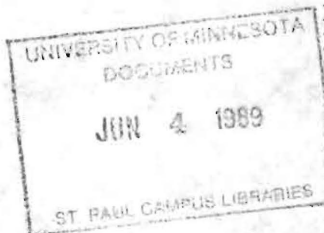


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Chemical Analysis of Soils Contaminated With Oilfield Brine

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Foreword

The purpose of this publication is to present practical guidelines for laboratory analyses of soils contaminated with oilfield brines. This information is intended for the use of commercial testing laboratories, the oil development industry, state and federal agencies involved in various phases of oil and gas development, and landowners who have concerns about brine contamination. The interpretation of these analyses will be discussed in a subsequent bulletin entitled "Diagnosis and Reclamation of Soils Contaminated with Oilfield Brine."

In most cases, the procedures are those commonly used for the analysis of saline and sodic agricultural soils with modifications for their adaption for brine-contaminated soils. The modifications given in this report are based upon research conducted by the Land Reclamation Research Center. The methods presented in this publication are for practical use by those trained in routine laboratory procedures. The necessary equipment and chemical solutions are generally available in commercial analytical laboratories. The complex solution and surface chemistry reactions that take place when brine reacts with the soil will not be discussed; persons interested in the more technical aspects are referred to the cited references.

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Introduction

Crude oil from the North Dakota oilfields usually occurs mixed with approximately equal amounts of brine which is separated and injected into deep disposal wells. The brine salts are predominately chlorides, usually consisting of 90 percent or more sodium chloride (NaCl), and the remaining salts are mostly calcium chloride (CaCl₂) and magnesium chloride (MgCl₂). A thousand gallons (approximately 24 barrels) of brine may contain over a ton of NaCl. Soils frequently become contaminated with brine due to leaks or spills at the pumping or battery site, to pipeline breaks, or to trucking mishaps.

The total salt content of brine-contaminated soils may initially be 10 or more times that of naturally occurring saline and saline-sodic soils. For example, electrical conductivity (EC) is a measure of soluble salts in a soil. In saturation extracts from agricultural soils, EC values above 2 mmho/cm in the surface soil and above 4 mmho/cm in the subsoil are considered to be detrimental to plant growth; EC values in naturally saline soils are usually less than 20. In brine-contaminated soils, we have measured EC values in excess of 200. The sodium adsorption ratio (SAR) is used to measure the relative activity of sodium in soils (sodicity). In agricultural soils, a topsoil SAR value above 4 and a subsoil value above 10 are considered to restrict plant growth; in agricultural soils, SAR values are usually below 20 or 25. In brine-contaminated soils, we have measured SAR values above 150. For this reason, procedures developed for analyses of naturally-occurring saline and sodic soils are not always directly applicable to brine-contaminated soils.

In the soils of western North Dakota, the naturally-occurring soluble salts are predominately sulfates of calcium (Ca), magnesium (Mg) and sodium (Na). Since salts in North Dakota oilfield brines are mostly chlorides (Cl), this means that Cl can be used as a tracer for the degree and extent of brine contamination. Sodium is not suitable for use as a tracer because naturally sodic soils frequently have relatively high levels of Na.

Sample Preparation

Samples may be obtained in the field by a number of different methods - with a shovel, with a hand probe or auger, or a truck-mounted hydraulic probe.

Field procedures for sampling brine-contaminated sites will be given in a subsequent publication, and only sample care in the laboratory will be discussed here.

Samples should be immediately placed in plastic bags for transport to the laboratory, allowed to air-dry completely, and then ground to pass 2 mm (10 mesh) screen. Ground samples should be stored in closed water-resistant containers until analyzed. Care must always be exercised during sample preparation to ensure against contamination by either other samples or any extraneous substances.

Analytical Procedures

The analytical methods given in this section are intended for routine analyses to identify the extent of brine-contaminated areas and to use in developing appropriate reclamation plans. Our research has shown that the methods presented here are sufficiently precise for use in practical field programs. When procedures include modifications from those developed for agricultural soils, data will be presented to substantiate these modifications.

Laboratory analytical determinations are reported here in the commonly accepted metric units, and concentrations are reported as milliequivalents per liter (meq/l) or per 100 g of soil (meq/100 g). Results are then converted to English units for the final computations. Rather than require bulk density determinations for each site, we have used the generally accepted average bulk density of 1.32 g/cm³. We then assumed that an acre/foot of soil weighs 3,600,000 lbs., and a 6-inch layer 1,800,000 lbs. Samples are usually taken in 1-foot increments to a depth of 4 feet; explicit directions for converting laboratory data for field use will be given in the subsequent bulletin on diagnosis and reclamation of brine-contaminated soils.

Method 1. Preparation of Saturated Paste and Determination of Saturation Percentage

The preparation of the saturated paste and subsequent analysis of the saturation extract is a generally accepted procedure for determining soil salinity and sodicity. The saturation extract is preferred because it is felt that it more nearly approximates field conditions in brine-contaminated soils than extracts of 1:1 and 1:5 soil:water mixtures.

Procedure:

Place 250 to 500 g of air-dry soil in a suitable container and add distilled water. Stir the mixture with a spatula until saturation is reached. At saturation, the soil glistens as it reflects light, flows slightly when the container is tipped, and slides freely from the spatula for all soils except those high in clay. Cover the container tightly and allow to stand overnight, then recheck the criteria for saturation. If free water has collected on the surface, add more soil and remix. If the paste has stiffened or lost its glisten, add more water and remix.

When saturation has been reached, pH of the paste should be determined (Method 2). To determine saturation percentage (SP), place a subsample of the saturated paste (25 to 30 g) in a weighed container, weigh container and paste, dry overnight at 105 degrees Celsius, and reweigh. To obtain the saturation extract, the remaining paste is transferred to a Buchner funnel fitted with highly retentive filter paper and filtered under vacuum. Discard or refilter the initial filtrate if it is turbid. About one-fourth of the added water can be removed under ordinary laboratory suction. Terminate filtration when air begins to pass through the filter or when sufficient extract has been obtained. The saturation extract will be used for determination of electrical conductivity (EC), soluble cations (Ca, Mg and Na) and Cl. Store saturation extracts in a refrigerator at 4 degrees Celsius until analyzed.

NOTE: For large numbers of samples, the use of a blender or mixer may be preferred for preparation of the saturated paste.

Calculations:

Saturation percentage (SP) is the percentage of water in the saturated paste based upon the weight of the oven-dry soil. Calculate the weight of the subsample of the paste and of the oven-dry soil by subtracting the container weight. Calculate saturation percentage (SP) as follows:

$$SP = \frac{\text{Wt. Paste} - \text{Wt. Oven Dry Soil}}{\text{Wt. Oven Dry Soil}} \times 100$$

Reference:

United States Department of Agriculture, 1984.

Method 2. Measurement of pH of Saturated Paste

The pH determination is a measure of the hydrogen ion concentration of the saturation extract and is not directly related to the soluble salt concentration. If the pH value for a specific sample differs markedly from values for other contaminated and uncontaminated samples from the same site, another

saturated extract should be prepared and the pH value redetermined. If a markedly different value is again obtained, sample contamination should be suspected.

Equipment:

Glass electrode pH meter; pH buffer solutions

Procedure:

Standardize the pH meter in the usual manner, and insert the electrodes into the saturated paste. Raise and lower the electrodes and rotate the paste container repeatedly until a representative pH reading is obtained.

Reference:

Sandoval and Power, 1977.

Method 3. Electrical Conductivity

Electrical conductivity (EC) is a reliable estimate of the total soluble salt concentration of the saturation extract, but does not measure the chemical composition of the salts. Measurements of soluble cations (Method 4) on a smaller number of selected samples can be used to determine the amount and kinds of salts, and these values can then be correlated with the EC values to determine the total amount of soluble salts in the contaminated site.

Equipment:

1. Conductivity meter
2. Conductivity flow cell with automatic temperature compensator

Reagents:

1. **Standard potassium chloride (KCl) solutions, 0.010 N and 0.100 N:**

Solutions of 0.010 N (0.7456 g KCl per liter) and 0.100 N (7.456 g KCl per liter) will have EC values of 1.41 and 12.86 mmhos/cm, respectively.

Procedure:

After the saturation extract (Method 1) and the standard solutions have reached room temperature, standardize the meter with the standard KCl solutions, then determine the conductivity of the saturation extract. Rinse the cell thoroughly between readings. Most conductivity meters can be adjusted to directly read the higher EC values of brine-contaminated soils. If not, dilution of the saturation extract may be required, and final readings must be adjusted accordingly. Because of the dilution effect on the ionic activity in concentrated solutions, EC values adjusted for dilution are not exact, but they are adequate for estimating the total amount of soluble salts present.

Reference:

Rhoades, 1982; Sandoval and Power, 1977.

Method 4. Soluble Cations

The dominant cations in brine-contaminated soils are Ca, Mg, and Na; the low concentrations of other cations that may be present are not a factor in the diagnosis and reclamation of these soils. The sodium adsorption ratio (SAR) is used to estimate the probable sodicity hazard after the brine salts are leached from the soil. The concentration of each cation in the saturation extract (Sat Ext) can be used to calculate the amount in the soil (meq/100 g) and the sum of all soluble cations to estimate the total soluble salts (TSS). The TSS and the amount of each cation are used in developing the reclamation plan and to correlate with EC values (Method 3) for estimating the amount and distribution of soluble salts in the entire site. Soluble cations only need to be determined on a sufficient number of representative samples to adequately correlate EC with TSS and to estimate the total amount of Ca, Mg, and Na in the site.

Equipment:

1. Atomic absorption spectrophotometer is preferred, although other procedures for analysis are satisfactory.
2. An automatic diluting apparatus is advisable if large numbers of samples are to be analyzed.

Procedure:

Standardize the spectrophotometer, using appropriate standard solutions, and determine the concentrations of Ca, Mg, and Na in aliquots of the saturation extract (Method 1). For samples highly contaminated with brine, aliquots may need to be diluted, sometimes by as much as 10 to 180 thousand times. If an internal standard such as strontium or lanthanum is used for the spectrophotometric analysis, adding the required concentration to the diluting solution will simplify laboratory procedures.

Calculations:

Report concentrations of each cation as milliequivalents per liter (meq/l) in the initial saturation extract by adjusting for dilution (multiply the measured concentration by the dilution factor). Calculate the sodium adsorption ratio (SAR) as follows:

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

in which all concentrations are expressed as meq/l.

In brine contaminated soils, the soluble salt content per unit weight of soil is needed. Calculate the milliequivalents of each cation per 100 grams of soil (meq/100 g) as follows:

$$\text{meq Sol Cat/100 g} = \frac{(\text{meq/l sat. ext}) \times SP}{1000}$$

in which SP is the saturation percentage (Method 1). The meq/100 g of total soluble salts (TSS) is the sum of the amounts of Ca, Mg and Na.

Reference:

Rhoades, 1982; Sandoval and Power, 1977.

Method 5. Chloride

Naturally occurring soluble salts in western North Dakota soils are mostly sulfates, while oilfield brines are predominately chlorides. Levels of Cl in samples from heavily and moderately contaminated areas are compared with those from uncontaminated areas to verify contamination by oilfield brines. Samples from a site suspected of contamination and from two adjacent noncontaminated sites are usually adequate.

Equipment:

1. Magnetic stirrer
2. Titration assembly

Reagents:

1. **Potassium chromate (K_2CrO_4) indicator:**
Dissolve 5 g K_2CrO_4 in about 75 ml water. Add a saturated solution of silver nitrate ($AgNO_3$) slowly until red silver chromate (Ag_2CrO_4) starts to precipitate. Set in dark for 24 hrs, filter to remove Ag_2CrO_4 and dilute to 100 ml.
2. **Standard silver nitrate ($AgNO_3$) solution: (0.025 N):**
Dissolve 4.2472 g reagent grade $AgNO_3$ in water and dilute to 1,000 ml. Determine exact normality as described in the following "Procedure" by titrating an aliquot of the 0.01 N KCl solution prepared for the conductivity standard (Method 3). Since $AgNO_3$ solutions are light-sensitive, place in dark bottle and store in dark.
3. **Sodium bicarbonate ($NaHCO_3$) saturated solution:**
Place about 15 g $NaHCO_3$ in 100 ml water, shake, and let stand overnight. Filter as needed into a dripping bottle.
4. **Methyl Orange Indicator:**
Dissolve 0.1 g methyl orange powder in 100 ml water.
5. **Phenolphthalein indicator:**
Dissolve 0.25 g phenolphthalein powder in 100 ml of 50 percent ethanol.

Procedure:

To determine the normality of the $AgNO_3$ standard solution, pipet exactly 25 ml of 0.010 N KCl (conductivity standard, Method 3) into a titration flask, add 5 drops K_2CrO_4 indicator, and titrate with $AgNO_3$ solution (Regent 2) until appearance of a reddish-brown precipitate. Approximately 10 ml of $AgNO_3$ solution

should be needed. At the same time, titrate a 25 ml distilled water blank to the same end point; subtract ml AgNO_3 required to titrate the blank from ml AgNO_3 required to titrate the sample aliquot to determine ml AgNO_3 required to titrate Cl in the aliquot.

To determine Cl in the saturation extract, place an aliquot in the titration flask, start the stirrer. Adjust pH to alkaline with methyl orange but acid to phenolphthalein; usually one drop NaHCO_3 saturated solution is adequate. Add K_2CrO_4 indicator (one drop per 5 ml of aliquot) and titrate with standard AgNO_3 solution until appearance of reddish-brown precipitate. For brine contaminated soils, the extract may need to be diluted. Titrate a distilled water blank of equal volume to the titrated aliquot; calculated ml AgNO_3 required to titrate Cl as described above.

Calculations:

Normality of AgNO_3 standard solution:

$$\text{Normality of } \text{AgNO}_3 = \frac{0.25}{(\text{ml } \text{AgNO}_3 - \text{ml blank})}$$

Concentration Cl in titrated aliquot:

Meq Cl/l =

$$\frac{1,000 (\text{ml } \text{AgNO}_3 - \text{ml blank}) \times \text{normality } \text{AgNO}_3}{\text{ml sample titrated}}$$

If the sample titrated has been diluted;

Meq Cl/l in Sat Ext =

Meq Cl/l in titrated aliquot x dilution factor

Reference:

Sandoval and Power, 1977.

Method 6. Extractable and Exchangeable Cations

To reclaim brine-contaminated soils, Ca amendments are applied to replace exchangeable Na remaining after displacement of the brine solution. At the same time, Na from the displaced brine solution replaces soluble cations in the lower levels of the soil, which in turn become sodic; the replaced cations (primarily Ca and Mg) move downward with the diluted brine solution. The content of extractable, soluble, and exchangeable cations at various depths in the root zone need to be determined to calculate the needed amount of Ca amendment. Extractable cations (Ext Ca) include both soluble cations (Sol Cat) and exchangeable cations (Exch Cat). In this procedure, Ext Cat are determined and Exch Cat calculated by subtracting the Sol Cat as determined in the saturation extract (Method 4). Extractable cations need to be determined on a limited number of samples (see Method 7, Calcium Requirement).

Equipment:

1. Centrifuge
2. 50 ml centrifuge tubes
3. Reciprocating shaker
4. Atomic adsorption spectrophotometer (or flame spectrophotometer)

Reagents:

1. Ammonium Acetate Extracting Solution (1.0 N NH_4OAc , pH 7.0):

Add 57 ml concentrated acetic acid (CH_3COOH) and 68 ml concentrated ammonium hydroxide (NH_4OH) to 700 or 800 ml distilled water, dilute to 1,000 ml, mix, and adjust to pH 7.0 by addition of concentrated CH_3COOH or NH_4OH .

2. Ethanol (EtOH), approximately 60 percent.

Dilute 600 ml EtOH to 1000 ml with distilled water.

Procedure:

Place the weighed soil sample (about 4 grams for fine textured and 6 grams for coarse textured soils) in centrifuge tube, add 33 ml of 1.0 N NH_4OAc , stopper, and place on reciprocating shaker for 15 minutes. Centrifuge until supernatant liquid is clear (usually 5 minutes at RCF 1,000) and carefully decant into a 100 ml volumetric flask. Repeat extraction once (total of 2 extractions) and decant into same flask. Make to volume, mix, and determine Ca, Mg, and Na as in Method 4.

Soluble salts should be removed from samples testing above EC 15 before extracting Exch Cat. This both facilitates complete extraction of Exch Cat and alleviates the need for diluting the extract for the cation determinations. Place the soil sample in a 50 ml centrifuge tube, add 33 ml of reagent 2, place on shaker for 15 minutes, then centrifuge. Carefully decant the supernatant liquid and discard. Extract the same sample twice more with 33 ml EtOH as above (total of three successive extractions). From the sample extracted with EtOH, extract exchangeable cations with NH_4OAc as described above.

Calculations:

Extractable cations (Ext Cat) include both soluble cations (Sol Cat) and exchangeable cations (Exch Cat). Calculations for each individual cation are as follows:

$$\text{Meq Ext Cat/100 g} = \frac{(\text{Meq/l Cat in Extract}) \times 10}{\text{g. of sample}}$$

Soluble cations in the saturation extract were determined previously in Method 4. When soluble salts are removed using EtOH, Ext Cat are a measure of Exch Cat.

Reference:

Sandoval and Powers, 1977; See Appendix for substantiation of modifications and additions to the referenced procedure.

Method 7. Calcium Requirement

This determination gives a measure of exchangeable Na remaining in the soil after the brine solution has been replaced and which must be replaced by Ca during reclamation. The extracting procedure is exactly the same as for Ext Cat (Method 6) except that only Na is determined in the extract; the amount of exchangeable Na determined in Method 6 can be used to calculate the calcium requirement (Ca Req). However, Ca Req needs to be determined on two or three times as many contaminated samples as for Cl and Ext Cat.

Equipment:

1. Centrifuge
2. 50 ml centrifuge tubes
3. Reciprocating shaker
4. Atomic adsorption spectrophotometer (or flame photometer)

Reagents:

1. Ammonium Acetate Extraction Solution

(NH₄OAc):

Reagent 1 in Method 6.

2. 60 percent Ethanol (EtOH):

Reagent 2 in Method 6

Procedure:

Place weighed soil sample (about 4 grams for medium textured and about 6 grams for coarse-textured soils) in centrifuge tube, add 33 ml 60 percent EtOH and shake for 15 minutes. Centrifuge, carefully decant and discard the supernatant liquid. Extract the same sample twice more with EtOH as above (total of three extractions). Add 33 ml NH₄OAc solution to the sample in the centrifuge tube, shake 15 minutes, and decant supernatant liquid into a 100 ml volumetric flask. Re-extract the same sample once more with NH₄OAc, decant the supernatant liquid into the same 100 ml volumetric flask, make to volume, and determine meq/l Na in the extracting solution.

Calculations:

The calcium requirement (Ca Req) is calculated as follows:

$$\text{Meq/100 g Ca Req} = \frac{\text{Meq/l Na} \times 10}{\text{g sample}}$$

This test is to be used to calculate the amount of calcium amendment needed to replace adsorbed Na and reclaim brine-contaminated soils. The recommended amendment is calcium chloride (CaCl₂•H₂O). The rate to be applied is calculated as follows to give the amount per acre or per 1,000 sq. ft. for a depth of 1-foot (assuming the sample tested represents a 1-foot depth):

$$\text{CaCl}_2 \text{ (lbs/a)} = \text{Ca Req (meq/100 g)} \times 2,700$$

$$\text{CaCl}_2 \text{ (lbs 1,000 sq ft)} = \text{Ca Req (meq/100 g)} \times 60$$

Reference:

Lang, K.J., et al., 1986. Abrol, et al., 1975; see following Appendix for confirmation of procedure.

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Appendix

Sodic soils are reclaimed by applying a suitable Ca amendment to replace exchangeable Na and then leaching the replaced Na out of the root zone using either irrigation or natural precipitation. When soils are contaminated with oilfield brine, the amount of soluble Na may be two or three times greater than that of exchangeable Na. However, when Ca amendments are added and leaching begins, the brine solution containing soluble Na is displaced downward, and only the remaining exchangeable Na needs to be displaced during reclamation. Consequently, to accurately calculate the required amount of Ca amendment needed, excess soluble salts, including soluble Na, must be removed from the sample before determining the remaining exchangeable Na. To do this, the gypsum requirement test of Abrol et al. (1975) was adapted by determining the number of successive ethanol extractions needed to adequately remove the high levels of soluble salts found in brine-contaminated soils.

After the excess soluble salts are removed, the amount of Ca amendment that needs to be applied to reclaim the soil, hereinafter termed the calcium requirement, can be calculated from determinations of the remaining exchangeable Na. The results of Lang, Merrill and Doll (1986) indicated that extraction of Na with 0.013 M CaCl₂ gave an accurate measurement of the Ca Req. Since 1.0 N NH₄OAc is used for extracting Exch Cat in the procedure given in this bulletin, the use of NH₄OAc for determining the Ca Req would simplify the procedure. Therefore, extractions with NH₄OAc and CaCl₂ were compared for determining the Ca Req.

Procedure:

A series of 14 soil samples were selected from sites which had been contaminated with oilfield brine; the electrical conductivity (EC) of the samples varied from 2.1 to 151.4 mmho/cm and the SAR from 3 to 178 (Table 1). A 5 g soil sample was placed in a 100 ml centrifuge tube and shaken with 33 ml 60 percent ethanol (EtOH) for 15 minutes, centrifuged until the supernatant liquid was clear, decanted into a volumetric flask, and Ca, Mg, and Na in solution determined using an atomic absorption spectrophotometer. All samples were successively extracted three times with EtOH, and a fourth successive extraction carried out on selected samples.

For comparison of extractants for determining Ca Req, 5 g soil were placed in 50 ml centrifuge tubes. To one set of duplicate samples, 33 ml of 1.0 NH₄OAc was added, and to another set 33 ml of 0.013 M CaCl₂ was added. Samples were shaken for 15 minutes, centrifuged until the supernatant liquid was clear, and decanted into a 100 ml volumetric flask, and Na determined by atomic absorption spectroscopy. Each sample was successively extracted three times.

Extraction of soluble cations with EtOH:

The total amount of Na removed by the successive EtOH extractions was approximately equal to the total amount of Na in the Sat Ext (Table 2). However, this is only an approximate comparison and should not be used for quantitative evaluations. The SP (Table 1) varied from 32 to 76 for these samples, so the soil/solution ratio for the saturated pastes was always less than 1:1, while a ratio of 5:33 was used in the EtOH extractions. Furthermore, the saturated pastes were allowed to equilibrate for approximately 24 hours as compared to 15 minutes for each successive EtOH extraction. However, this rationale does not entirely explain why more Na was extracted

Table 1. Saturated paste and extract analyses of brine contaminated soils.

Sample No.*	Saturated Paste		Saturated Extract				SAR
	pH	SP	EC mmho/cm	Ca meq/l	Mg meq/l	Na meq/l	
1	7.7	51	7.4	23.0	56.9	29.8	5
2	7.3	52	13.3	47.9	45.2	22.7	3
3	7.3	36	24.0	91.0	87.0	98.6	10
4	7.5	51	44.0	21.5	10.6	453.9	113
5	7.5	53	69.6	45.3	21.6	742.6	128
6	7.5	45	82.5	56.2	28.0	840.8	136
7	7.2	45	114.7	145.1	90.9	1262.1	116
8	7.1	76	2.1	12.0	0.4	5.8	2
9	7.8	69	12.2	8.4	1.3	98.0	44
10	7.6	41	20.3	59.6	2.9	145.2	26
11	7.2	54	43.2	24.3	5.3	447.8	116
12	7.4	41	63.3	61.3	11.3	625.4	104
13	7.4	47	84.9	100.5	31.6	984.3	121
14	—	32	151.4	164.4	36.5	1787.1	178

*Samples 1-7 are from a site in McKenzie County, and samples 8-14 from Bottineau County.

Table 2. Soluble Na removed from brine-contaminated soils by successive extractions with 60% EtOH.

Sample No.	Amount of Na (meq/100 g soil)					Total
	Initial*	EtOH Extraction				
		1	2	3	4	
1	1.5	0.8	0.4	0.2	0.2	1.6
2	1.2	1.0	0.2	0.1	—	1.3
3	3.6	2.7	1.1	0.2	—	4.0
4	23.2	18.9	2.5	0.8	—	22.2
5	39.4	32.4	8.3	1.4	0.8	42.9
6	39.6	31.3	6.1	1.0	0.8	39.2
7	56.8	47.6	6.5	1.9	0.5	56.5
8	0.4	1.3	0.2	0.1	—	1.6
9	6.8	5.1	1.1	0.2	—	6.4
10	6.0	5.1	1.3	0.2	—	6.6
11	24.2	16.5	5.3	0.7	0.3	22.8
12	25.6	15.3	5.3	0.6	—	21.2
13	46.3	33.0	11.7	1.3	0.4	46.4
14	57.2	59.7	24.6	4.4	1.0	89.7

*Calculated from Na concentration in saturation extract given in Table 1; not directly comparable with Na extracted with EtOH because of differences in soil/solution ratios and time.

with EtOH than was contained in the Sat Ext for samples 8 and 14 (Table 2).

However, these results do indicate that essentially all of the soluble Na is removed by the EtOH extractions. Of the total amount of Na extracted, an average of 75 percent was removed by the first extraction, 21 percent by the second, and 4 percent by the third extraction. In comparison with the total amount extracted, that removed in the fourth extraction was negligible.

The total amounts of Ca and Mg extracted with EtOH were appreciably less than that in the saturation extract (Tables 3 and 4). This is due to the low solubility of many of the Ca and Mg compounds in the soil as compared to the Na compounds, so that more Ca and Mg became soluble during the 24-hour saturated paste equilibration than during the relatively short EtOH extraction. When the total amount of Ca and Mg removed by EtOH is considered, the amount removed by each of the successive extractions follows the same pattern as the removal of Na.

These results indicate that three successive extractions are necessary to adequately remove soluble Na from the contaminated samples with high contents of soluble salts (as illustrated by samples 5, 6, 7, 13 and 14 in Table 2).

Comparison of extractants for calcium requirement determinations:

The amount of Na extracted with NH_4OAc was about equal to that extracted with CaCl_2 (Table 5) in-

dicating that NH_4OAc can be used for Ca Req determinations instead of CaCl_2 as suggested by Lang, Merrill, and Doll (1986).

The results of the successive extractions with each reagent (Table 5) indicate that 97 percent to 98 percent of the total Na is removed by the first two extractions. Therefore, two successive extractions with 1.0N NH_4OAc are adequate for Ca Req determinations.

Table 3. Soluble Ca removed from brine-contaminated soils by successive extractions with EtOH.

Sample No.	Amount of Ca (meq/100 g soil)					Total
	Initial*	EtOH Extraction				
		1	2	3	4	
1	1.2	0.1	0.1	0.1	0.1	0.4
2	2.5	2.2	0.2	0.1	—	2.5
3	3.3	2.0	0.6	0.1	—	2.7
4	1.1	0.4	0.1	0.1	—	0.6
5	2.4	1.2	0.1	0.1	0.3	1.7
6	2.5	1.2	0.1	0.1	0.3	1.7
7	6.5	5.3	0.1	0.0	0.1	5.5
8	0.9	0.5	0.1	0.1	—	0.7
9	0.6	0.1	0.0	0.1	—	0.2
10	2.4	1.1	0.1	0.1	—	1.3
11	1.3	0.2	0.1	0.0	0.0	0.3
12	2.5	0.3	0.1	0.0	—	0.4
13	4.7	2.3	0.3	0.1	0.3	3.0
14	5.3	4.3	1.2	0.1	0.1	5.7

*Calculated from Ca concentration in saturation extract given in Table 1; not directly comparable with Ca extracted with EtOH because of differences in soil/solution ratio and time of extraction.

Table 4. Soluble Mg removed from brine-contaminated soils by successive extractions with EtOH.

Sample No.	Amount of Mg (meq/100 g soil)					Total
	Initial*	EtOH Extraction				
		1	2	3	4	
1	2.9	0.2	0.1	0.1	0.1	0.5
2	2.4	2.2	0.3	0.1	—	2.6
3	3.1	2.0	0.7	0.1	—	2.8
4	0.5	0.2	0.0	0.1	—	0.3
5	1.1	0.6	0.1	0.1	0.4	1.2
6	1.3	0.6	0.1	0.1	0.3	1.1
7	4.1	3.1	0.1	0.0	0.1	3.3
8	0.1	0.1	0.0	0.0	—	0.1
9	0.1	0.1	0.0	0.0	—	0.1
10	0.1	0.1	0.0	0.0	—	0.1
11	0.3	0.1	0.0	0.0	0.1	0.2
12	0.5	0.1	0.0	0.1	—	0.2
13	1.5	0.7	0.2	0.1	0.1	1.1
14	1.2	1.0	0.4	0.0	0.1	1.5

*Calculated from Mg concentration in saturation extract given in Table 1; not directly comparable with Mg extracted with EtOH because of differences in soil/solution ratio and time of extraction.

Table 5. Sodium removed by each of three successive extractions with either CaCl₂ or NH₄OAc for determination of calcium requirement.

Sample No.	Sodium Extracted (meq Na/100 g soil)							
	CaCl ₂				NH ₄ OAc			
	1	2	3	Total	1	2	3	Total
1	0.48	0.14	0.04	0.66	0.90	0.20	0.04	1.14
2	0.20	0.06	0.02	0.28	0.22	0.12	0.04	0.38
3	0.30	0.06	0.02	0.38	0.32	0.08	0.04	0.44
4	5.46	0.76	0.18	6.40	5.80	0.60	0.08	6.48
5	4.40	0.60	0.22	5.22	4.20	0.86	0.16	5.22
6	4.38	0.70	0.10	5.18	4.02	0.66	0.10	4.78
7	4.54	0.36	0.32	5.22	4.28	0.50	0.08	4.86
8	0.22	0.04	0.02	0.28	0.20	0.08	0.02	0.30
9	5.46	0.94	0.18	6.58	5.62	0.68	0.10	6.40
10	0.92	0.12	0.02	1.06	0.94	0.14	0.04	1.12
11	7.36	1.42	0.24	9.02	8.00	0.98	0.16	9.14
12	4.56	0.92	0.12	5.60	4.80	0.52	0.08	5.40
13	4.12	0.58	0.10	4.80	3.80	0.44	0.08	4.32
14	3.14	0.38	0.08	3.60	2.28	0.64	0.08	3.00