Salts and Chlorides Remediation

The remediation of salts and chlorides is not a process of consumption but rather a process of binding, buffering, immobilization, detoxification, filtering, or conversion into a non-toxic soil mineral. This is accomplished in a variety of both cationic and anionic processes and reactions. The following information will provide some additional information that will assist in how some of these processes occur and a foundation on what these potential contaminants do in soil.

**Impact of Salt/Chloride 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 Ca²⁺ and Mg²⁺ 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.

The term “chloride” does not refer to any specific compound but is a category of substances that are either present in the soil or groundwater or are added to drilling muds or hydro-fracturing fluids to facilitate development of a gas/oil well. The most common chlorides of interest include sodium chloride, calcium chloride, magnesium chloride, ammonium chloride, potassium chloride, and barium chloride. Therefore the remediation of “Chlorides” may encompass a variety of compounds that can respond differently to treatments due to a variety of variables and conditions. It is also known that within any remediation of salts and chlorides that a variety of charges and reactions are required due to the fact that Cations migrate to negative charges and anions migrate to positive charges. Therefore, multiple charges of treatment products will be required to react appropriately with the different charges of the various components in the soil and water.

Why is the PEB important to the salt remediation process?

PEB naturally binds, adsorbs, and coordinates sodium cations and chlorine anions which allow excessive amounts of salts/chlorides to become more mobile in terms of sodium cations and chloride anions, which eliminates the salt's/chlorides ability to bind to soil particles, especially clay. This reaction allows sodium/chlorides to be safely leached and naturally filtered through the soil profile. Any sodium/chloride residue creates a new mineral formation resulting in sodium, chloride, cation and anion conversion into physically and mechanically bound status, thus eliminating salt toxicity resulting in desalination and salt toxicity reduction/elimination. This process also improves the growing profile by reversing negative osmotic pressure, reducing electrical conductivity, increasing soluble organic matter allowing proper nutrient and moisture retention, percolation, and uptake, therefore allowing new plants to establish and regenerate soil back to a healthy and productive state. In aqueous solutions, the reactions are similar, resulting in the precipitation of most of the sodium, chlorides and metals with the remaining soluble forms being neutralized into non-toxic forms.

How does SA-1000 work?

SA-1000 possesses several beneficial characteristics that buffers the treatment environment, creates a foundation for maximum biological, geological and chemical reactions, is both hydrophobic and hydrophilic, and is designed to work effectively in both soil and aqueous environments. Through these various reactions with contaminants, SA-1000 attracts various contaminants, reverses their negative
impact in their environment and reduces/or eliminates the harmful impact through the following processes:

- **SA-1000** adsorbs and coordinates sodium cations and chlorine anions which allow excessive amounts of salt to become more mobile in terms of sodium cations and chloride anions that have a natural ability to safely filter through the soil or precipitate out of water. Any sodium residue creates a new mineral formation resulting in sodium, chlorine, cation and anion conversion into physically and mechanically bound status, thus eliminating salt toxicity resulting in desalination and salt toxicity reduction/elimination.

- **SA-1000** with bio-available calcium is immediately soluble and active compared to gypsum applications. See results within a couple weeks.

- In soil, **SA-1000** creates fresh soil organic matter that results in increased CEC, reduced Electrical Conductivity (EC), better water holding capacity through osmotic pressure reduction, and soil porosity/structure that results in healthy, active soil for re-use.

- **SA-1000** will naturally stimulate toxic organic and mineral pollutants decomposition into neutral soil mineral compounds such as converting Chromium VI to Chromium III which is accomplished by an abundance of hydroxyl and phenol groups. These functional groups are key to the metal complexation resulting in the binding of various metals which protects the environment.

**SA-1000 Technical Mechanisms (Salts/Chlorides)**

- The bio-polymers that makeup SA-1000 are chemically, biologically and geologically active material. In other terms, PEB is a nonspecific material that provides a positive impact to many, if not all, soil compounds (organic and mineral matter, soil bacteria, plant, etc.); organic pollutant (oil hydrocarbon and others); mineral toxicant (heavy metals, salts, etc.); soil function and properties (water holding capacity, porosity and density, CEC, EC, etc.) as well as plant growth / development processes. These are caused by PEB which is a poly fractional organic-mineral composition and colloidal origin (PEB contains molecules with different molecular mass); biopolymer or polyelectrolyte nature (PEB molecules are biologically synthesized molecules – biopolymer, while at the same time these polymers - molecules are electrolyte – or rather a polyelectrolyte); volumetric structure (three dimensional molecules with ability to conformational changes – ability to change their shapes), functional groups and a number of local positively and negatively charged active centers – negatively charged centers located primarily on the outer/external edges and positively charged centers located primarily in the inner/internal sites of these molecules. This unique molecular structure allows SA-1000 to be effective on both sodium cations and chloride anions.

- It is well known that soil particles bear negative electrical charges and this results in cations (positively charged ions) absorption on their surfaces. *Note: Soil particles form a soil “skeleton” that means they are not available for moving through soil profile (in most cases).* These cations form thin or thick hydrated layer around each soil particle. This electrically charged layer is called a “Double Electrical Layer”. This property primarily causes soil Cation Exchange Capacity (CEC). There is primarily hydrogen, calcium, magnesium, sodium; potassium and some other cations are present in this layer. Depending on makeup of the soil, the type of cations that dominates various soils could vary significantly. According to modern agro chemistry the best cation is
calcium. If sodium cations dominate in this layer and the layer is thick, the sodium cations can move into soil pore solution due to diffusion, in this case, soil gets toxic for plant and soil bacteria (due to several mechanisms including high osmotic pressure). However, most sodium cations are strongly bound with soil particles and even soil washing with plenty of water does not remove any significant amount of sodium. That is why sodium removal is possible through ions exchange mechanisms: usually calcium (calcium sulfate – bio-available calcium) is used to replace sodium by calcium and sodium is available for removal from soil due to rainfall, natural diffusion processes, etc. If soil has high CEC (for example, black soil; clay; clay loam), soil can accumulate high levels of sodium without detectable sodium toxicity to plants because sodium cations are strongly bound and sit in “double electric layer”. Soil with low CEC cannot absorb high levels of sodium that is why in “light” soil (sandy soil; sandy clay; etc.) even a small amount of sodium results in great toxicity for plant/soil bacteria. 3 Tier PEB’s increase CEC because activated bio-polymers have many active functional groups which have increased ions exchange capacity. The greater CEC, the greater the amount of sodium is absorbed and the lower its toxicity. Our PEB is the real molecular solution with dominated mass around 27,000 Daltons up to 100,000 Daltons. Therefore, with a sodium cation mass being 23 D (chlorine ion 36 D) a single PEB molecule is greater/heavier than a sodium ion by 1,174 times. The greater/heavier the molecules, the less mobile they are. Once sodium ions are absorbed by the PEB molecule, it makes sodium ions less mobile and respectively less toxic. It is possible to say roughly, that each PEB molecule works like a soil “particle” which forms a “Double electrical layer” with sodium resulting in reduced sodium mobility/toxicity.

- Our PEB molecules are volumetric: meaning three dimensions. Sodium ions can travel inside volumetric molecules and interact with their negatively charged sites. This can be described in terms of “sodium coordination”. Note: It can be explained in very simple terms. - For example, the Moon is coordinated by the Earth (due to gravity) and this doesn’t allow the Moon travel freely. But if the Moon gets extra energy, it can leave the Earth because there are no other forces or bonds which keep them together.

- In the soil or waste water PEB molecules absorb and coordinate sodium cations on negatively charged external surfaces and chlorides anions on the positively charged centers. Due to “diffusion” by water, chlorides ions have a significantly greater concentration on the inside portion of the molecule, while the sodium ions are captured in greater concentration on the outside of the PEB molecules rather than in the surrounding water. In soil this results in lowering sodium and chlorides concentration in soil pore solution and greater concentration around solid phase. The lower sodium and chlorides content in soil pore solution, the less salt toxicity to the plants. Though this process of absorption and coordination still binds sodium and chlorides ions, they still remain mobile and soluble without the inhibiting effects to the soil, water, and the environment trying to survive in it.

Note: PEB molecules interaction with calcium, magnesium and two others with greater valent cations resulting in PEB molecules coagulation and precipitation. Calcium, magnesium, etc. make conformational changes or in other terms change PEB
molecules shapes to more spherical which include sodium and chloride inside such spheres. This is the sodium and chlorides occlusion that results in less mobility/toxicity of these ions.

- Solid phase formation in soil or sediment formation in waste water due to PEB coagulation by calcium, magnesium, etc. significantly changes the mechanisms of sodium and chlorides diffusion in solid-liquid media. Sodium and chlorides distribution between liquid phase (water) and solid phase (coagulated PEB in soil and sediment in waste water) results in greater sodium and chlorides content in solid phase. This difference can be detected by sodium and chlorides content determination in liquid phase before and after PEB application. Liquid phase electro conductivity can be read also before and after PEB application. Electro conductivity reduction is more than expected.

*Note: without solid phase or sediment formation a PEB application could result in electro conductivity increase due to its electrolytic nature.* Sodium and chlorides diffusion in solid phase and sediment is still great because they are not strongly bound; they are just absorbed and coordinated. This diffusion allows sodium and chlorides leaving the top soil into deeper layers. This results in top soil desalination. If this sediment in waste water is located on the surface of native ground (loam, sandy loam, etc.) it can result in sodium and chlorides diffusion to deeper layers and salt content reduction in waste water.

*Note: PEB molecules which were coagulated to sediment are not mobile. They can catch sodium in the same manner as it does cationic resins in case of sodium prevalent content over calcium, magnesium, etc. In this case sodium replaces calcium, magnesium, etc. and calcium chloride, magnesium chlorides content can increase while lowering sodium chloride concentration in water.*

- As previously stated, PEB is a biologically active product which catalyzes the processes of new soil organic matter formation due to fresh organic matter and organic residue humification into colloidal PEB and primarily to Humus. Freshly formed colloidal PEB is negatively charged in wet soil having a high CEC that results in sodium ions absorption and protons $\text{H}^+$ release. Protons replace sodium and form $\text{H}^+\text{Cl}^-$ . So, original $\text{NaCl}$ turns to $\text{H}^+\text{Cl}^-$ . Protons and chlorides are very mobile which results in rapid filtering and movement from the soil top layer. Freshly formed colloidal PEB can absorb and keep protons and chlorides “mechanically” bound thus reducing or eliminating chlorides toxicity. *Note: PEB also acts as a biologically active product in soil. First of all, PEB stimulates autotroph group of bacteria which use mineral compounds such as ammonia/ammonium; sulfur; iron, etc. as energy source. This group of bacteria can utilize carbon dioxide as carbon source. But carbon dioxide is a gas and not available for this bacteria. Carbon dioxide dissolution in soil pore solution or waste water results in bicarbonate formation. Bicarbonate in soil or waste water is rapidly available for autotroph and they turn bicarbonate into bacterial organic matter. If soil is contaminated, for example by sodium bicarbonates, bicarbonates consumption by bacteria results in free sodium ions release and their absorption by soil negatively charged particles – CEC or leaching from soil in form of sodium hydroxide ($\text{NaOH}$). So,
PEB is most effective for soil which is contaminated by bicarbonates – sodium bicarbonate, magnesium bicarbonate, etc.

- **PEB** acts as effective bio stimulator for plant and soil native microbiology. PEB can be applied by mixing into the soil or as foliar spray. PEB molecules regulate soil and plant’s cells osmotic pressure. It is known, that the higher salt content in water, the greater the osmosis pressure and greater the salt toxicity will be to the plants. High osmosis pressure makes water unavailable for plant resulting in their drying and death. PEB molecules reduce osmosis pressure making water available for plant.

- As we also stated, PEB is geologically active product. It means that PEB catalyzes the process of new soil mineral formation acting as a “matrix” which collects dissolved cations (primarily magnesium, calcium) and anions (primarily hydroxyl groups, silicates) into new clayey minerals. Sodium and chlorides are “mechanically” occluded between mineral’s crystals and lose their mobility and toxicity to plants. These processes in soil a reasonable period of time and result are detectable in several weeks: sodium and chlorides reduction while soil clay mineral content may increase.

**Proper Site Characterization and Analytical Data for Maximum Performance Results:**

Basic sodium and chloride testing will ONLY provide one small piece of the puzzle………what is the level of loading! Understanding the makeup and use of the site, soil structure, and analytics that detail the impact of the sodium/chloride to the specific site are all critical to development of an effective remediation process that can yield maximum results in the shortest period of time. Without a complete site picture, the remediation process will, in most cases, will not perform to the required expectations resulting in retreatment, additional time, and additional expense that can be avoided with proper testing and investigation of the site.

**Required site testing:** (the best method for overall site analysis is composite soil sampling)

- pH
- Bicarbonate Alkalinity
- Carbonate Alkalinity
- Electrical Conductivity (EC)
- Total Soluble Salts (TSS)
- Calcium
- Potassium
- Magnesium
- Sodium
- Chloride (Anions)
- Nitrate as N (Anions)
- Sulfate as SO4 (Anions)
- Cation Exchange Capacity (CEC)
- Exchangeable Sodium Percentage (ESP)
- Sodium Absorption Ration (SAR)
- Soil Texture Analysis (Sand, Silt, Clay)
**Required site specific information:**

- General topography of site
- Site accessibility
- Principal site use (Pasture, Agricultural, Stabilization)
- Regulatory Standard
- Surface/Groundwater impact or influence (location of creeks, rivers, ponds and depth to groundwater if known)
- Age/Volume of Spill
- Makeup of the water spilled (Produced Water, Frack Water, Hydrocarbon present, Metals, other potential remediation concerns presented by spill, MAY REQUIRE ADDITIONAL TESTING DATA)
- Depth of contamination (Soil Texture Testing at incremental depths may be required)
- Depth to groundwater, type & potential water uses

Frequent work within a general geographic area may limit the amount of information required for all sites through experience though it is not uncommon for soil structure to vary significantly from location to location. Due to the relatively low cost for all tests, establishing a consistent testing regime will insure consistent results and a portfolio of proven reference data for replicatable results and success.