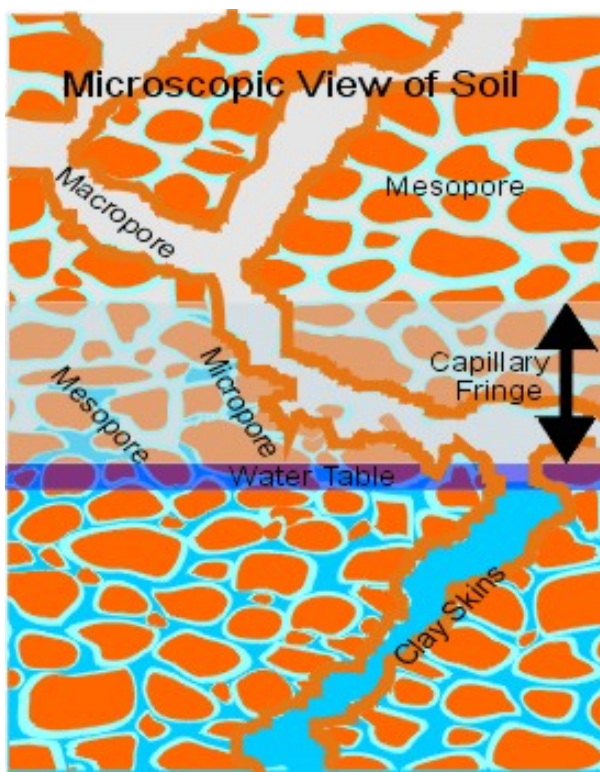
The major consequence of a saltwater spill is the loss of soil aggregation and the inability of soils to properly mobilize soil moisture due to osmotic stress. In short, dispersion destroys soil fertility.



Parts of the A horizon:

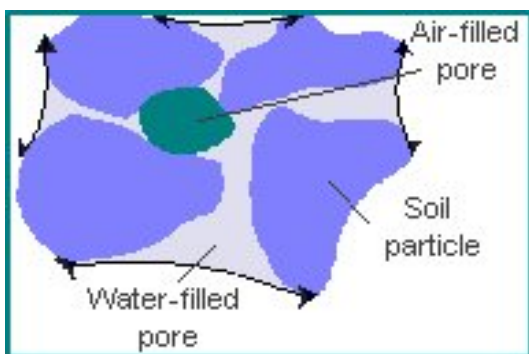
- Solids
- Liquids
- Gases

Aggregate/peds



Macropores	0.80 – 5+ mm
Mesopores	0.03 – 0.08 mm
Micropores	0.005 – 0.03 mm
Ultramicropores	0.0001 – 0.005 mm
Cryptopores	< 0.0001

Soil aggregates are larger and more stable in native prairie than in cultivated crops.



Factors which hold aggregate in equilibrium:

- Electronic charges
- Microorganism activity in the rhizosphere (bacteria, actinomycetes, mold, yeast)
- Bacterial “glues”
- Organic material – humus (clays, iron oxides)
- Balanced water chemistry
- Buffering capacity of soil chemistry

D. Soil pH

The pH value determines to what degree the soil environment is acidic or alkaline. The pH of a solution is the logarithm of the reciprocal of the hydrogen ion concentration where $\text{pH} = \log 1/\text{H}^+$ and H_2O is ionized as an H^+ cation (acid) and an OH^- anion (base).

A pH value between 6.5 and 7.5 is considered optimum for the growth of many plants. Although many plants respond to an optimum pH, this value usually covers a range from 0.5 units below to 0.5 units above the optimum level. It should be noted one pH unit is a factor of 10. Therefore, plants have a fairly broad pH tolerance.

The pH of soil influences the absorption and availability of nutrients to plants. There are two general sources of soil nutrients. Some nutrients are absorbed on colloids and some are available to plants as ions in solution. In both cases the various nutrients are present as ions. In most cases the cations (positively charged ions) are absorbed on colloids and the anions (negatively charged ions) are in solution.

Soil is a highly buffered ecosystem. Hydrogen ions in the soil solution are in equilibrium with negative exchange sites on the soil particles. In cation exchange, hydrogen acts as a reserve pool which continuously supplies hydrogen ions to the soil.

In areas of high rainfall, soil tends to be acidic due to the leaching effect on the exchange sites. In arid and semi-arid regions, soils tend to be basic. Basic soils have higher concentrations of calcium, magnesium, and sodium carbonates.

The pH of soil varies significantly in thin soil zones. These variations in pH are due to differences in both macro and micro ecosystems. The microbial population near root surfaces is an example of such an ecosystem. The rhizosphere bacteria population significantly impacts pH this microsystem and thus affects plant growth and the progress of soil remediation. Restoring the rhizosphere bacteria population and activity significantly increases available nutrients to the soil.

Since most soils in North Dakota are basic, the addition of sulfur with fertilizer is an important part of the remediation. As pH approaches 8.7, the addition of sulfur can be justified. To lower the pH of an 8 inch deep loam soil 0.5

pH units, 1,000 lbs of sulfur per acre is required. Sulfur lowers the pH thus increases the solubility of gypsum.

E. Soil Moisture

The volume and movement of water in the soil is the single most important factor determining plant growth. Depending on the plant, water comprises 50% to 90% of the plant tissue. Photosynthesis and nutrient availability depend on water. Water is the solvent in which all chemical reactions take place.

Similarly, water is the most important factor determining remediation of salt water and hydrocarbon spills. Approximately 12-14 inches of rain are required to remediate 10,000 uS/cm of electrical conductivity per year, depending on soil type.

Gravitational force pulls water down through the soil matrix and is the predominant influence on water movement in soil.

Water can also move by capillary action due to hydrogen bonding and the subsequent magnetic attraction of water molecules to one another. Capillary forces can overcome gravitational forces and move water in a direction other than straight down into the soil. Both gravitational and capillary water movement is influenced by soil particle type and distribution in the soil.

Water around soil particles is controlled by adhesive and cohesive forces. "Adhesion water" is held tightly and does not move. In contrast, "cohesion water" is held more loosely on soil particles and can be utilized by plants. Cohesive forces and capillary forces move water against gravitational forces in the root zone to increase water utilization by plants.

The osmotic potential of water becomes important in a saline soil. At high salt concentrations, a higher osmotic potential decreases the movement of water into plants. Additionally, more energy is required to move water into the root at higher osmotic potentials.

Following a rain event, the soil is saturated as soil pores fill with water. Gravitational forces drain water from the root zone. Depending on the soil and amount of rain, the draining process is completed in 48 to 72 hours. As the soil drains, the soil reaches a “field capacity” state. At this point, air will fill the large pores and each soil particle will have a thick film of moisture (cohesion water). Plant uptake and evaporation will continue to deplete the cohesion water and shrink the soil-water film. As the film becomes thinner it is more difficult for the root to absorb water. As this process continues and capillary water and additional rain fall does not replenish the root zone, a “wilt point” will develop.

During this process of saturation and drainage, calcium ions can replace the sodium ions and remediation can occur. It is important that water move evenly through the soil as it drains out of the root zone. Therefore, pre-work of the soil to produce a “remediation seed bed” to facilitate water drainage out of the root zone is helpful to the total remediation process. Soil texture will determine the “water retention” capacity of a soil. A loamy soil will remediate at a faster rate than a sandy or heavy clay soil.

APPENDIX F

Soil Chemistry

A. Chemical Elements

All matter is made up of elements. There are 107 known elements. These elements make up what is known as the periodic table. The atom is the smallest unit of an element. In turn, atoms are made up of three particles, protons, neutrons, and electrons.

Positively charged particles are protons, neutral particles are called neutrons, and negatively charged particles are called electrons. In the configuration of the atom, protons and neutrons inhabit the nucleus, the center of the atom. Around the nucleus in various orbits are the active electrons. Different configurations of the electrons and nucleus will change atomic properties and behavior. The total weight of all electrons, protons, and neutrons make up the atomic weight of the atom. Atoms combine to form molecules. Molecules combine with other molecules to form compounds.

Soils contain all the natural chemical elements of the periodic table. However, only a few elements make up 95 percent of the earth's mass. The majority of the elements in the periodic table are present only in trace and micro amounts.

In soil, there are 17 elements which impact plant growth. The distinction between essential elements and toxic elements is the type of element and concentration of the element.

Most of the elements are present as ions in soil solution and flow to roots in a water solution. Plants have a wide range

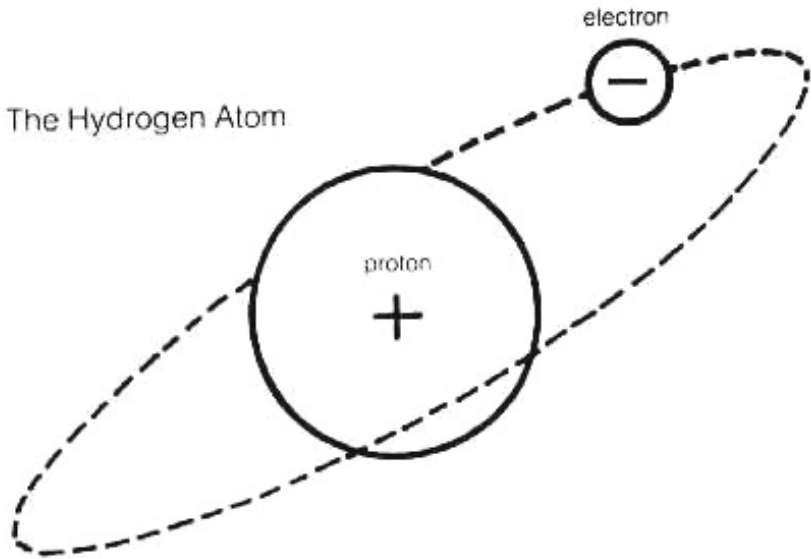
of tolerance to elements and can select the ions required by the plant. However, in cases of salt water spills, the balance of Na^+ (sodium) ions and Cl^- (chloride) ions are now artificially increased. This imbalance impacts both soil structure and plant physiology.

Chemical reactions in soil are rapid compared to water and air environments. As a general comparison, reaction rates in air can be measured in days and years, in water, hours, and in soil, seconds and minutes.

Soils are colloidal, meaning that they are made up of very small particles (1 to 1000 nm). Each colloidal particle has surface area. It is this surface area on which chemical reactions in soils take place. Not surprisingly then, soils have an astoundingly sizeable surface area for chemical reactions to occur.

Although many chemical reactions are possible in the soil/water interface, only a few elements dominate the impact of salt water spills and thus impact the soil remediation process. Water, sodium chloride, and calcium sulfate are the dominant species we are concerned with in salt water spills and the remediation of the impact. The elements of primary importance are: H^+ and O_2^{2-} in water, Na^+ and Cl^- in salt and Ca^{++} , S, O_2^{--} in gypsum.

Hydrogen is the simplest element in the periodic table. Hydrogen has one electron and one proton as shown below.

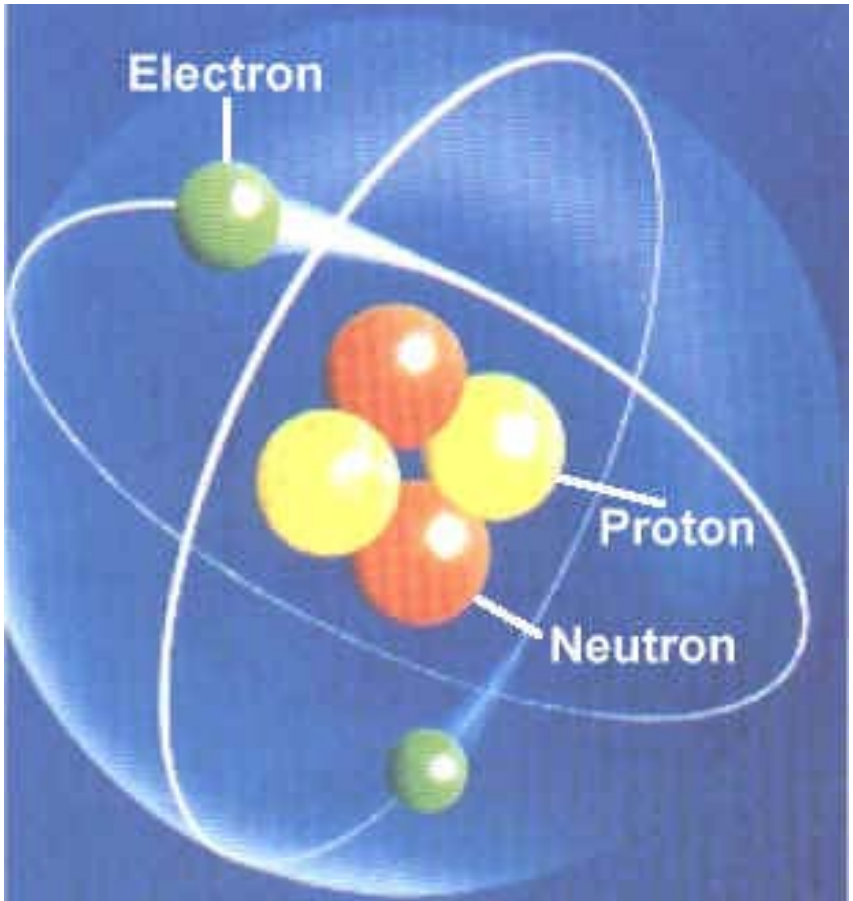


From:

<http://www.airpower.maxwell.af.mil/airchronicles/aureview/1984/jul-aug/roberds.html>

An atom is the smallest unit of an element. Atoms are made of three particles:

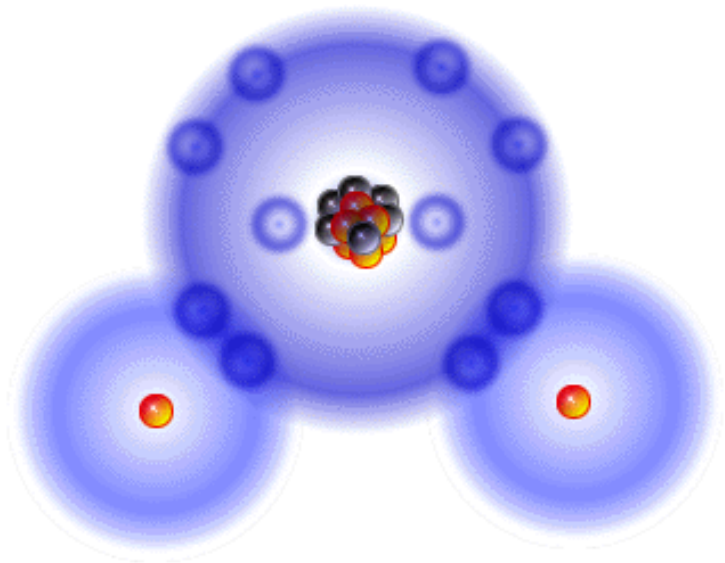
1. Electron – a negatively charged particle
2. Proton – a positively charged particle
3. Neutron – a neutral particle



Atoms combine to form molecules.

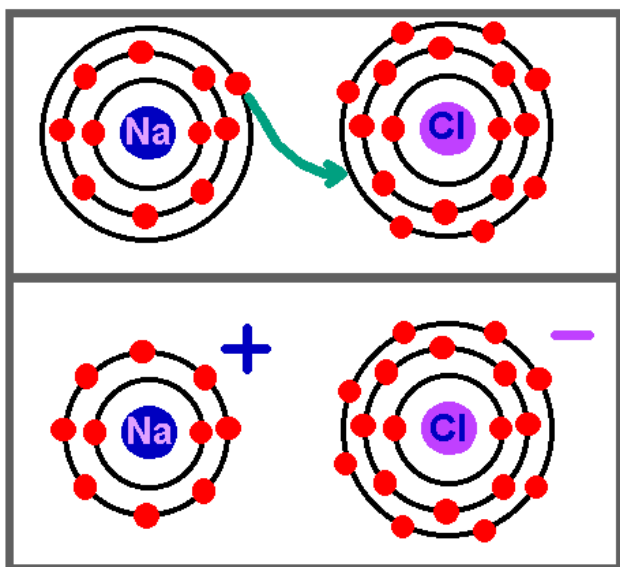
- Molecules form compounds.
- State of ionization: Normal compounds (atoms) have equal numbers of electrons and protons. If an imbalance occurs, the molecules (atoms) become ions.
- $\text{H}_2\text{O} = 2\text{H}^{2++} + \text{O}^{--}$
- $\text{H}_2\text{O} = \text{protons} + \text{anions}$

Water Molecule

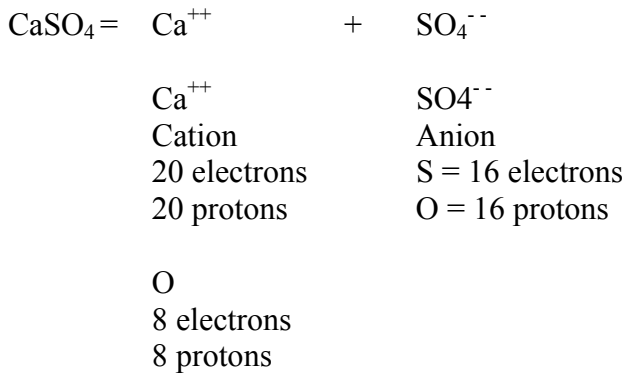


Sodium chloride

$\text{NaCl} =$	Na^+	+	Cl^-
	Sodium		Chlorine
	Na^+		Cl^-
	Cation		Anion
	11 electrons		17 electrons
	11 protons		17 protons
	10 electrons		18 electrons
	11 protons		17 protons



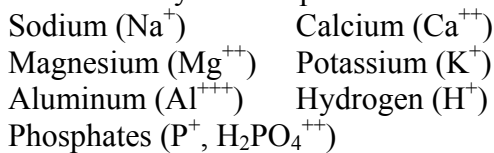
Calcium sulfate



Cations/Anions

Cations (positively charged molecules)

Cation exchange capacity (CEC): the total number of cations absorbed by the soil particles.



Basic soils: Na^+ , Ca^{++} , Mg^{++} , K^+

Sodium has the lowest absorption strength.

Acid soils: Al^{+++} , H^+

Cations -- continually absorbed and replaced on clay particles.

Soil particles are negatively charged and are in balance with positively charged cations. That resistance/repellency creates spaces between soil particles, creating aggregation.

Anions (negatively charged molecules):

Chloride Cl^-

Sulfate SO_4^{--}

Carbonate CO_3^{--}

Bicarbonate HCO_3^{--}

Nitrate NO_3^-

Anions are mobile.

Soils have a low anionic exchange capacity.

B. Dispersion In Soils

Salt water spills impact soils and plants by dispersing soil particles and causing osmotic stress on plants. Soil dispersion destroys soil structure and osmotic stress reduces the ability of plants to utilize water. The negatively charged ions in soil are primarily from clay micelles and organic material.

1. Salt water impact and soil aggregation
 - Na^+ ion becomes the dominant cation as compared to Ca^{++} and Mg^{++} ions.
 - The larger Na^+ ions break the soil aggregate bonding causing soil to disperse. Na^+ ion has a weak chemical charge.
 - Total salt concentration (EC) increases.
 - Soil solution has lost its chemical balance due to the high increase in Na^+ and Cl^- ions.
 - High levels of Cl^- ions can cause direct toxicity to plants. However, chloride ions are negatively charged so they move rapidly through the soil and out of the root zone.
 - Rain on soil with high Na^+ ion concentration will accelerate the dispersion process.

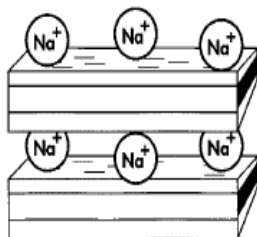
2. Salt water impact on osmotic pressure

- As total salt concentration increases the osmotic pressure in the water increases.
- In high osmotic environments, plants must spend more energy to absorb water.
- The soil matrix may have sufficient water but the plants cannot utilize the water, show stress, and wilt.

DISPERSION

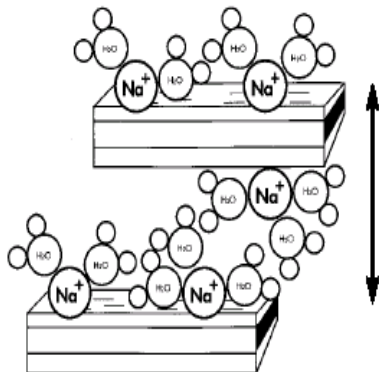
Sodic clay

sodic clay (high ESP)



In a sodic soil, sodium, Na^+ is adsorbed onto the surface of the clay. It is a large ion with a weak charge. The positive ions bind the negatively charged clay particles together.

sodic clay + water



As water is added to a sodic soil the water is attracted to the sodium. The ions hydrate, forcing the plates apart. The ions' role in binding the clay platelets is overcome, and the clay swells then disperses with water.

CLAY BRIDGE STRENGTH

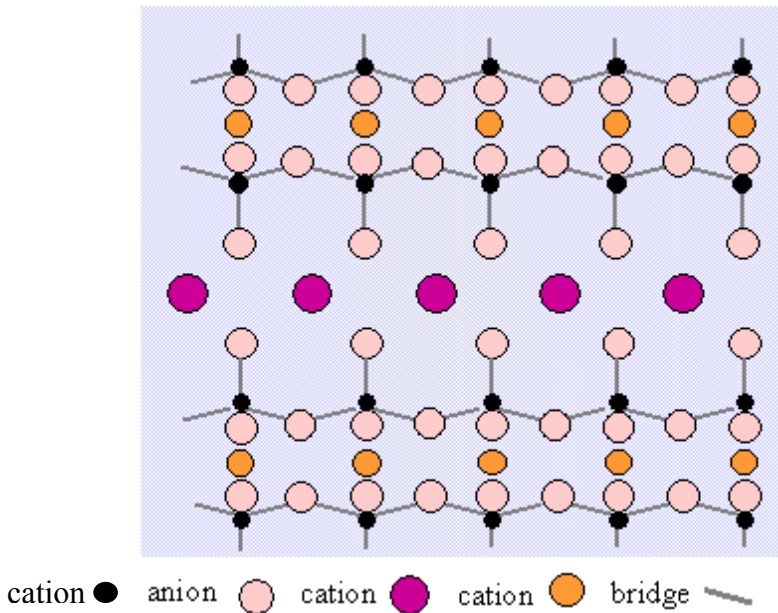


Figure 3:

The sandwich structure of silicate clays.

Layers of silica ions (●) bridged with two oxygen ions (●), form bonds with other cations (●) and (●). The strength of the bond differs with the cation. Weak bonds such as those formed with sodium ions cause clay particles to break up in water, clogging soil pores and increasing the mechanical resistance to root growth.

C. Acidity and Alkalinity of Soils

1. pH/acidity/alkalinity

In the soil remediation process, acidity and alkalinity are measured by determining the pH of the soil solution. Although the pH is not a true measurement of acid/base buffered reaction in soil, it does reflect the range of acidity vs. alkalinity.

A pH meter measures the hydrogen ions in solution. The higher the hydrogen ion concentration, the more acidic the soil and the lower the pH number. As discussed earlier, pH is the logarithm of the hydrogen ion concentration.

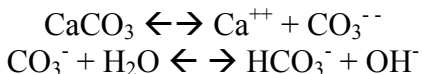
The majority of North Dakota soils are basic or alkaline. This is due to the high base saturation of the soil. The calcareous nature of the soil promotes the hydrolysis of the calcium carbonate resulting in a high (basic) pH. The actual pH of a soil with a base saturation below 100 percent depends on the balance between hydroxyl ions and hydrogen ion reaction. If the sodium saturation exceeds 15 percent, the hydrolysis of sodium produces lye. This reaction will increase the pH. High sodium soils are called sodic soils.

The pH of soil will affect the availability of plant nutrients. In the remediation process, pH is not considered a remediation issue until it reaches 8.7. At a pH of 8.7, the solubility of gypsum is significantly reduced and will increase remediation time.

2. Sources of alkalinity

- Predominant cations in soil are Ca^{++} , Mg^{++} , K^{+} , and Na^{+} .

- The hydroxyl (OH⁻) ions are principally carbonates (CO₃⁻) and bicarbonates (HCO⁻).
- Anions originate from the dissolution of such minerals as calcite (CaCO₃).



- In regions of low precipitation (18-20 inches), rainfall is not sufficient to leach away cations formed by mineral weathering.

3. Source of acidity

- Production of H⁺ predominantly from soluble Al⁺⁺⁺ and Fe⁺⁺⁺.
- Carbon dioxide produces acids in the root zone from respiration by roots and organic acids from microbial activity.
- Rainfall – generally slightly acidic.

D. Amendments in Remediation

Gypsum

Gypsum is the main remediation amendment. Gypsum is CaSO₄⁺ + 2 H₂O and is a widely distributed mineral in the earth's crust. It has limited solubility in water at 0.24 g/100 ml of water. Calcium (Ca⁺⁺) in gypsum replaces Na⁺ ions on the micelle clays and re-establishes aggregation in the soil.

The initial stages of remediation are the establishment of a soil structure – aggregation. Gypsum is a naturally occurring mineral. Other sources of calcium can be used. Calcite limestone is predominately CaCO₃, dolomitic limestone is CaMgCO₃ and MgCO₃, burned lime is CaO,

and hydrated lime $\text{Ca}(\text{OH})_2$; all can supply Ca^{++} ions for remediation. Never-the-less, gypsum is the best source of calcium and the easiest product to handle for soil remediation. It should be noted that burned lime and hydrated lime are difficult to use and their use is not recommended.

Leonardite (HumexTM)

Leonardite is a naturally occurring mineral. HumexTM is a trade name of the material available commercially. HumexTM is leonardite which is mined and ground to a specific particle size.

Leonardite contains humus, humic acids, fulvic acids, and trace minerals. As an amendment, it aides Na^+ ion exchange, improves soil structure, and is an instant soil builder. Leonardite also increases microorganism activity and increases biodegradation of hydrocarbons. Leonardite is also used to reduce and increase biodegradation of weed killer chemical.

Fertilizer

The remediation process uses fertilizer to increase nutrients in the top 6 inches of soil. Fertilizer will increase the number of bacteria and thus improve soil physical condition and nutrient content. Fertilizer also increases rate of hydrocarbons biodegradation.

Use 10/20/10/10 fertilizer or equivalent. The 10/20/10/10 complex is nitrogen, phosphate, potassium, and sulfur.

Sulfur

Sulfur is primarily used to reduce and control high pH (alkalinity) in soil. Sulfur is also considered an essential nutrient in plant growth.

It takes 2,200 lbs/acre of sulfur to reduce pH by one unit (one pH unit is a ten-fold difference). The 2,200 lbs/acre is equal to 50 lbs of sulfur per 1000 sq ft in 8 inches of loamy soil.

At a soil pH greater than 8.6, increase sulfur by 25 lbs/1000 sq ft (1,100 lbs/acre).

Manure amendments

- Add 3 inches of manure and work material into top 4 inches of soil. The manure should be 8 to 10 years old, if possible.
- Three inches of manure is equal to approximately 6 tons per acre.
- **Need landowners consent to use manure.**
- In most cases the manure has to come from the land owner's property.
- Manure can carry numerous weed seed species. The number of live weed seeds is reduced by the aging process which is the reason to use manure that is 8 to 10 years old.
- **Manure has a high nitrate content. Do not use manure near ponds, streams, water supplies, and residences.**
- Note: manure will replace 60% of the HumexTM, 40% of the gypsum, and all the fertilizer. Need to work soil two times in the second year and once in the third year to stimulate biodegradation.