Evaluation of Limiting Constituents Suggested for Land Disposal of Exploration and Production Wastes

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
AND
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FOREWORD

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SECTION 1

INTRODUCTION AND EXECUTIVE SUMMARY

Onshore exploration and production (E&P) activities generate a limited variety of wastes. Ninety-eight percent of E&P waste (by volume) is composed of produced water, most of which is disposed of via Class II injection wells. The remaining 2% is composed of drilling wastes (drilling muds and wellbore cuttings that yield pit solids and liquids) and associated wastes which include production solids, tank bottoms, oily emulsions, and so forth. E&P wastes that are not recycled or managed at off-site facilities are commonly disposed of on site in pits or landspread over larger areas.

The objective of this study was to develop salinity and petroleum hydrocarbon threshold values for one-time landspreading, on-site burial, or road spreading of these E&P wastes. Definition, technical justification and guidance for the application of these threshold values is provided. Measurable parameters which serve as indices for proper management of salinity and petroleum hydrocarbons include: electrical conductivity (EC), sodium adsorption ratio (SAR), and exchangeable sodium percentage (ESP) for salinity; and oil and grease (O&G) for petroleum hydrocarbons.

The threshold guidance values generally recommended for land-applied waste:soil mixtures are EC <4 millimho per centimeter (mmho/cm), SAR <12, ESP <15%, and O&G <1%. The parameter thresholds have been developed to be generally applicable for any waste containing salts or petroleum hydrocarbons including E&P wastes under ordinary conditions. Previous studies cited within this document provide supporting technical justification for selection of the threshold values.

In general, waste:soil mixtures that test below the threshold values are shown to have minimal impact to soil and vegetation for one-time applications. Yield reductions for many crops is less than 15% in the first year after application. Under certain restrictive conditions, the guidance threshold values have to be adjusted or crops temporarily changed to more tolerant species. Depending on drainage, crop cover, and soil amendments (gypsum and fertilizer), a soil with a loading no greater than that recommended should recover over a few seasons. **The operator must determine whether the guidance values apply over the short- or long-term, or whether site-specific conditions warrant more or less restrictive values.**

In general, the references cited within this report provide support for the recommended guidance values to avoid potential groundwater contamination. In addition, API is developing a contaminant fate and transport model to verify the appropriateness of the threshold values for a range of hydrogeologic environments found at E&P sites.

SECTION 2

TECHNICAL JUSTIFICATION AND LITERATURE REVIEW

2.1 Limiting Constituents

Salts and hydrocarbons have been identified as the principal limiting constituents of concern relative to onshore E&P operations because they may induce a phytotoxicity or, in the case of sodium salts, may deteriorate soil structure interrupting normal soil-plant-water relationships and causing excessive erosion (Miller and Honarvar, 1975; Ferrante, 1981; Freeman and Deuel, 1984; Nelson et al., 1984). Salts and hydrocarbons associated with E&P wastes may pose a significant threat to surface and groundwater resources when not properly managed (Henderson, 1982; Murphy and Kehew, 1984).

2.2 Salinity

Salinity is a general term reflecting the levels of available cations and anions in aqueous solution. Major ions include sodium (Na), calcium (Ca), magnesium (Mg), potassium (K), chloride (Cl), sulfate (SO_4), bicarbonate (HCO_3), carbonate (CO_3) and hydroxide (OH). EC reflects the ionic strength or total level of these constituents, while SAR and ESP consider the influence that specific ions may have under particular circumstances.

2.2.1 Definitions

Charged particles in solution will conduct an electric current to an extent determined primarily by the concentration and type of ionic species present, hence the term electrical conductivity. EC is measured directly in reciprocal units of resistance and conveniently reported in mmho/cm. Since dissolved solids are predominately dissolved salts in the form of dissociated charged particles, EC may be used as an indirect, approximate measure of total dissolved solids (TDS).

TDS is defined in chemical terms as the unfilterable residue associated with aqueous fluids resulting from the evaporation of a known quantity of water, and is reported in terms of mass per unit volume (mg/liter). This residue is predominately composed of salts, but may include organic materials (humic substances or anthropogenic compounds) or mineral colloids passing through the filter.

An exact relationship exists between concentration of a specific salt in pure water and electrical conductance of that solution (Barrow, 1966). However, this relationship is inaccurate at high-salt concentration, solutions of mixed salt species, or presence of nonionic dissolved species. Of more immediate use have been empirical correlations between TDS and EC for various aqueous solutions:

$$TDS = (A) \ X \ (EC)$$

with the regression constant "A" (slope), being used as a conversion factor. Values of "A" have been found to range naturally from 540 to 960 cm.mg/mmho.liter (Hem, 1985). For naturally occurring saline/sodic soils a constant of 640 may be assumed (U.S. Salinity Laboratory Staff, 1954). Using the above equation, one calculates a TDS of 2560 mg/liter at a corresponding EC of 4 mmho/cm, and "A" of 640 cm.mg/mmho.liter. A recent analytical review of E&P wastes by the EPA (1987), and parallel review by the API (1987), suggested that an "A" value of 613 more accurately estimates TDS in E&P wastes when calculated from EC. This value is used in subsequent TDS calculations within this document.

TDS is generally not an accurate measure of salinity for many E&P wastes, due to errors associated with hydrocarbons and fine clay passing the filtration step. If one wants the perspective of salinity on a mass basis, it is best estimated from EC. EC has long been the parameter of choice in defining salinity hazards associated with production agriculture.

2.2.2 Concerns

2.2.2.1 Plants and Soil

Although some elements, such as boron, are toxic to plants, generally the ill effects of salinity are caused by increased osmotic pressure of soil solution in contact with plant roots (Haywood and Wadleigh, 1949; U.S. Salinity Laboratory Staff, 1954). Osmosis is a process that controls the movement of water between solutions and depends upon the number of dissolved molecules or ions (salinity). Water flows from lower to higher osmotic pressure. Plants have an osmotic pressure associated with their cell solution which varies greatly between plant species and to some degree between cultivars within species. If the osmotic pressure in soil solution outside the plant exceeds that inside, the plants wilts. The point of permanent wilting is reached when the plant can not recover even when exposed to less saline water. There is a direct relationship between osmotic pressure and EC:

$$\text{Osmotic Pressure (OP), atm.} = 0.36 \times \text{EC, mmho/cm}$$

Salts also affect plants by disrupting normal nutrient uptake and utilization (Kramer, 1969). The mechanism is one of simple antagonism, whereby a given salt specie in excess inhibits the plant intake of required elements. The effect is usually manifested as a deficiency resulting in lowered yield expectations or overall crop quality.

There is no one critical or threshold salinity level where all plants fail to grow or maintain acceptable yields (Maas and Hoffman, 1977). General crop response to soil salinity is shown in Table 1 (U.S. Salinity Laboratory Staff, 1954). The sensitivities of various agricultural crops to salt are shown in Figures 1 through 3 generated from equations and data in Maas (1986). For example: At an EC of 4 mmho/cm, barley, cotton, and bermuda grass are not affected by salt, whereas yields are expected to decrease for rice and corn (0-15%), alfalfa and sugarcane (15-30%) and beans (30-50%). Yield response intervals shown in Figures 1 through 3 were developed from agricultural

Table 1. General Crop Response as a Function of EC.

(After U.S. Salinity Laboratory Staff, 1954)

EC (mmho/cm)	Effect on Crop Yield
0 - 2	None
2 - 4	Slight to none
4 - 8	Many crops affected
8 - 16	Only tolerant crops yield well
> 16	Only very tolerant crops yield well

systems receiving salt-containing irrigation over the long term and may overestimate the anticipated response for a one-time land disposal of E&P wastes. Based on Lunin (1967), the authors believe that salinity guidelines for continual use systems can reasonably be doubled for a one-time application; the rationale being that salt accumulated outside the bulk soil mass (in pores and on ped surfaces) is more easily displaced than that penetrated into and reacted with the bulk soil mass.

If the salinity is initially too high for a given crop after land applications of waste, soils will generally recover following rainfall or irrigation containing less salt because excess salts are leached when adequate drainage is present. Growth of more salt tolerant plants may be desirable during the interim

Fiber, Grain, and Special Crops

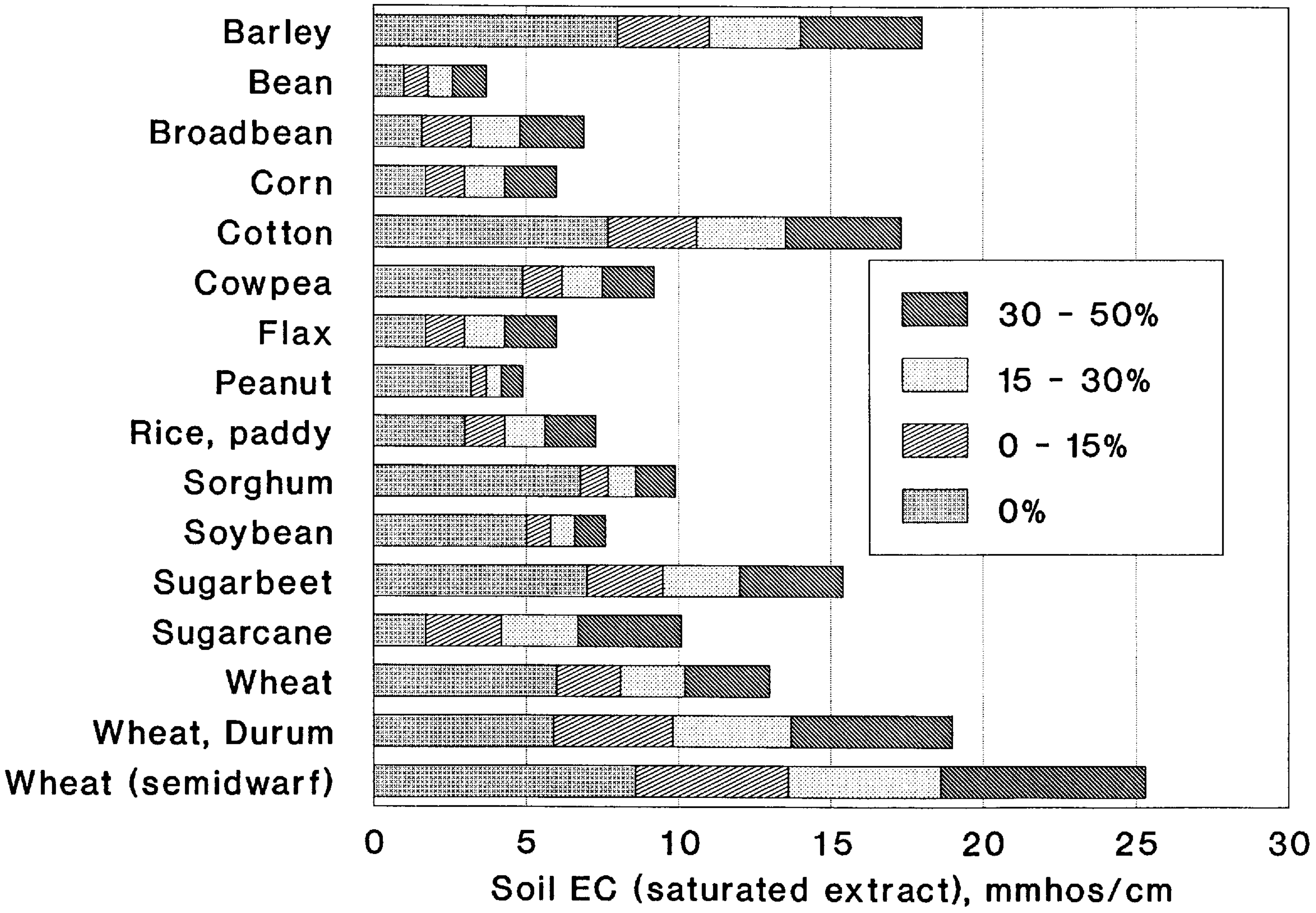


Figure 1. Yield decrease due to soil salinity (Maas, 1986)

Grasses and Forage Crops

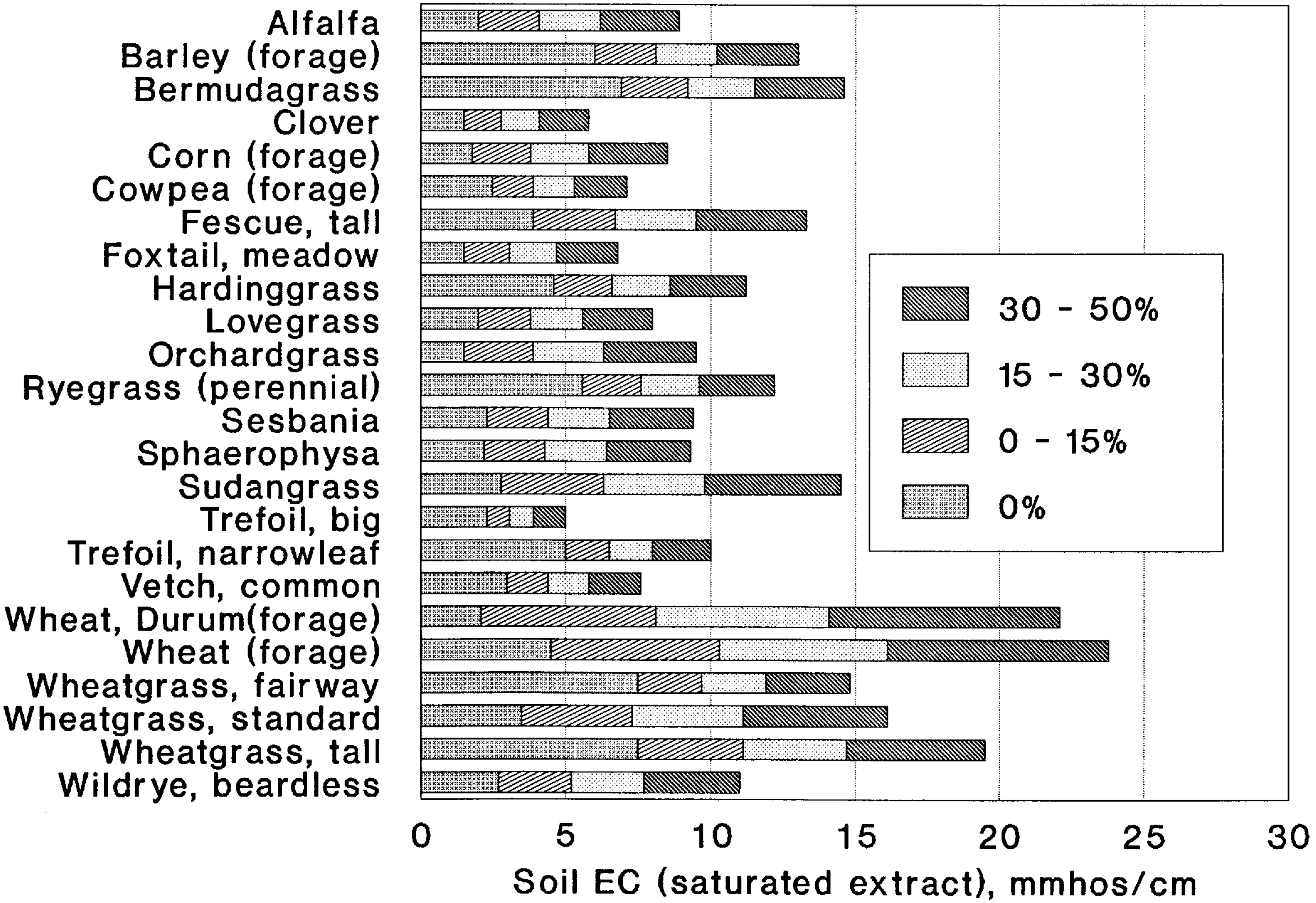


Figure 2. Yield decrease due to soil salinity (Maas, 1986)

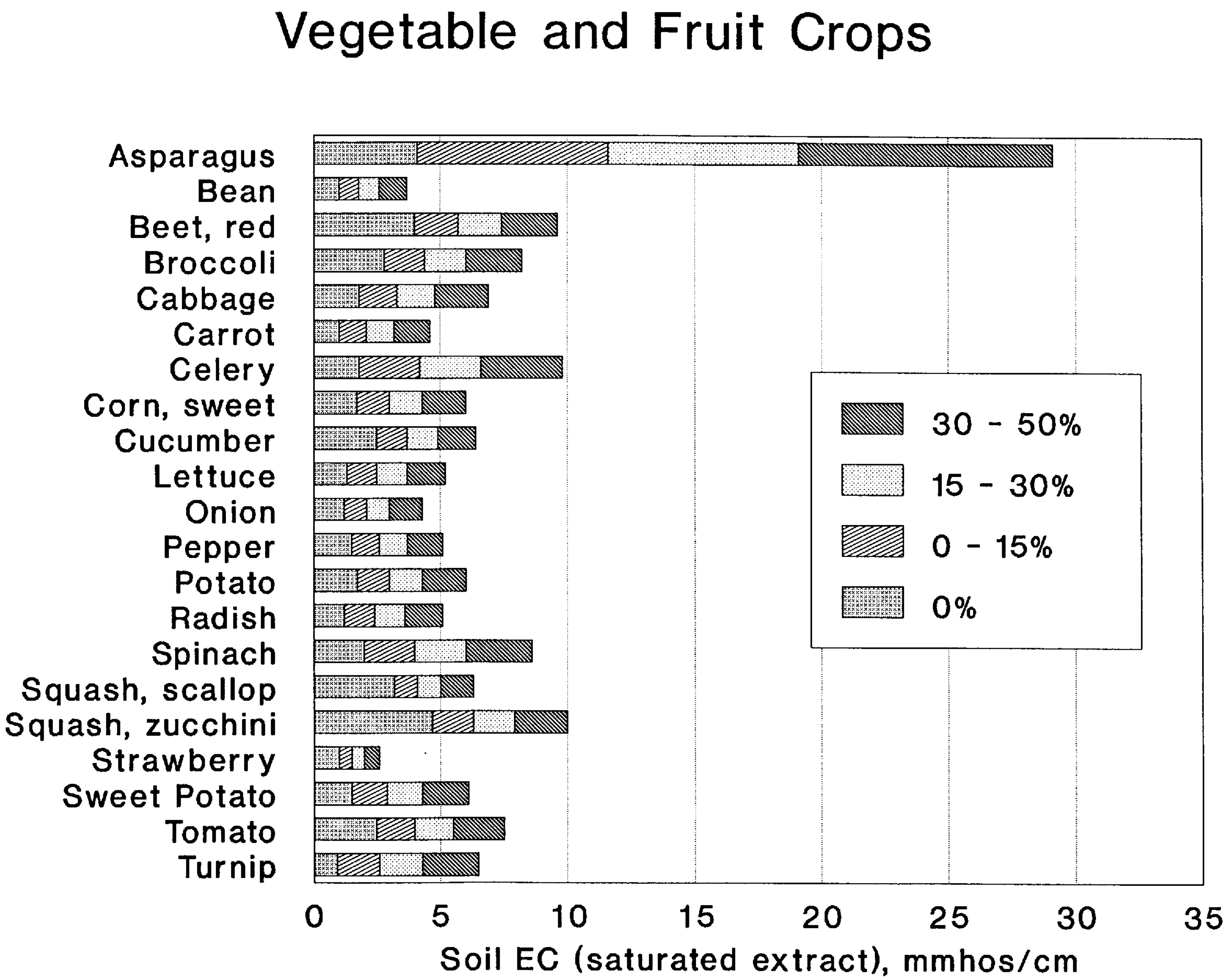


Figure 3. Yield decrease due to soil salinity (Maas, 1986)

between application and recovery (Foth and Turk, 1972). Reclamation of salt-containing soils may be hastened through the application of calcium sulfate (gypsum) which results in the replacement of exchangeable sodium by calcium (Oster and Rhoades, 1984). Plants grown on gypsiferous soils will tolerate an EC approximately 2 mmho/cm higher than those shown in Figures 1 through 3 (Mass, 1986). This is because gypsum is dissolved at moisture equivalents used in preparing saturated soil extracts for analysis but not at moisture equivalents normal to field conditions.

USDA Handbook 60 (U.S. Salinity Laboratory Staff,1954) classifies water with EC values above 2.25 mmho/cm as unfit for agricultural purposes except under very special circumstances. Soils with salinity levels > 4 mmho/cm are considered saline. The recommended criteria of 4 mmho/cm is too high for the more salt sensitive crops (Table 1), and some adjustments may have to be made relative to intended land use. Miller and Pesaran (1980) found that high concentrations of soluble salts in mud-treated soil hindered plant growth in a 1:1 mud:soil mixture. Extracting their data where EC of the mud:soil mixture was < 8 mmho/cm, yield decreases averaged only 7% for green beans and 13% for sweet corn. Nelson et al. (1984) measured average yield decreases of 20% and 38% for swiss chard and rye-grass, where EC ranged from 6.3 to 18.6 mmho/cm. In these studies EC was above the recommended criteria of < 4 mmho/cm. Tucker (1985) reported adding drilling mud with resulting EC values from 1.3 to 5.3

mmho/cm with no adverse effect on bermudagrass and at 1.7 mmho/cm with no adverse effect on alfalfa. He also reported a significant decrease in EC with time following application, reflecting the leaching of salts out of the root zone.

The expected yield decrease associated with a one-time EC application guideline of 4 mmho/cm is <15% for most crops. In those cases where precipitation, drainage, or crop type places special restrictions on waste management, some adjustments may have to be made relative to waste addition levels or intended land use while the soil recovers.

2.2.2.2 Water Resources

In areas of net infiltration, the soluble salts are transported from the surface to lower soil zones. Murphy and Kehew (1984) found that soluble salts from a pit containing saturated brine drilling fluids (EC > 200 mmho/cm) posed a threat to localized groundwater resources. However, the EC of 200 mmho/cm greatly exceeds the recommended threshold of 4 mmho/cm. Bates (1988), working with a freshwater drilling fluid, demonstrated that Cl was not retained in the zone of incorporation when mixed with surface soil.

The criteria of 4 mmho/cm (2452 mg/liter TDS for "A" = 613) can be expected to have no measurable impact on groundwater even in the most sensitive hydrological settings. Water and associated dissolved constituents do not move through soils as an isolated unit (plug flow), instead there is a natural redistribution controlled by water potentials, pore dynamics, dispersion, and diffusion (i.e., chromatographic effect). Recent field research studies conducted by Owens et al. (1985) and Bruce et al. (1985) perhaps best illustrate this principal in that they were conducted at concentrations comparable in magnitude to the 4 mmho/cm threshold. Both studies observed the redistribution of surface-applied bromide (Br) by rainfall infiltration and percolation.

The Owens group demonstrated better than a 7-fold decrease in Br after passing through only 2.4 m of well-drained silt loam and fractured shale due to attenuation processes mentioned above. Under conditions similar to their study, a surface loading of NaCl equivalent to 4 mmho/cm (2452 mg/liter TDS) would result in an EC <0.6 mmho/cm and corresponding Cl of < 213 mg/liter at a depth of 2.4 m. Bruce et al. (1985) showed Br redistribution from as great as 1800 mg/liter at the surface to <20 mg/liter below a depth of 3 m after nearly 4 years and 4.7 m of rainfall. The Br level was 100 mg/liter at a depth of 1.5 after 4 years with none detected below 3.8 m. If one substitutes Cl for the Br salts used in these studies it becomes apparent that percolating water will be at or below the EPA secondary drinking water quality standard of 250 mg/liter Cl (40 CFR, Part 143, Sec. 143.3) within a few feet of the source at controlled land applications (EC < 4 mmho/cm).

2.2.3 Criteria

In summary, the EC criteria of 4 mmho/cm based on a one-time application serves to protect vegetation, land and groundwater resources at most drilling and production locations, including those located in sensitive regions, if amenable to a temporary adjustment in plant species. The criteria may be adjusted to meet special requirements.

2.3 Sodicity (ESP and SAR)

2.3.1 Definitions

2.3.1.1 Exchangeable Sodium Percentage (ESP)

The capacity of a soil to adsorb positively charged ions (cations) is called the cation exchange capacity (CEC) and may be expressed in meq/100 g.

It follows that the exchangeable cations in a soil are those positively charged ions held on the surface exchange sites and in equilibrium with the soil solution. The major cations calcium (Ca), magnesium (Mg), sodium (Na), and K (potassium) are called basic cations, and the percentage of the CEC occupied by these cations is called the base saturation. Fertile soils have a base saturation greater than 80% with the cations distributed mainly as Ca and Mg.

ESP is a measure of the degree to which the soil exchange sites are saturated with sodium and is calculated as follows:

$$\text{ESP,\%} = (\text{NaX} / \text{CEC}) \times 100$$

where NaX (exchangeable Na) and CEC are expressed in meq/100g.

2.3.1.2 Sodium Adsorption Ratio (SAR)

Ca and Mg are generally needed in relatively large amounts to maintain good soil structure (physical status relative to tilth and permeability) and fertility, but they form salts of low solubility in soils. Na salts are much more soluble and readily dominate soil solutions, often with a detrimental impact.

SAR is an empirical mathematical expression developed by the USDA Salinity Laboratory as an index to detrimental sodium effects in soils (U.S. Salinity Laboratory Staff, 1954). SAR is computed as follows:

$$SAR = Na / \sqrt{(Ca + Mg)/2}$$

where concentrations are expressed in meq/liter. Concentrations are determined by direct chemical analysis of pit liquids or aqueous extracts of waste solids or soils. An empirical equilibrium expression developed by the USDA Salinity Laboratory relating the ESP of the solid phase to the SAR of irrigation water or soil solution is given below:

$$ESP = 100\ (-.0126 + .01475\ SAR)\ /\ 1 + (-.0126 + .01475\ SAR)$$

2.3.2 Concerns

High Na levels (SAR >12) in soil solution cause Ca and Mg deficiencies in plants by both antagonistic reactions and shifting of solubilities by common ion effect (Kramer, 1969; U.S. Salinity Laboratory Staff, 1954).

Soils reacted with solutions of high SAR are at risk of becoming sodic. A soil is termed sodic when the ESP exceeds 15% of the CEC (U.S. Salinity Laboratory Staff, 1954). The most distinguishing feature of sodic soils is their lack of structure and tendency to disperse in water. A dispersed soil condition has a devastating impact on plants by limiting the free exchange of air and infiltration of water (Reeve and Fireman, 1967; Bresler et al., 1983).

Research conducted by Tucker (1985) involving land disposal of waste drilling fluids indicated that SAR < 10 and ESP < 15% are required for maintaining good soil structure and normal plant growth. Miller and Pesaran (1980) measured ESP for 1:1 and 1:4 mud:soil mixtures and found average yield decreases of 12% for green beans and 20% for sweet corn at an average ESP of 11.5%. These results are from samples with ESP ranging from 0.6-19.7% and EC < 8 mmho/cm.

SAR is somewhat less critical in that it represents the more easily altered solution phase. Deuel and Brown (1980) showed that the detrimental effect for water with an EC of 2.6 mmho/cm and SAR of 16.1 was directed proportionate to the solid-phase Ca in receiving soil. The occurrence of appreciable amounts of gypsum in the soil, either naturally or by amendment, may permit the disposal of highly sodic E&P wastes, particularly if the ionic strength of total salt is relatively low. Freeman and Deuel (1984) reported the successful pit closure in terms of the soil and plant environment (SAR < 15, ESP < 15%) by land disposal of E&P waste solids with SARs > 200 and ESP > 90, when salinities were < 4 mmho/cm. Treatment consisted of blending waste solids with native soils at chemically defined mix ratios in conjunction with gypsum and fertilizer amendments.

2.3.3 Criteria

Therefore, the API Environmental Guidance Document recommends a SAR of <12 and ESP of <15% for a single application land disposal of E&P wastes. These values are widely accepted thresholds recommended by the USDA for preventing soil sodicity (U.S. Salinity Laboratory, 1954). Field and laboratory studies with drilling muds have also shown them to be reasonable values.

It is important to note that guidance values pertain to final disposition or closure status: These values do not limit the composition of the wastes that can be land disposed. However, operators must be prepared to provide necessary management inputs for wastes applied to land in exceedance of recommended values.

2.4 Hydrocarbons

2.4.1 Composition and Analysis

Crude oil and diesel are the principal hydrocarbons associated with E&P wastes (Miller et al., 1980; Thoresen and Hinds, 1983; Whitfill and Boyd, 1987). They are sometimes added to water base drill systems to lubricate the drill bit and pipe string. O&G levels in freshwater drilling wastes are generally < 4% (Freeman and Deuel, 1986). Other E&P waste such as tank bottoms, emulsions, and oil-contaminated soil may have higher concentrations of O&G.

Crude oil and diesel fractions are comprised of a complex array of saturate and aromatic hydrocarbons (Thoresen and Hinds, 1983, Oudot et al., 1989). Both fractions are readily partitioned from water by solvent using a separatory funnel or extracted from solid mineral components using a Soxhlet apparatus (Brown et al.,1983). Hydrocarbons extracted are assayed gravimetrically and reported collectively as oil and grease (O&G). Methylene chloride is the solvent of choice owing to its efficiency for extracting petroleum hydrocarbons without co-extracting significant quantities of naturally occurring organic matter (Brown and Deuel, 1983).

2.4.2. Concerns

2.4.2.1 Plants and Soils

A considerable amount of research has been carried out on the detrimental effects of crude oil and gas on plants and soils (Baldwin, 1922; Murphy, 1929; Schollenberger, 1930; Harper, 1939; Plice, 1948; Schwendinger, 1968; Garner, 1971; Odu, 1972). The most phytotoxic compounds are lower molecular weight aromatic hydrocarbons present initially or formed as metabolites of the various degradation processes (Baker, 1970; Patrick, 1971). Several studies (Murphy, 1929; Plice, 1948; Honarvar, 1975; Udo and Fayemi, 1975) reported marked inhibition of germination and corresponding yield reduction for row crops planted to soils receiving crude or waste oil applications in excess of 2% by weight. Pal and Overcash (1978) reported that the growth of vegetables and row crops were affected at an oil application of 1% by weight. Yields were generally 50% of control at 2% oil by weight. Bulman and Scroggins (1988) showed that plant growth was good on field plots with oil content of 3.5% or less but poor on plots with oil content of over 5%. At another site they found reduced crop growth in the first season after applying 1% and 2% oil in the soil. However, areas that received levels of 0.5% oil showed enhanced crop growth.

Frankenberger and Johanson (1982) reported certain crude oil components and refined petroleum products added to soil at 20% to 60% disrupt the oxidative and soil microflora activity requisite for biological assimilation following oil spillage events with oxidation being slowest for heavier molecules.

Miller et al. (1980) found that a 1% soil loading with diesel fuel resulted in decreased yields of 49% and 69% for beans and corn, respectively. Replanting after 4 months resulted in near normal growth. Younkin and Johnson (1980) grew reed canary-grass in soil initially containing 0.45% diesel fuel and found an initial germination decrease of 69%, a first harvest yield decrease of 79% and no yield decrease with a second harvest (75 days after diesel addition). Overcash and Pal (1979) determined an oil level of about 1% of soil weight as the threshold for reduced yields, and with 1.5 - 2% causing yield reductions greater than 50%. These effects occur immediately after application before hydrocarbon is assimilated by the various loss mechanisms. Table 2 lists the oil tolerance for selected crops (Overcash and Pal, 1979). Crop investigations as early as 1919 suggested that oil damage in soil was due to poor aeration-water interactions rather than direct toxicity (Carr, 1919). Work by Ellis and Adams (1961) suggested that iron and manganese released under anaerobic conditions contribute to the phytotoxic response to soil contamination by petroleum hydrocarbons. Phytotoxic response was lowered after assimilation of the hydrocarbon by the soil.

Table 2. Oil Tolerance for Selected Crops

Crop Type	Single Oil Application
yams, carrots, rape, lawngrasses, sugar beets	< 0.5% of soil weight
ryegrass, oat, barley, corn, wheat, beans, soybeans, tomato	< 1.5% of soil weight
red clover, peas, cotton. potato, sorghum	< 3.0% of soil weight
perennial grasses, coastal bermuda grass, trees, plantain	> 3.0% of soil weight

These studies indicate that under hydrocarbon loadings >1%, E&P wastes may be detrimental toward plant growth. However, at 1% or less of mixed hydrocarbons, little or no yield reduction is expected based on existing information. This is the rationale for the selection of the 1% limit. Also, recovery of the site is expected after a few months to one growing season, following a one-time application.

2.4.2.2 Water Resources

Several general observations of oil mobility in soil bear directly on any assessment of potential groundwater contamination. Plice (1948) observed that when oil enters the soil as a liquid, there is a natural segregation whereby the higher molecular weight, more viscous compounds are held near the surface while the lighter fractions penetrate deeper. Also, while the overall concentrations tend to decrease with depth, the composition toward the lighter end aromatic fraction tends to increase (Duffy et al., 1977; Weldon, 1978).

The recent review by EPA (1987) of E&P wastes showed only produced waters contained significant levels of the notably more mobile hydrocarbons including benzene, toluene, ethyl benzene, and xylenes (Roy and Griffin, 1985). These compounds were present in diesel oil-base drilling fluids but at concentrations that would be readily attenuated in subsurface strata by an adsorptive mechanism (El-Dib et al., 1978). Mobilities are also restricted by the chromatographic effect of liquids moving through a porous media (Waarden, Groenewoud, and Bridie, 1977). Oil floats, and its movement through soils is restricted to those pores of passable diameter, not saturated with water. Movement is further retarded by the "Jamin effect" or obstruction of a non-wetting fluid in a porous media (Schiegg, 1980).

At low levels of hydrocarbon addition to surface soils, leaching has not been found to be a problem. Watts et al. (1982) found no migration at a 30- to 45-cm depth after applying 14% industrial waste oil to the top 15 cm. Raymond et al. (1976) added about 2% oil to the top 15 cm and determined that 99% remained within the top 20 cm after 1 year. With loading rates of 3 and 13% of soil weight per year, Streebin et al. (1985) found no significant oil migration below the zone of incorporation. Oudot et al. (1989) found the potential for leaching of unmodified hydrocarbons toward the groundwater was slight at a loading of 2% oil in soil. The one-time 1% level recommended for production waste additions to soil is therefore not expected to create any leaching problems.

2.4.3 Biodegradation

It has been demonstrated that soils have an adequately diverse microbial population and capacity to degrade E&P waste hydrocarbons (Raymond et al., 1967; Atlas and Bartha, 1972; Jobson et al., 1972; Kincannon, 1972; Westlake et al., 1974; Horowitz et al., 1975; Sveinung et al., 1986). Saturates and light-end aromatics are degraded first, with kinetics or rate of degradation controlled by concentration and composition of hydrocarbons, nutritive status, aeration, moisture and temperature (Schwendinger, 1968; Francke and Clark, 1974; Huddleston and

Meyers, 1978; Dibble and Bartha, 1979; Brown et al., 1983; Flowers et al., 1984; Bleckmann et al., 1989). Mechanisms and pathways of biodegradation of petroleum hydrocarbons are quite complex and are beyond the scope of this paper. Suffice it to say that the narrower the carbon:nitrogen ratio (60-100 C:N) and the nearer the moisture and temperature are to optimum levels (60-80% of the moisture retained in soil at 0.33 bar pressure and 35-38°C, respectively), the greater the rate of degradation.

Watts et al. (1982) measured a 2-year half life for a 14% by volume loading of oil to soil. Streebin et al. (1985) also found a half life of about 2 years for API separator sludge at a similar loading rate. At a loading rate of 2% in the field, 94% of hydrocarbons were removed after 3.5 years (Oudot et al, 1989). Lynch and Genes (1987) determined a half life of 77 days on a field plot containing up to 1% polyaromatic hydrocarbons in soil with 5% benzene extractable hydrocarbons.

It has been demonstrated that degradative processes attenuate the more mobile, light-end aromatic and water-soluble petroleum hydrocarbons when applied to the surface with little potential for contaminant migration (Raymond, 1975; Brown et al., 1983; Brown and Deuel, 1983; Whitfill and Boyd, 1987; Bleckmann et al., 1989). Whitfill and Boyd (1987) reported that soils may be treated with up to 5% oil by weight with no adverse environment impact. Several studies have shown that controlled oil applications actually improve soil physical conditions and fertility status (Plice, 1948; Mackin, 1950; Ellis and Adams, 1961; Baker, 1970; Giddens, 1976).

2.4.4 Criteria

The API Environmental Guidance Document recommends a 1% oil and grease threshold for land disposal of E&P wastes based on attenuation and degradation processes that will occur under landspreading conditions. This value is predicated on the concept of minimum management, whereby an operator may load a soil (add hydrocarbon) at an appropriate mix ratio (E&P waste:soil) not to exceed 1% oil and grease. Available information demonstrates that 1% hydrocarbon by weight was a reasonable threshold initiating only temporary plant yield reductions.

2.5 Summary

This information supports the guidance values that have been developed for the land disposal of exploration and production wastes. For a one-time application the guidance values are EC < 4 mmho/cm, SAR < 12, ESP < 15%, and O&G <1%. These guidance values have been developed to be generally applicable for any waste containing salts or petroleum hydrocarbons including E&P wastes. They are designed to protect the environment under conditions most likely to be found at E&P locations. While being generally applicable, it is up to the operator to determine whether they apply to his particular site.

SECTION 3

PIT OPERATIONS AND LAND DISPOSAL

3.1 Pit Operations

3.1.1 Sealing Process

One factor that limits the potential of contaminant migration from waste drilling fluids managed in earthen pits and buried on site is the effective sealing offered by dispersed particulates (Rowsell et al., 1985).

Many drilling muds are primarily clay-water suspensions that function to clean any cuttings from beneath the drill bit and carry them to the surface, seal and stabilize the bore hole, and lubricate the drill string and bit. A significant portion of this mud is circulated to the reserve pit as waste drilling fluid along with the drill cuttings. Clay and fine silt particles associated with mud and cuttings penetrate the natural earthen surface defining the pit walls and bottom. This seals the pit forming a natural liner system. The more clay and the smaller the pore diameter of the native soil the quicker the seal.

It has been observed by the author of this paper that pits constructed in coarser textured soils, and loamy or clayey soils in an aridic soil moisture regime, are penetrated deeper by waste drilling fluids and require more fine particulates to develop a natural liner condition than in moist loamy or clayey soils. The soil layer composing this "natural" liner not only serves as a physical barrier, but also has chemisorptive properties further reducing the potential for pollutant migration.

Prewetting the surface of pits constructed in coarse textured soils or loamy and clayey soils exhibiting vertical cracks may reduce the depth of penetration and the amount of fine particulates needed to effect a natural liner seal.

3.1.2 Pit Liquids

3.1.2.1 Operative Criteria

Pit liquid is defined as the aqueous phase above settled solids. The API Environmental Guidance Document recommends an operative criteria of 4 mmho/cm (2452 mg/liter TDS for "A" = 613). See Section 2.2.1 for parameter definitions and comparative discussion. EC serves as an index parameter for decision-making purposes relative to pit liquid disposal options. Pit liquid analyses do not necessarily reflect what is in the pit solids, separate analyses are required to obtain a complete understanding of pit contents.

3.1.2.2 Sampling and Analysis

Numerous grab samples at various depths improve statistical probability of obtaining a representative sample. Containers that can be opened below the surface at a selected depth interval are a must when sampling multiphase liquids (oil layer over water).

Expensive sampling equipment is usually not necessary and more often than not fails under field trials. Scrupulous cleaning of sampling hardware is requisite in preventing cross contamination between sample locations.

The specific analytical protocol is given in the Appendix.

3.1.2.3 Pit Liquid Disposal

The EC criteria may be relaxed (subject to state and local regulations) where the native soil or freshwater wetlands are of poorer quality than the wastes themselves.

Pit liquids approaching the threshold criteria should not be applied to agricultural soils except as a one-time application, and with careful management of potentially damaging levels of sodium. Careful management should include, at a minimum, a laboratory bench scale equilibrium study to define an acceptable loading rate and/or a contingency plan for saline-sodic soil reclamation.

3.1.3 Pit Solids

3.1.3.1 Operative Criteria

EC, SAR, ESP and O&G must be measured for pit solids in order to provide sufficient information to properly land dispose according to guidance values (4 mmho/cm, 12, 15% and 1%, respectively). Land disposal may include such techniques as burial or landfill, and landspreading. Roadspreading is not recommended for pit solids.

EC and O&G are operative parameters for materials buried or landfilled. EC, O&G, SAR and ESP are used for managing waste disposal by landspreading.

3.1.3.2 Sampling and Analysis

Sampling of pit solids can be achieved by simply pushing a hollow tube, open at both ends, into the solids across all layers such that the composition of the sample is representative of the entire matrix. Earthen pits are sampled to consolidated native soil. A lined pit is sampled to the top of the liner. An end cap or other suitable plugging device usually will allow a back suction to form keeping the sample in the core barrel on retrieval.

Experience has shown that the best approach to sampling a large pit is to divide it into sections with an area of approximately 5000 ft^2. A minimum of 10 cores are then taken in each section and composited to form a section sample. Section samples may be analyzed separately and averaged as representative of pit solids, or composited by weight or volume prior to analysis.

E&P waste:soil mixtures are sampled after closure to verify correct landspreading procedures. Multiple corings are made for preparing composites representative of the zone of incorporation.

Analytical protocols specific for each parameter are detailed in the attached Appendix.

3.1.3.3 Pit Solids Disposal

The most limiting constituent for managing E&P wastes by landspreading is salt (NaCl). Sodicity (SAR for pore liquids and ESP for solids) is a major concern but easily managed by calcium amendment (i.e., gypsum) if the total salt is kept in check. Petroleum hydrocarbons, as O&G, are best managed in the natural environment by the landspreading technique.

In practice, E&P waste solids are added to the receiving soil then disked to an appropriate depth such that the final waste:soil mixture meets the constituent threshold criteria.

Landspreading is best suited in the more humid and warmer sectors of the country (precipitation > 25 in/year). Higher rainfall affords a greater margin for error. E&P waste solids are very difficult to manage from a standpoint of spreading and mixing. This generally results in what may be termed as "hot spots." Organics will degrade, but salts require leaching by rainfall to move them out of the intended root zone. Also amendments to alter sodic soil conditions require significant soil moisture for cation exchange to occur and displace desorbed Na.

Burial or landfill is best suited to a semi-arid (rainfall < 20 in/year) or drier climate with no potential for leaching to the subsurface. The recommended criteria could be relaxed in semi-arid regions after evaluation of the site for any potential environmental impact.

3.2 Summary of Guideline Thresholds and Application

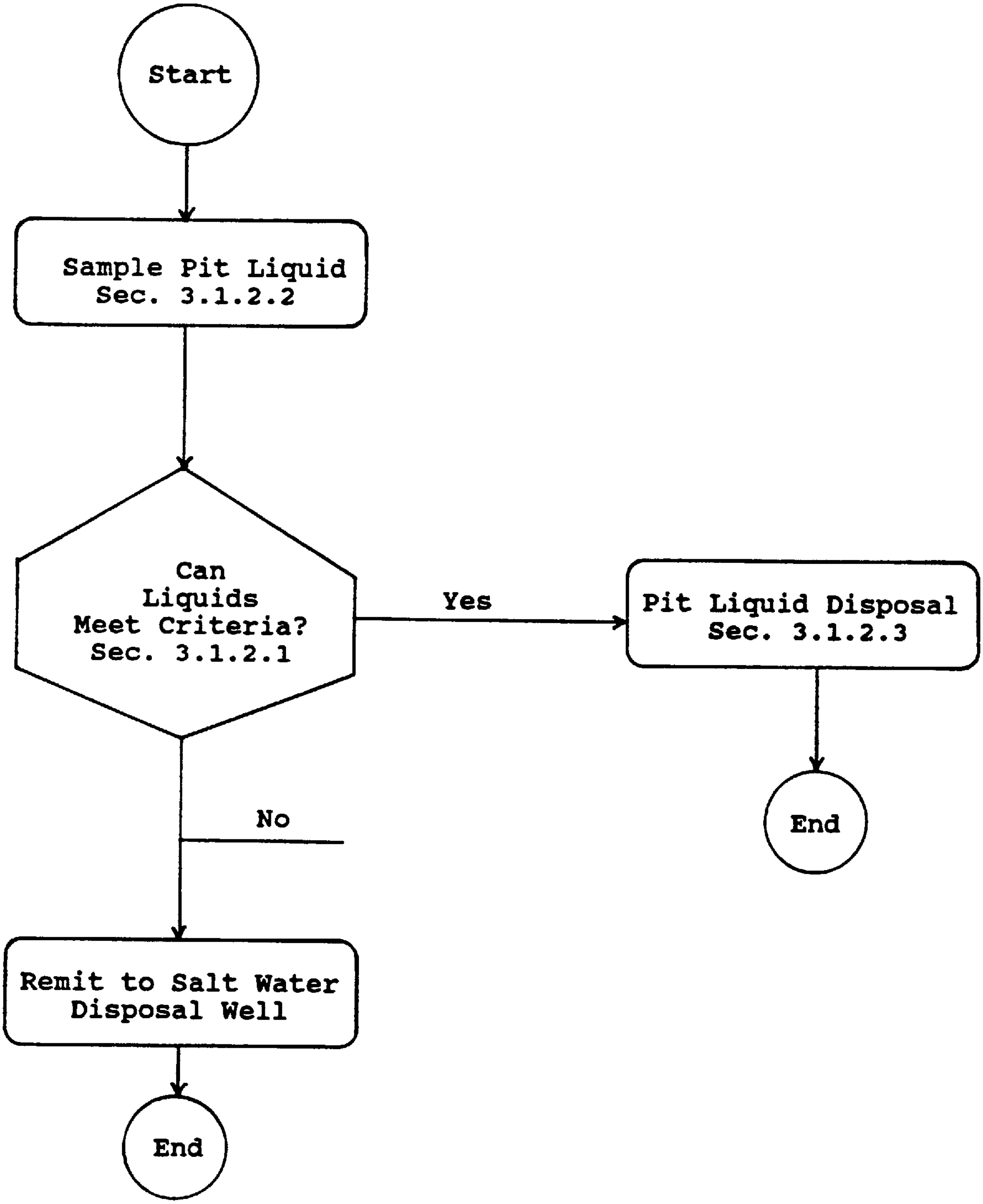
A summary of guideline thresholds and application relative to waste type, method of disposal, and criteria is given in Table 3. E&P waste type is differentiated between liquid and solid phases. Pit solids may have utility as construction fill in arid and semi-arid regions, but generally do not constitute a suitable weight-bearing and driving surface. Therefore, roadspreading is not recommended as a method of disposing pit solids. Roadspreading applications are defined in the API Environmental Guidance Document.

Table 3. Summary of E&P Waste, Disposal Technique, and Operative Criteria

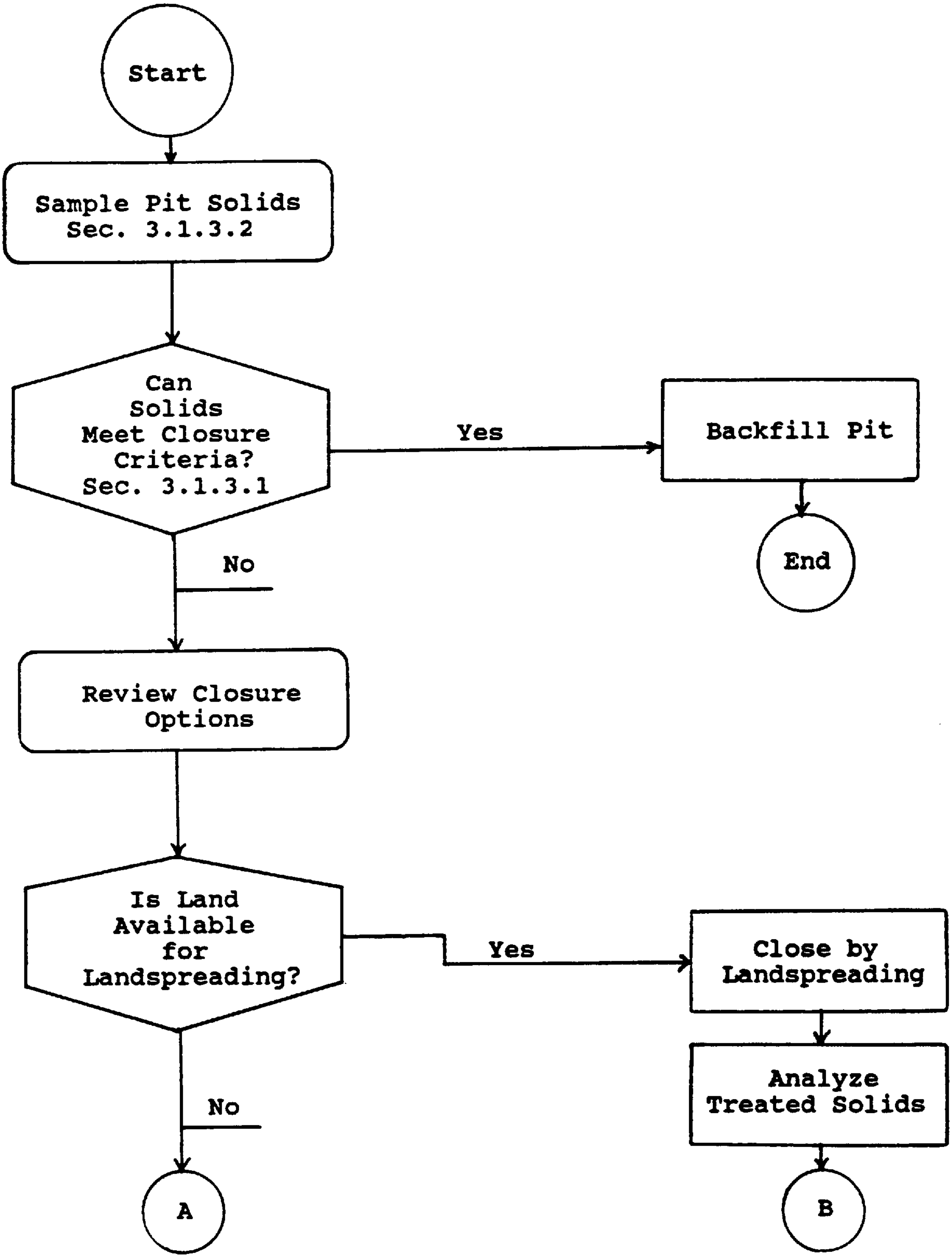
E&P Waste	Disposal Technique	Criteria EC	 SAR	 ESP	 O&G
		mmho/cm	ratio	%	%
Liquid	roadspreading	4	NA*	NA	NA
	landspreading	4	12	15	1
Solids	landspreading	4	12	15	1
	burial or landfill	4	NA	NA	1

NA* - not applicable

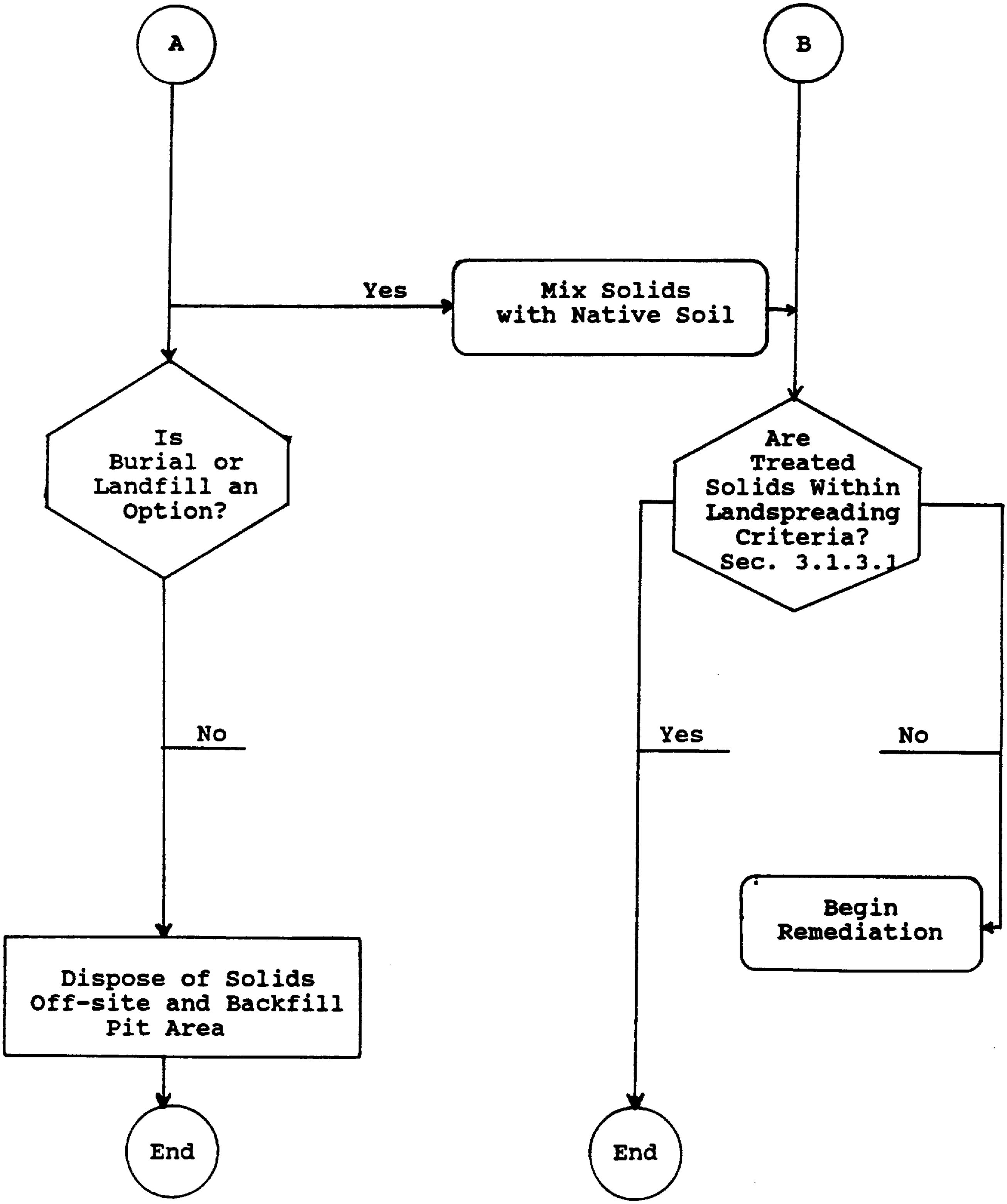
3.3 Flow Diagram for Pit Liquid Disposal



3.4 Flow Diagram for Pit Solids



3.4 Flow Diagram for Pit Solids (Continued)



3.5 Parameters and Example Calculations for Management of Pit Wastes by Land Treatment

3.5.1 Pit Material and Native Soil Characteristics

Parameter[+]	Pit[++] Liquid	Pit[*] Solids	Native[*] Soil	Threshold[#] Level
Moisture, %	NA	243	NA	NA
TDS, mg/liter	1,410	24,830	272	NA
EC, mmho/cm	2.3	40.5	0.4	4
SAR, ratio	4	25	<1	12
Na, meq/liter	9.3	260	0.4	NA
Ca, meq/liter	10.9	199	2.5	NA
Mg, meq/liter	1.7	16	0.9	NA
CEC, meq/100 g	NA	13.5	39.6	NA
Na, meq/100 g	NA	2.8	0.3	NA
Ca, meq/100 g	NA	18.5	24.8	NA
Mg, meq/100 g	NA	0.3	7.5	NA
ESP, %	NA	20.7	<0.1	15
O&G, %	0.2	10.1	<0.1	1
Volume, bbl	12,938	21,897	NA	NA

[+] Parameters are reported on a dry weight basis unless noted otherwise.

[++] NA means the parameter meets the guidance threshold or is not applicable for that matrix.

[*] Soluble constituents were determined for saturated paste extracts of pit solids and native soil.

[#] An ESP of 12% is recommended in establishing land requirements for Na management.

3.5.2 Determination of Limiting Constituent(s)

3.5.2.1 Pit Liquid Management

a) Comparison of pit liquid analyses and threshold values show no chemical limitation for land application.

b) Native soil loading capacity for Na using an ESP of 12%, and materials distribution depth of 6 in/acre.

Given: 1 acre-6 in = 2,000,000 lb

1 mg/kg = 1 lb/1,000,000 lb

Na, mg/kg = CEC meq/100g X (ESP/100) X 23 mg/meq X 10

= 39.6 X 0.12 X 23 X 10

= 1093

Na, lb/acre-6 in = 1093 mg Na/kg soil X 2

= 2186

c) Total Na mass of pit liquid.

Na,lb = (9.3 meq/l X 23 mg/meq X 3.8 l/gal X 42 gal/bbl X 12,938 bbl/pit) / (1000 mg/g X 454 g/lb)

= 973

d) Land requirement on Na mass basis, assuming a materials distribution to a depth of 6 in

Acres = (973 lb Na) / (2186 lb Na/acre-6 in)

= 0.45

e) Liquid management limitation.

Pit liquid, acre-in = (12,938 bbl X 42 gal/bbl) / (27,152 gal/acre-in)

= 20

f) Native soil has an infiltration rate of 1.12 in/hr but drops to less than 0.1 in/hr within 10 min. A dry surface can receive about 1.3 in without producing runoff.

g) Acreage needed for a one-time application so as not to generate runoff.

Land needed, acre = 20 acre-in/1.3 in application

= 15.4

h) Construction of temporary levees for containment during infiltration reduces land requirement.

3.5.2.2 Pit Solids Management.

a) Comparison of pit solid analyses and recommended thresholds show EC, SAR, ESP and O&G as potential limiting constituents.

b) Given the fact that the exchangeable Ca is high in both waste solids and the receiving soil, one would not consider SAR limiting.

c) Pit solids contained 243% moisture (M) on a dry weight basis. The equivalent percent water on a wet weight basis is 70.85%.

Dry wt, g = (100 g wet wt X 100) / (100 + 243% M)

= 29.15 g

solids, % = (29.15 g / 100 g) X 100

= 29.15%

d) Volume of dry solids used to calculate land requirement.

Dry solids, bbl = 21,897 bbl wet X .2915

= 6383

e) TDS land requirement (based on relationship from Section 2.2.1).

2452 mg/l = (6383 bbl)(24,830 mg/l) + (X bbl)(272 mg/l) / (6383 bbl + X bbl)

X bbl = 65522

acre-6 in = (65522 bbl) / (3875 bbl/acre-6 in)

= 16.9

f) EC land requirement.

4 mmho/cm = (6383 bbl)(40.5 mmho/cm) + (X bbl)(0.4 mmho/cm) / (6383 bbl + X bbl)

X bbl = 64717

acre-6 in = (64717 bbl) / (3875 bbl/acre-6 in)

= 16.7

g) ESP land requirement.

12% = (6383 bbl)(20.7%) + (X bbl)(0.1%) / (6383 bbl + X bbl)

X bbl = 4667

acre-6 in = (4667 bbl) / (3875 bbl/acre-6 in)

= 1.2

h) O&G land requirement.

1 % = (6383 bbl)(10.1%) + (X bbl)(0.1%) / (6383 bbl + X bbl)

X bbl = 64539

acre-6 in = (64539 bbl) / (3875 bbl/acre-6 in)

= 16.7

i) The land-limiting constituent is EC, requiring 64717 bbl of native soil to effect management (EC <4 mmho/cm). The land requirement is met by spreading waste solids over 16.7 acres then mixing it to a depth of 6 inches.

j) Wet solids are spread over the receiving soil at a depth of 2 in, allowed to dry, then mixed with soil to a depth of 6 in by a disk operation.

Depth wet solids, in = (21,897 bbl/16.7 acre) /(647 bbl/acre-in)

= 2.03

k) A salt-sensitive crop such as strawberries would require 68 acres to effect management (EC <1 mmho/cm).

1) Nitrogen (N) is added to the receiving soil in the form of ammonium sulfate or urea at rates to provide an O&G:N ratio of 150:1. Phosphorus (P) and potassium (K) are added to provide a N:P:K ratio of 4:1:1.

O&G, lb/acre = (O&G, 1%) X (10,000 ppm/%) X (2 ppm/lb/acre

= 20,000

N requirement, lb/acre = (20,000 lb O&G/acre) / 150

= 133

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APPENDIX

E&P SAMPLE PREPARATION

1.0 Scope and Application

1.1 This method is used to prepare samples for analysis by the protocols listed below:

1.1.1 Sodium Adsorption Ratio

1.1.2 Exchangeable Sodium Percentage

1.2.3 Cation Exchange Capacity

2.0 Summary of Method

2.1 The sample is homogenized, dried at 105C and ground prior to the individual analyses.

3.0 Apparatus and Materials

3.1 Oven capable to 105C (+/- 2C)

3.2 Grinding apparatus

3.3 Drying pans

3.4 Balance

4.0 Procedure

4.1 Homogenize the sample thoroughly.

4.2 Weigh a pan to the nearest 0.1 g that is large enough to hold 250-g sample.

4.3 Weigh 100- to 200-g homogenized sample to pan, and place pan in oven at 105C until a constant weight is achieved. Record weights to calculate moisture content.

4.4 Grind the material so that it will pass a 2-mm sieve. Sample is now ready for analysis.

5.0 Procedure for Hydrophobic Material

5.1 Tests for hydrophobicity

5.1.1 Visible blobs of oil or grease

5.1.2 The sample presses into a single, damp-looking mass when crushed with mortar and pestle and will not hydrate with water.

5.1.3 Sample leaves an oily mark when pressed between two pieces of filter paper.

5.1.4 Sample feels damp when pinched between fingers.

5.2 Place sample in muffle furnace and heat to 250C for 1hr.

5.3. Increase temperature to 350C at 50C intervals allowing smoke to dissipate between adjustments. Do not allow sample to catch fire or exceed 390C.

5.4 Cool the sample and grind it to pass 2-mm sieve. The sample is now ready for the appropriate analyses.

6.0 Calculation

6.1 Moisture Content

$$\text{Moisture,\%} = (W - D)/(D - P) \times 100$$

where: W = wet weight of sample + pan, g

D = dry weight of sample + pan, g

P = weight of pan, g

SATURATED PASTE EXTRACT

1.0 Scope and Applications

1.1 Saturation percentage is a condition of soil related to field moisture and associated plant response. It is reproducible and approximately equivalent to twice the percentage moisture at field capacity (0.3 bar) and four times the percentage moisture at permanent wilting (15 bar). This method is used to obtain a saturation extract for the following analyses:

1.1.1 TDS

1.1.2 EC

1.1.3 SAR

2.0 Summary of Method

2.1 Water is added to a known amount of sample until the point where no more water can be added without forming free water layer.

3.0 Interferences

3.1 Excessive stirring puddles the sample and reconstitute the dispersed condition of most E&P waste solids. Puddled soils represent a gross overestimation of the saturation percentage.

4.0 Apparatus

4.1 Container of 250-ml capacity.

4.2 Buchner funnel, filter paper, vacuum source, and collection vessel.

5.0 Procedure

5.1 Weigh 100-g, dried, ground and sieved solids into 250-ml container.

5.2 Add distilled water to fill pores, stirring gently as needed to achieve saturation. The solid:water mixture is consolidated occasionally by tapping container on workbench.

5.3 At saturation the mixture glistens as it reflects light and flows slightly when the container is tipped.

5.4 Allow paste mixture to stand 1 hr and check for conditions of paste. Mixture should not stiffen nor should free water form at the surface.

5.5 Add solid sample material if free water forms or more distilled water if mixture stiffens.

5.6 Record the weight of water used to achieve saturation and transfer to the vacuum filter apparatus. Vacuum extraction should be terminated when air begins to pass through the filter.

5.7 Extract is used to measure TDS, EC and SAR

6.0 Calculation

Saturation Percentage (SP),% = (W - D)/(D - C) X 100

where:

W = wet weight of sample + container

D = dry weight of sample + container

C = weight of container

7.0 References

U. S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. Agriculture Handbook 60.

TDS

1.0 Scope and Application

1.1 This can be applied to E&P aqueous phase samples including produced water, pit liquids and saturated paste extracts.

2.0 Summary of Method

2.1 Total dissolved solid is mineral matter passing a standard glass filter, which remains after drying at 180C to constant weight.

3.0 Interferences

3.1 The principle interference is from fine clay fractions and organic colloids passing the filter and stablizing at 180C.

4.0 Apparatus and Materials

4.1 Evaporating dishes

4.2 Filtration equipment

4.3 0.45-um filters

4.4 Drying oven, for operation to 180C (+/- 2C)

4.5 Analytical balance, capable to 0.1 mg

5.0 Procedure

5.1 Assemble filtration equipment and insert 0.45-um filter.

5.2 Apply vacuum and wash disk with three, 20-ml volumes of distilled water. Discard washings.

5.3 Filter measured volume of homogenized sample through filter, wash with three, 10-ml volumes of distilled water, allowing complete drainage between washings.

5.4 Transfer filtrate to weighed evaporation dish previously cleaned by ignition to 550C for 1 hr.

5.5 Evaporate water at 180C to a constant weight. Evaporation dish is cooled in desiccator prior to weighing.

6.0 Calculation

TDS, mg/liter = (A - B) X 1000/sample volume, ml

where: A = weight of residue + dish, mg

B = weight of dish, mg

7.0 References

7.1 Standard Methods for the Examination of Water and Wastewater. 1985. 16th Edition. APHA. AWWA. WPCF. Method 209 B. Total Dissolved Solids Dried at 180C.

EC

1.0 Scope and Application

1.1 Electrical conductivity is an indicator of the quantity of soluble salts in an aqueous sample. This method applies to pit liquids and saturated paste extracts.

2.0 Summary of Method

2.1 EC is measured direct with the reading corrected to specific conductance at 25C.

3.0 Apparatus and Materials

3.1 Temperature-compensating conductivity meter

3.2 Conductivity cell

3.3 Reagents

3.3.1 ASTM Type II water

3.3.2 0.01 N potassium chloride

4.0 Procedure

4.1 Rinse conductivity cell and fill with calibration standard. Read and record conductivity.

4.2 Rinse conductivity cell and fill with sample. Read and record conductivity.

5.0 Calculations

5.1 Cell Constant, C

$$C = (1.413 \text{ mmho/cm}) / (EC_{KCL} \text{ mmho/cm})$$

where:

EC_{KCL} = measured conductance, mmho/cm

5.2 Specific Conductance of Sample

$$EC = (EC_m)(C)$$

where:

EC_m = measured conductance of sample, mmho/cm

C = cell constant

6.0 References

6.1 Rhoades, J.D. 1982. Soluble Salts. p. 172-173. In A.L Page (ed.) Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. 2nd Edition. (Ed.) ASA Agronomy Monograph 9.

SAR

1.0 Scope and Application

1.1 This method is applicable to most E&P wastes including pit liquids and water extracts of pit solids or waste solid:soil mixtures.

2.0 Summary of Method

2.1 Soluble cations are determined by atomic absorption spectrophotometry or other suitable instrumentation for pit liquids or water extracts of solid-phase samples. The sodium adsorption ratio (SAR) is calculated from the cationic distributions.

3.0 Procedure

3.1 Calibrate instrumentation using standards of known concentration.

3.2 Read concentrations of Na, K, Mg and Ca direct for pit liquid samples and aqueous extracts including saturated pastes.

4.0 Calculations

4.1 Conversion to meq/liter

$$\text{Na, meq/liter} = (\text{Na mg/liter}) / (23 \text{ mg/meq})$$

$$\text{K, meq/liter} = (\text{K mg/liter}) / (39 \text{ mg/meq})$$

$$\text{Ca, meq/liter} = (\text{Ca mg/liter}) / (20 \text{ mg/meq})$$

$$\text{Mg, meq/liter} = (\text{Mg mg/liter}) / (12 \text{ mg/meq})$$

4.2 SAR

$$\text{SAR} = (\text{Na, meq/l}) / \sqrt{(\text{Ca, meq/l} + \text{Mg, meq/l})/2}$$

5.0 References

5.1 Rhoades, J.D. 1982. Soluble Salts. p. 173-174 A.L Page (ed.) Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. 2nd. Edition. ASA Agro. Monograph 9.

EXCHANGEABLE CATIONS

1.0 Scope and Application

1.1 This method is applicable to most soils and E&P waste solids and is used to determine the distribution of cations adsorbed on the solid phase.

2.0 Summary of Method

2.1 The sample is saturated with an excess of ammonium acetate resulting in an exchange of adsorbed cations. The cations released into solution are then quantified as extractable cations and when adjusted for soluble cations are reported as exchangeable cations.

3.0 Interferences

3.1 Sparingly soluble salts may give erroneously high cation distribution values.

4.0 Apparatus and Materials

4.1 Centrifuge and centrifuge tubes

4.2 Mechanical shaker

4.3 Atomic absorption or other suitable instrumentation

5.0 Procedure

5.1 Weigh 5 g of sample to a 50-ml centrifuge tube.

5.2 Add 30-ml 1.0<u>N</u> ammonium acetate reagent to the tube, stopper, shake for 5 min and centrifuge to yield a clear, supernatant liquid.

5.3 Decant the supernatant as completely as possible into a 100-ml volumetric flask. Repeat step 5.2 two more times combining extracts.

5.4 Dilute to volume, mix, and determine the amounts of the various extracted cations using AAS or other suitable instrumentation.

5.5 Soluble cations must be determined for an aqueous extract of the same sample if not determined previously.

6.0 Calculations

6.1 Extractable Cations

extractable cation, meq/100g = (cation concentration of extract in meq/liter X 10) / (sample wt in g)

6.2 Soluble Cations

soluble cation, meq/100g = (cation concentration of saturation extract in meq/liter) X (saturation percentage) / 1000

6.3 Exchangeable Cations

exchangeable cation, meq/100g = (extractable cation in meq/100g) - (soluble cation in meq/100g)

7.0 References

7.1 Thomas, G.W. 1982. Exchangeable Cations. p. 159-161. In A.L. Page (ed.) Methods of Soil Analysis. Part 2 - Chemical and Microbiological Properties. 2nd. Edition. ASA Agron. Monograph 9.

CATION EXCHANGE CAPACITY

1.0 Scope and Application

1.1 This method is applicable to most soils and E&P waste, including calcareous and non-calcareous samples.

2.0 Summary of Method

2.1 The sample is saturated with an excess of sodium acetate solution, resulting in an exchange of other cations by sodium. Subsequently, excess sodium is rinsed from the sample followed by quantitative desorption of sodium by ammonium. The concentration of displaced sodium is then determined by atomic absorption, emission spectroscopy, or an equivalent means as available and approved by EPA.

3.0 Interferences

3.1 Soluble salts and gypsum will interfere with the CEC determination if they are present in sufficient quantities. These may be overcome by washing the solids with water before saturating with sodium, or employ a more exhaustive saturation procedure.

4.0 Apparatus and Materials

4.1 Centrifuge and centrifuge tubes

4.2 Mechanical shaker

4.3 Volumetric flask: 100 ml

4.4 Atomic absorption or equivalent instrumentation

5.0 Reagents

5.1 Sodium acetate 1.0 N buffered to pH 8.2

5.2 Ammonium acetate 1.0 N buffered to pH 7.0

5.3 Isopropyl alcohol: 99%

5.4 Sodium standards in 1.0 N sodium acetate

6.0 Sample Preparation

6.1 See E&P Sample Preparation

7.0 Procedure

7.1 Weigh 5-g sample into a 50-ml centrifuge tube.

7.2 Add 30 ml of 1.0 N sodium acetate, stopper and shake for 5 min, then centrifuge to clear supernatant.

7.3 Decant and discard supernatant, and repeat step 7.2 three more times to effect sodium saturation.

7.4 Add 30 ml of 99% isopropyl alcohol, stopper and shake for 5 min, then centrifuge to clear supernatant.

7.5 Decant alcohol and discard supernatant, and repeat step 7.4 three more times to effect washing of solids.

7.6 Add 30 ml of ammonium acetate, stopper and shake 5 min, then centrifuge to clear supernatant liquid. Decant supernatant into a 100-ml volumetric flask.

7.8 Repeat step 7.6 two more times decanting into the same volumetric flask.

7.9 Dilute the volumetric to mark with ammonium acetate,and determine sodium concentration by atomic absorption or other instrumentation

8.0 Calculations

8.1 CEC

CEC, meq/100 g = (sodium, meq/liter X 10) / (sample wt, g)

8.2 ESP

ESP, % = (Exchangeable Sodium, meq/100g) / (CEC, meq/100g) X 100

9.0 References

9.1 Chapman, H.D. 1965. Cation Exchange Capacity. p. 891-900. In C. A. Black (ed.) Methods of Soil Analysis. Part 2-Chemical and Microbiological Properties. ASA Agron. Monograph 9.

OIL & GREASE

1.0 Scope and Applications

1.1 This method is used to recover O&G by chemically drying wet E&P waste solids and then extracting by Soxhlet apparatus.

2.0 Summary of Method

2.1 Anhydrous sodium sulfate is used to combine with water and enhance recovery of petroleum hydrocarbon. After drying, the O&G is extracted with methylene chloride using the Soxhlet apparatus.

3.0 Apparatus and Materials

3.1 Soxhlet extraction apparatus

3.2 Analytical balance

3.3 Extraction thimble

3.4 Grease-free glass wool

3.5 Vacuum distilling apparatus

3.6 Desiccator

4.0 Reagents

4.1 Concentrated hydrochloric acid

4.2 Anhydrous sodium sulfate

4.2 Nanograde methylene chloride

5.0 Procedure

5.1 Weigh 25 g (+/- 0.5g) of wet E&P waste solid of soil into 150-ml beaker.

5.2 Acidify to pH 2 with concentrated hydrochloric acid.

5.3 Add anhydrous sodium acetate as necessary to dry solids.

5.4 Transfer sample to extraction thimble, covering sample with glass wool, then place in Soxhlet apparatus.

5.5 Add methylene chloride and commence extraction at 20 cycles/hr for a minimum of 6 hr.

5.6 Using grease-free glass wool filter extract into a pre-weighed boiling flask, previously rinsed with solvent.

5.7 Connect boiling flask to vacuum distillation head and evaporate solvent.

5.8 Place boiling flask in a dessicator to cool and remove trace water on glass.

5.9 Weigh boiling flask and record weight gain.

6.0 Calculations

6.1 O&G

O&G,% = (weight gain in flask, g) / (sample wt, g) X 100

where:

sample wt, g = (wet weight X 100) / (100 + % moisture)

7.0 References

7.1 Test Methods for Evaluating Solid Waste. 1986. Method 3540. Soxhlet Extraction. EPA SW-846. USEPA Washington D.C.

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