



## Treatment of Salt Affected Soil in the Oil Field

### Abstract

Soils, drill cuttings and other solid wastes which are exposed to high levels of salt through spillage from drilling and producing operations, pipe line breaks or leaks, become saturated with sodium. Although the EPA and the industry have demonstrated that the vast majority of such wastes are non-hazardous, in actuality, they have an adverse impact on the fertility of the soil.

The degree of salt saturation is influenced by the soil mineralogy. Many native soils containing high montmorillonitic clays have the capacity of adsorbing sodium species in their crystal structure. Sodium adsorbed montmorillonitic clays being dispersed affect the physical structure of soil and, in turn, adversely influences its permeability. High salt content of soil also has a profound influence on its osmotic pressure. Consequently, it has a detrimental influence on the health of the commercial crops or native vegetation.

The physical structure of the soil can be chemically modified, allowing improved drainage of undesirable salt species. To store its physical structure and to make it permeable, the industry has practiced cationic amendment of sodium contaminated soil. Traditionally used gypsum, being sparsely soluble in water is unable to provide a readily available source of cationic species for amendment. A carefully designed product containing readily available cationic source along with other nutrients for the growth of vegetation has been highly successful. Field results from various geographical locations with different soil composition and degree of contamination showing rapid reductions in the sodium contents and, in turn, also having a dramatic effect on the restoration of vegetation are discussed in this paper.

### Introduction

The components of soil can be classified into the following groups: sand, silt, humus and clays. Sand and silt are siliceous. They are relatively inactive from ionic exchange point of view. Humus and clays, which contribute to the fines, are highly surface active particulates. They are negatively charged in an aqueous environment. Consequently, they readily attract and hold positively charged ionic species.

In soil, the primary cationic species of the accumulated salts are  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$ . The anionic species, on the other hand, are  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^-$ . Their sources are primarily from the soil forming mineral matters. Of these, the presence of  $\text{Na}^+$  is considered particularly detrimental, as it has toxic effect on plants and vegetation. As  $\text{Na}^+$  is weakly adsorbed and is inefficient in neutralizing the negative charge sites, it tends to disintegrate the soil structure and reduces the soil permeability and tilth. This, in turn, adversely affects the seed germination and the overall plant growth.

In arid and semi-arid regions, runoff water collected in certain areas of land evaporates and the salts in the water accumulate. In these areas water also moves upward from artesian sources and shallow water tables. Through evaporation, salts are deposited to form saline, saline-sodic, or sodic soils. These soils are prevalent in arid and semi-arid regions where the rainfall is inadequate to leach out the accumulated salt. While nature has been responsible for most of the soil salinity problem, accidental spillage or leakage from the industrial sources such as the oil & gas industry have been the major human introduced causes for salt contamination. The primary sources of contaminants from the oil & gas industry are the produced water, spent drilling fluids, treating fluids and leakage from the crude oil pipe lines.

After a brine spill,  $\text{Na}^+$  cations present in overwhelming concentration displace other cationic species, such as calcium, magnesium, and potassium from the clay structure. Adsorption of  $\text{Na}^+$  species disperses clay particles, which subsequently diminishes the drainage characteristics of soil. While  $\text{Na}^+$  ions are involved in the ion exchange process and adsorb at clay surfaces, the  $\text{Cl}^-$  ions function as indifferent ions and remain in the liquid phase. Further irrigation with fresh water or rainfall tends to drain free  $\text{Cl}^-$  or  $\text{Na}^+$  ions of the soil system to a greater depth. However, due to the dispersed nature of clay particles, water permeability of the soil is drastically diminished. This results in puddling of water at the soil surface.

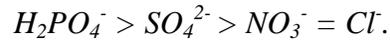
The environmental industry has a track record of only limited success in the remediation of salt affected sites. This can be attributed to the lack of understanding of the soil-salt interactions and also due to the absence of chemicals specifically designed to accelerate the remediation. Similar to the farming community, the oil & gas industry traditionally has used gypsum for the treatment of sodium affected soil but again with limited success. While gypsum is a source for calcium, its solubility being extremely low ( $< 0.03 \text{ g}/100 \text{ ml water}$ ), it is not readily available to the soil. Consequently, the process of remediation is very slow. The slow rate of remediation is even more pronounced in the arid regions, where water is scarce and irrigation at regular intervals can be expensive. Calcium chloride<sup>1</sup> and calcium nitrate have also been used. In both cases calcium species are readily available. However, with the environmental pressure on the nitrate level of the effluents, use of calcium nitrate has become prohibitive.

Based on the ionic exchange principle, cationic electrolytical chemicals effectively displace the toxic sodium species in the soil matrix, removing it from the root zone to allow growth and development of plants and vegetation. This paper reviews the principles related to the remediation of salt affected sites, with test data demonstrating the effectiveness of a cationic electrolytic chemical in field applications.

### **Ion Exchange in Soil**

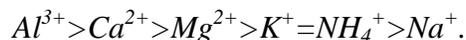
Ion exchange occurs in soils at the mineral surfaces, organic matters, and roots. Cation exchange is generally considered to be more important, since the anion exchange capacity of most soil is comparatively much smaller than the cationic exchange capacity. Anion Exchange Capacity (AEC) of a soil increases with pH; and it is much greater in soils containing kaolinitic clays and those containing hydrous oxides of Fe and Al than it is in soils which contain montmorillonitic

clays. Anions such as  $\text{Cl}^-$  and  $\text{NO}_3^-$  may be adsorbed, although not to the extent of  $\text{H}_2\text{PO}_4^-$  and  $\text{SO}_4^{2-}$ . The order of adsorption strength is as follows:



In fact, in most soils,  $\text{H}_2\text{PO}_4^-$  is the primary anionic species adsorbed. Some acidic soils may adsorb significant quantities of  $\text{SO}_4^{2-}$ . In most cases the anionic adsorption by soil particles can be attributed more to specific adsorption or chemisorption than simple Coulombic adsorption due to counter ionic interactions.

The major exchangeable cations in soil are  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{H}^+$ . Other exchangeable cations, which are minor components of soil but have nutrient values, are  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}^{2+}$  and nitrogen as  $\text{NH}_4^+$ . However,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$  and  $\text{Na}^+$  are the dominant exchangeable cations in most soils. Their abundance generally parallel the energy of the adsorption sequence, with  $\text{Ca}^{2+}$  most abundant and  $\text{Na}^+$  or  $\text{K}^+$  the least abundant. Valence is the major factor affecting the likelihood that a cation will be adsorbed. A trivalent  $\text{Al}^{3+}$  is more likely to be adsorbed than a divalent  $\text{Ca}^{2+}$  which is more strongly adsorbed than a monovalent  $\text{Na}^+$ . For cations of similar valence, the smaller cations will have the greater charge density per unit volume and, therefore, attract more water molecules and form a larger primary hydration shell. These water molecules cause the hydrated radius of a smaller cation to be larger than the hydrated radius of a larger cation. For this reason,  $\text{Ca}^{2+}$  with hydrated ionic radius of 6A adsorbs with a much stronger energy than  $\text{Mg}^{2+}$  with hydrated ionic radius of 8A. Similarly, and  $\text{NH}_4^+$  or  $\text{K}^+$  with their respective hydrated ionic radii of 2.5A and 3A adsorbs with much stronger energy than  $\text{Na}^+$  with hydrated ionic radius of 4A. Further more, as  $\text{NH}_4^+$  and  $\text{K}^+$  can readily shed their primary hydration shell and become much smaller in size, they can preferentially replace  $\text{Na}^+$  in the soil structure. The general order of selectivity or replaceability of some important hydrated exchangeable cations is as follows:



It is difficult to place  $\text{H}^+$  in this series.  $\text{H}^+$  ion is unique because of its very small size and high charge density. Its adsorption strength can be placed between  $\text{Al}^{3+}$  and  $\text{Ca}^{2+}$  ions. However, it is weakly bonded to clay surfaces, whereas it is strongly bonded to the acidic group of the organic matters of soil. That is,  $\text{H}^+$  ions are preferably or specifically adsorbed at the soil organic matters and nonspecifically adsorbed at the clay surfaces. This indicates restricted use of acids for sodic soil amendment.

The cation exchange capacity (CEC) of a soil represents the total quantity of negative charge available to attract positively charged ions in solution. It is expressed in terms of milliequivalents of negative charge per 100 g of oven dried soil (meq/100 g). The CEC also represents the total meq/100 g of cations held on the negative charge sites of the soil particles.

The CEC of a soil is strongly influenced by the nature and amount of mineral and organic compounds present. Soils containing high clay and organic matters have higher cationic

exchange capacity than sandy soils which are low in organic matter content. The CEC of soil with different textures is given in Table 1.

**TABLE 1 - CEC VALUES OF DIFFERENT SOIL TEXTURES**

<u>Soil Textures</u>	<u>CEC ( meq/100 g )</u>
Sands ( light colored )	3 - 5
Sands ( dark colored )	10 - 20
Loams	10 - 15
Silt loams	15 - 25
Clay and Clay loams	20 - 50
Organic soils	50 - 100

It is evident that a soil with high clay content or organic matters has high CEC value, and will tend to adsorb a larger amount of cationic species. However, the capacity for the adsorption of cations will also depend on the base saturation of the soil, which is defined as the percentage of total CEC occupied by basic cations, e.g.  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$  and  $\text{Na}^{+}$ . The percentage base saturation is expressed as follows:

$$\% \text{ Base Saturation} = ( \text{total bases} / \text{CEC} ) * 100 \quad ( 1 )$$

*where total base and CEC are in terms of meq/100 g.*

In terms of field operations, the CEC differential between the soils on a mass basis can some time be deceiving. This value should also be evaluated in the light of the bulk density of the soil forming materials. For example, one pound of an organic soil may represent a volume that is several times larger than one pound of mineral soil. Similarly, the pH of the soil has a significant influence on the CEC value. Its influence is more pronounced on the soil containing high organic matter. For example, the CEC of the organic matter increases from 36 meq/100 g at pH 2.5 to 213 meq/ 100 g at pH 8 and the respective increase in the CEC of the clay is from 38 meq/100 g to 64 meq/100 g.

There is a direct relationship between CEC and Exchangeable Sodium Percentage ( ESP ) which can be expresses as follows:

$$ESP = ( Na_{Ex} / CEC ) * 100 \quad ( 2 )$$

*where  $Na_{Ex}$  is the exchangeable sodium.*

ESP can also be calculated by the following empirical relationship based on the Sodium Adsorption Ratio ( SAR ) of the soil:

$$ESP = 100 (-0.0126 + 0.01475 SAR) / [1 + (-0.0126 + 0.01475 SAR)] \quad (3)$$

SAR is calculated as follows:

$$SAR = Na / [ (Ca + Mg) / 2 ]^{0.5} \quad (4)$$

where the concentrations of Na, Ca and Mg are expressed in meq/liter.

The degree of dispersion in a soil depends on its mineralogical composition, in particular on its clay content. The clay component of soil can be classified into two broad mineralogical categories: kaolinite and montmorillonite. A soil with high kaolinitic clays and with a lower cationic exchange capacity may require as high as 40% Na saturation in its cationic exchangeable structure. On the other hand, a soil with high montmorillonitic clays with a high cationic exchange capacity may require as low as only 15% Na saturation before the soil is dispersed. However, soils with low clay content are less subject to problems as they have a low cationic exchange capacity and are also more water and air permeable.

### **Effect of Soil Electrochemistry on Vegetation**

Soil contaminated with sodium can be classified into three groups: saline, sodic and saline/sodic. Saline soils have saturated Extract Conductivity (  $EC_{se}$  ) > 4 mmhos (or mS)/cm, pH < 8.5, and ESP < 15 %. The concentration of soluble salts is sufficient to interfere with vegetation or plant growth.

Sodic soils occur when ESP > 15 %,  $EC_{se}$  < 4 mmhos/cm, and pH > 8.5. In the sodic soil, the excess Na disperses the colloidal fraction soil and the presence of  $Na^+$  creates nutritional disorder in most plants.

A combination saline/sodic soil has the salt concentration with  $EC_{se}$  > 4 mmhos/cm and high ESP of >15 %; however it has pH < 8.5. In contrast to saline soils, when the salts are leached out, the exchangeable sodium hydrolyzes and the pH increases which results in a sodic soil.

In many cases, when the damage of soil is due to salt spillage, a combination of saline/sodic condition may prevail. However, when soil is exposed to a high concentration of salt resulting in ESP > 15 % and SAR > 12.8, there is a risk of the soil becoming sodic.

At high concentrations of salts, in the presence of mixed salt species or in the presence of non-ionic dissolved components, such as organic species, a relationship between  $EC_{se}$  and Total Dissolved Solid ( TDS ) becomes inaccurate. However, in most salt spillage situation, the following statistical correlation<sup>3</sup> is useful:

$$TDS ( mg/liter ) = A * EC_{se} ( mmhos/cm ) \quad (5)$$

where A is a constant.

Based on API<sup>4</sup> and EPA<sup>5</sup> data the values of A for naturally occurring saline/sodic soils

and soil exposed to Oil & Gas field salt spillage are 640 and 613, respectively.

The high EC<sub>se</sub> value of soil increases the osmotic pressure of the soil solution. As the plant or vegetation roots in contact with this soil solution do not possess the ability to overcome the osmotic pressure of the soil, they die from a lack of water<sup>6</sup>. A statistical correlation between osmotic pressure and EC<sub>se</sub> does exist. This means that easily determinable EC<sub>se</sub> allows estimation of the potential danger for crops from increased osmotic pressure of the soil solution.

The uptake of salts from contaminated soil disrupts nutrient uptake and utilization. Consequently, excess salt in the soil solution reduces the availability of essential plant nutrients, resulting in the drop in plant yield and in many cases total devastation. There is no one threshold salinity level of all plants or vegetation. Generally, vegetables are more sensitive to salts than grains and grasses. A general crop tolerance levels to salt has been developed by the US Salinity Laboratory<sup>7,8</sup> as given in Table 2, which indicates no effect on plant yields at EC<sub>se</sub> lower than 2 mmhos/cm.

**TABLE 2 - GENERAL CROP RESPONSE AS A FUNCTION OF EC<sub>se</sub>**

<u>Ec<sub>se</sub> ( mmhos/cm )</u>	<u>Effect on Crop Yield</u>
0 - 2	None
2 - 4	Slight
4 - 8	Many crops affected
8 -16	Only tolerant crops yield well
> 16	Only very tolerant crops yield well

**TABLE 3 - REDUCTION IN CROP YIELD AS A FUNCTION OF SOIL ESP**

<u>Type of Soil</u>	<u>ESP</u>	<u>Average % Reduction in Crop Yield</u>
Slightly Sodic	7 - 15	20 - 40
Moderately Sodic	15 - 20	40 - 60
Very Sodic	20 - 30	60 - 80
Extremely Sodic	> 30	> 80

At a higher EC<sub>se</sub> value than 16 mmhos/cm, either there is a drastic reduction in plant yield or there is a complete devastation. Crop yield is also affected by the sodicity or ESP of the soil, as shown in Table 3.

### **Treatment of Salt Affected Soil**

As can be seen in Table 3, at all levels of sodic conditions the crop yield is affected. In extreme

conditions (  $ESP > 30$  ), which can be the case in many oil field brine spill sites, there can be complete devastation with the site being devoid of any vegetation. In these salt affected soils, if the mineralogy of soil is favorable, excess salinity can be leached from the soil by rainfall or by the application of irrigation water. However, the soil with high CEC value, i.e. the soil with high montmorillonitic clay content, sodium species adsorbed in the clay structure need to be replaced allowing it to drain down in the soil bed out of the root zone.

**Remediation Strategy.** Prior to treatment of salt affected soil, it is important that the site is carefully characterized. Factors such as volume and frequency of salt spillage, soil characteristics, topography of the land and the stratigraphic layout or horizontal band, commonly known as horizons of the sub-soil, have an influence on the remediation design. In many cases, if the spillage has been occurring frequently for some length of time without any remediation, under given soil mineralogical condition, the land could suffer semi to permanent damage. In such cases, restoration of the site for the growth of vegetation may require additional nutrients. With time, surface topography can change due to soil erosion. Although the remaining top soil may have a favorable physical structure conducive to the water drainage, it can be devoid of nutrients and has an unfavorable environment for the re-growth of vegetation.

For designing the remediation program for the salt affected site, it is also important to identify the depth of the sub soil saturated zone. However, wicking of the salt to the upper zone will depend on the physical nature of soil layers. Many naturally occurring saline soils result from the near surface saturated zone. In these cases, the ability of soil to drain moisture is drastically reduced where soil pores are almost saturated with water. In some cases, where the saturated zone is very close to the surface, it is almost impossible to remediate the site without having an artificial drainage system installed. Yet, it is important that the site is frequently irrigated for downward water flux to prevent the upward migration of salt due to the wicking effect.

**Field Test Results.** The following are some examples from areas within Texas and Oklahoma under variety of settings, soil types and weather conditions where the salt contaminated sites were treated with the cationic electrolytic chemicals:

***Lamesa, West Texas.*** In this case, salt contamination was due to underground pipeline leaks located in cotton and peanut fields where the salt affected crops died immediately. The salt damage ranged from 1 ft. to 2 ft. depths. At the time of soil treatment tilling and disking was not possible due to the living crops surrounding the affected areas. Water from the existing irrigation system was used for the dilution and application of the cationic electrolytic chemical. Rainwater was the only source of post treatment irrigation of the treated soil. Test results are summarized in Table 4.

**TABLE 4 - REMEDIATION OF SALT CONTAMINATED SITE AT LAMESA, TX**

<u>Location</u>	<u>General Soil Type</u>	<u>Na ( mg/Kg )</u>		<u>% Na Reduction</u>
		<u>4/2/96</u>	<u>8/2/96</u>	
1	Clayey Loam	1660	173	89.5
2	Clayey Loam	750	218	70.9
3	Clayey Loam	1770	860	51.4
4	Clayey Loam	530	220	58.4
5	Clayey Loam	3370	68	97.9

As can be seen in Table 4, at these locations in about four months after the soil treatment sodium content of the soil was reduced by 58-97%. Crops were completely restored by the following growing season.

**Houston, Texas.** Test results are shown in Table 5. At this location the salt damage occurred from pipeline leaks located in grassland areas. The locations at this site were each of about ½ acre size. At location 1, the pipeline was located above the ground and a leak flowed into a nearby stream and wooded area. At location 2, the leak occurred underground affecting the vegetation along the pipeline areas and into a highly wooded area. In both cases, all vegetation and trees were killed immediately. Both sites were treated with the cationic electrolytic chemical. For the application of this chemical, water was brought in from an outside source. Posttreatment irrigation was primarily from the natural rainfalls. No tilling or disking was possible due to thick brush and vegetation surrounding these areas. Grass seeds were applied after one week of the site treatment.

**TABLE 5 - REMEDIATION OF A SALT CONTAMINATED SITE IN HOUSTON, TX**

<u>Location</u>	<u>General Soil Type</u>	<u>Na ( mg/Kg )</u>		<u>% Na Reduction</u>
		<u>10/1/96</u>	<u>11/7/96</u>	
1	Clayey Loam	842	120	85.7
2	Clayey Loam	1190	218	81.7

As shown in Table 5, sodium levels were reduced by 81-85% in about five weeks after the site treatment. Total vegetation of the site was restored in approximately four months.

**Kilgore, Texas.** In this case, the salt spillage occurred due a storage tank into a pastureland. The total affected area was estimated to be about 15,000 ft<sup>2</sup>. As the site was a pastureland, tilling was possible at the time of chemical applications. The soil was generally classified as clayey loam. Following the application of the chemical, the site was immediately irrigated with water. In this case, a set of samples were collected after only three hours of chemical application. These samples were taken from the top 6 in. of the soil, and they were

analyzed for sodium content, SAR and ESP. Test results are summarized in Table 6, which indicate that within a short period of three hours there were significant reductions in the sodium content, SAR and ESP values of the treated soil. This behavior suggests rapid rate of interactions between the cationic chemical and the soil system.

**TABLE 6 - REMEDIATION OF A SALT CONTAMINATED SITE AT KILGORE, TX**

<u>Sample</u>	<u>Na ( mg/Kg)</u>			<u>SAR</u>			<u>ESP %</u>		
	<u>Before</u>	<u>After</u>	<u>% Red.</u>	<u>Before</u>	<u>After</u>	<u>% Red.</u>	<u>Before</u>	<u>After</u>	<u>% Red.</u>
1	5626	1950	65	44	14.5	67	75.2	4.6	94
2	3993	1516	62	27.5	2.6	91	41.3	8.7	79

**Concluding Remarks**

Accidental spillage and leakage of pipe lines are the major sources of oil field related salt contamination of native soil. The effect of the damaging sodium ions of salt on the fertility of soil is influenced by the mineralogical composition of soil and its chemical properties. Those cationic species which have more specific adsorption properties for the soil minerals, particularly clay structures, are effective as the soil amending additives. Compositions containing readily available calcium ionic source have proven to be very effective. While freshly contaminated sites are readily amendable with the application of chemicals, old contaminated sites require specific preparations and could take a longer time. Water being the work-horse for the removal of sodium species from the vegetation or plant root zone, degree and frequency of irrigation have critical effects on the site remediation process.

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