Commercial Value Assessment of Newly Discovered Anhydrite Soil in the Coastal Lands of Abu Dhabi Emirate

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Abstract

A unique anhydrite (CaSO₄) rich soil has been discovered during the soil inventory of the coastal lands of Abu Dhabi Emirate. The next challenge was to assign a taxonomic name using the world most used Soil Taxonomy of the United States Department of Agriculture (USDA). As anhydrite soil had not been reported previously in the USDA soil taxonomy hierarchy, the closest soil was gypsic (CaSO_{4.2}H₂O), and therefore, it was imposed to anhydrite soil, which is far from perfect. Based on this, a proposal for a change in USDA Soil Taxonomy was prepared. The proposal suggests addition of anhydritic diagnostic horizon and mineralogy class, as well as Anhydritic Aquisalids subgroup in Aridisols soil order. The suggested changes are shared in this paper. Both gypsum and anhydrite have commercial value based on composition, purity, mining cost, and extent of deposit. In this paper representative anhydrite samples from five potential locations have been investigated for their physical, chemical, purity and mineralogical composition using standard analytical procedures. The solution chemistry is dominated by cations Ca > Na > Mg > K and anions $SO_4 > Cl > HCO_3$. The anhydrite was identified as dominant mineral, occurring as single mineral, and in association with halite and calcite. It has been concluded that four out of five samples have purity ranging from 73 to 98% as required for a commercial product (> 70%), only one sample showed 51% purity which have impurities such as quartz, plagioclase, dolomite, and magnesite. The interesting feature observed is that anhydrite (CaSO₄) is not converted to gypsum (CaSO₄.2H₂O) when coexisting with water in the coastal lands of Abu Dhabi Emirate. The high salinity coupled with high

temperature of crystallization in hyper arid coastal lands of Abu Dhabi Emirate could be the reason to favor anhydrite formation over gypsum.

Keywords: Anhydrite; Abu Dhabi Emirate; coastal land; Soil Taxonomy; commercial value; UAE.

1. Introduction

Abu Dhabi Emirate is the largest among seven Emirates of the United Arab Emirates (Fig. 1). Its major ecosystems comprise the coast, numerous islands, mountainous areas, gravel plains and sandy desert. Nearly 80% of its area is desert, to the north and west is an extensive area of coastal flats locally known as "sabkha". Isolated sabkha surrounded by dune and gravel desert also exists which is called inland sabkha. Abu Dhabi Emirate experiences extremely high temperatures during summers (45-50°C) with mean temperature being 28°C and short mild winters with temperature as low as 3°C ([1]. Humidity is the highest along the coastal fringes and decreases inland. The mean annual rainfall is about 111 mm [2].

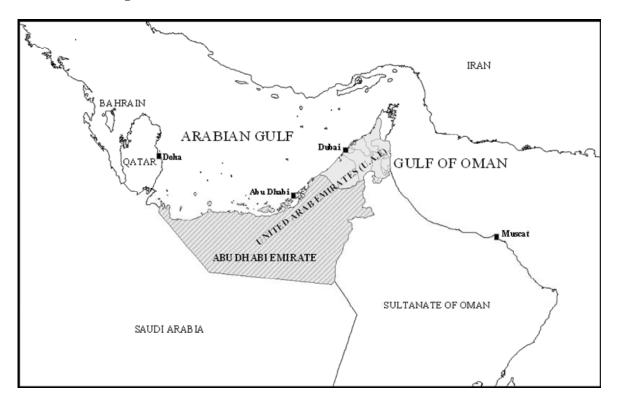


Figure 1: Location of Abu Dhabi Emirate in the Arabian Peninsula

All terrestrial life ultimately depends on soil, energy, and water. Soil is a vital part of the environment and plays a key role in environmental interaction, linking the atmosphere, water resources and land use. Understanding the capabilities and limitations of this resource is crucial for sustainable and profitable development. In this regards a scientific soil inventory has been completed for better understanding and management of coastal lands of Abu Dhabi Emirate [3]. During this coastal lands inventory a new soil rich in anhydrite was discovered, which has neither been reported in world soil literature nor included in the world most used Soil Taxonomy of the United States Department of Agriculture [4 and 5].

Anhydrite was first discovered in 1794 in a salt mine near Hall in Tirol. In this occurrence nearer the surface anhydrite has been altered to gypsum by absorption of circulating ground water.

Werner gave the name anhydrite (CaSO₄) in 1804, because of the absence of water of crystallization, as contrasted with the presence of water in gypsum. Anhydrite is derived from the Greek *anhydro*, meaning "waterless" in contrast to gypsum (CaSO₄.2H₂O) which contains water. Anhydrite is a rare mineral, since most existing specimens alter to the much more common mineral gypsum from the addition of water. However, based on formation conditions some specimens only partly alter to gypsum, leaving one part anhydrite and the other part gypsum. Recently, it has been confirmed that regardless of available soil literature on anhydrite conversion to gypsum, it occurs as pure mineral even when coexist with water [6 and 7].

Anhydrite usually occurs in arid regions. It is commonly found as an evaporative deposit in a marine environment, often interbedded with halite, and also associated with calcite, and frequently found with gypsum. Great care is to be exercised during sample collection and preservation to avoid conversion to gypsum. It is recommended that this mineral be stored in a dry area or with silica gel.

The objective of the present study is to assess the commercial value of the newly discovered anhydrite soil in the coastal lands of Abu Dhabi Emirate. The assessment is made using number of techniques to characterize anhydrite material, including but not limited to solution chemistry and mineralogical composition. For more information about the soils of the coastal lands of Abu Dhabi Emirate, the reader is referred to these publications [3,6,8].

1.1. Mineral chemistry and properties of anhydrite

The structure of anhydrite comprises sulfate (SO₄) tetrahedra and calcium coordinated by eight oxygens. The CaSO₄ is the chemical formula of anhydrite and molecular weight is 136.14 g. The standard elemental composition is (calcium 29.44%; sulfur 23.55%; oxygen 47.01%) and oxides as (calcium oxides 41.19%; and SO₃ 58.81%). The major x-ray diffraction spectra appear at 3.49°A, 2.849°A and 2.328 °A. It is colorless, white, bluish white, violet white and dark gray. Diaphaniety is transparent to sub transparent to translucent. It occurs as massive, fibrous, and distinctly fibrous fine-grained forms. It also occurs as plumose (aggregate like plume-like forms). Hardness is 3.0-3.5 Mohs scale, specific gravity is 2.97 g/cm³, luster is vitreous to pearly, streak is white, and it is non radioactive.

1.2. Formation of anhydrite

Anhydrite, unlike gypsum, is an anhydrous calcium sulfate (CaSO₄). It is gypsum without the water. Compared with gypsum, anhydrite is less common. It is commonly known that the addition of water to powdered anhydrite will result in the formation of gypsum crystals. Reverse is true for gypsum that has its water driven off will convert to anhydrite. Gypsum-anhydrite and anhydrite-gypsum conversions do happen naturally. It has been reported in the literature that from calcium and sulfate rich solution, calcium sulfate is crystallized to gypsum, but when the solution contains an excess of sodium or potassium chloride, anhydrite is deposited if temperature of crystallization is above 42°C [9]. This is one of the several methods by which the mineral has been prepared artificially, and is identical with its mode of origin in nature; the mineral is common in salt basins, crystallized through evaporation of entrapped saline water in depressions. Under natural conditions, anhydrite cannot be hydrated easily. To form gypsum from anhydrite at low temperatures, dissolution and reprecipitation may be necessary. Anhydrite has retrograde solubility in water with temperature, but increases in solubility with pressure. Experimental formation of anhydrite under aqueous conditions which simulate evaporitic fluids has been explored by a number of researchers. Increased salinity decreases the temperature at which gypsum can transform to anhydrite, thus appearing to favor anhydrite formation, although the exact mechanism(s) of anhydrite formation in evaporites may still require further investigation.

1.3. Uses of Anhydrite

- Anhydrite is used for the production of sulfuric acid and as filler in paper.
- The mineral has been used as a soil conditioner and, while not as economically beneficial as other minerals, it has been used to make sulfuric compounds (gypsum is generally much more cost effective).
- Anhydrite uses include: soil conditioner; mixed with cement to control the rate of curing; manufacture of gypsum wallboard; mineral filler in joint compounds, plastics and paints; a source of sulfur

2. Materials and Methods

2.1. Procedures used to evaluate commercial value of anhydrite

Five anhydrite samples were collected from different sites (Table 1) to allow more representative evaluation of physical, chemical and mineralogical composition.

 Table 1:
 Geographical coordinates of sample collection sites

ID Number	Northing	Easting
1	24°20.203	54 ° 21.501
2	24 ° 10.438	54 ° 13.520
3	24 ° 10.026	54 ° 13.565
4	24 ° 09.896	54 ° 13.648
5	24 ° 09.813	54 ° 13.739

Evaluation of commercial value of anhydrite requires establishment of its percent purity in the deposit, chemical and mineralogical composition and cost of mining. The latter requires more detailed investigation on the market requirement and economics of anhydrite mining. In this paper the latter has not been focused, but will become focus in future studies. Following procedures have been used.

2.1.1. Color

The color is established using standard Munsell Color Chart [10], which requires hue, value and chroma. Where *hue* is the dominant spectral color, *value* is degree of lightness or darkness in relation to a neutral gray scale, and *chroma* is the relative purity or strength of the spectral color. Munsell color notation is (Hue value/chroma). Pure white color of anhydrite indicates its high purity, presence of impurities departs white to other colors.

2.1.2. Purity

The purity is determined by dissolving anhydrite sample in sufficient water to assure all material is dissolved, and then precipitation with acetone, the precipitate is dissolved in water and electrical conductivity is measured, which is converted to anhydrite percentage using standard calculation procedure [11].

2.1.3. Solution Chemistry

It is determined by completely dissolving small quantity of anhydrite material in sufficient volume of water. The suspension is then filtered to remove impurities and to determine solution chemistry. Soluble cations (sodium, potassium, calcium and magnesium) are measured using flame photometer and atomic absorption spectrophotometer, soluble anions - carbonates by acid titration using phenolphthalein indicator to colorless end point; bicarbonates by acid titration using methyl orange

indicator to orange color end point [11], chlorides by chloride meter and sulfates by difference between total cations and (CO₃+HCO₃+Cl) expressed in milli equivalents per liter.

2.1.4. Evaluation of dissolution rate

Dissolution rate of five anhydrite samples was determined by dissolving 0.15g of anhydrite material in 100 ml deionized water. The suspension was shook at an interval of five minutes on an end to end shaker and electrical conductivity (EC) measured for each suspension. The process continued until steady state EC reading was achieved.

2.1.5. Mineralogical investigation

The x-ray diffraction (XRD) is by far the most powerful technique to provide finger prints of anhydrite in the form of d spacing. The Philips x-ray diffractometer model PW/1840 was used for mineralogical investigation. Air-dried (30 °C) samples were used to record x-ray patterns using Cu-K α radiation, using variable divergent, receiving and scattering slits. The step size was 1°2 θ /min. The procedure is similar to method 7A2i [11]. A Philips X-ray diffraction model PW/1840, with Ni filter, Cu-K α radiation (λ = 1.542 °A) at 40 kV, 30 mA and scanning speed 0.02°/S was used. Diffraction peaks between 2 and 60° 2 θ were recorded. The corresponding d-spacing and the relative intensities (I/I°) were calculated and compared with standard data.

3. Results and Discussion

3.1. Breakthrough in soil information

The anhydrite soil was recognized during the soil inventory of coastal lands of the Abu Dhabi Emirate [3]. The inventory revealed thirteen different soils at the soil family level of the soil taxonomy (ST) of the United States Department of Agriculture (USDA). Among these, an anhydrite (CaSO₄) rich soil was mapped over a large area. The next challenge was to assign a taxonomic name to the anhydrite soil using the USDA Soil Taxonomy. As anhydrite had not been reported previously in any category, it was initially classified under the gypsic soil category.

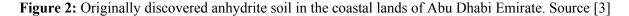
3.2. Proposal to the USDA for a change in Soil Taxonomy

To ensure recognition of anhydrite soil in USDA Soil Taxonomy, a formal proposal was submitted to the USDA to consider for a future change of the Soil Taxonomy at only three different levels. This is possible as the USDA Soil Taxonomy has been continuously upgraded through an iterative process since its first publication in 1975 [12] through the addition of new orders, suborders, great groups and sub groups. The proposal will go through intensive review prior to final acceptance and inclusion in USDA Soil Taxonomy. Proposal suggests three additions; 1) *Anhydrite* soil mineralogy class; 2) *Anhydritic* subsurface diagnostic horizon and; 3) *Anhydritic Aquisalids* soil subgroup in Aridisols order. Details of the proposal can be seen in recent publication [13]. The authors believe that the inclusion of anhydrite in the USDA Soil Taxonomy will be break though in soil information and will benefit the international soil science community to provide a scientific means to classify soils rich in anhydrite.

3.3. Gypsum and anhydrite material

Gypsum (CaSO₄.2H₂O) is well recognized in world soil literature, based on its purity and commercial value, gypsum is commonly used in agriculture as conditioner to offset sodicity problems by improving soil structure. However, there are differences between gypsum and anhydrite materials. Anhydrite is 21% lighter in weight than gypsum. The relatively high solubility and light weight of anhydrite compared to gypsum means that its use is more economical and effective as less material and time will be required for reclamation, thus providing benefits to farmers. The originally discovered [3]

anhydrite is presented in Figure 2. Whitish material is anhydrite deposition in the soil profile over a hypersaline (EC > 200 dS/m) water table at 70 cm depth.







3.4. Evaluation of commercial value of Anhydrite material

3.4.1. Dissolution of anhydrite material

All five samples revealed different dissolution rates with respect to time and resulted electrical conductivity; however, all samples attained maximum dissolution (saturation) within first 15-25 minutes shaking time (Table 2). The less pure sample (ID1) presented lowest initial and final EC, this is due to impurities of alumino silicate minerals, which are insoluble in water, and hence has low

commercial value relative to other samples. The impurities are recognized as plagioclase, quartz, dolomite and magnesite through XRD analyses (see Table 5).

Table 2: Dissolution rate of anhydrite material over a period of shaking time

Sample ID	Weight dissolved	Volume (ml)	EC 2 min	EC 5 min	EC 10 min	EC 15 min	EC 20 min	EC 25 min	EC 30 min
110	(g)	(ml)			microSiemens/cm (μS/cm)				
1	0.15	100	980	1040	1070	1130	1130	1130	1130
2	0.15	100	1121	1330	1370	1410	1430	1460	1460
3	0.15	100	1260	1350	1450	1520	1540	1560	1560
4	0.15	100	1120	1240	1310	1380	1380	1380	1380
5	0.15	100	1230	1320	1400	1430	1450	1460	1460

EC = Electrical conductivity

3.4.2. Color assessment

Standard Munsell Color Assessment [10] revealed very pale brown (10 YR 8/2) color of relatively impure anhydrite (ID 1), pinkish white (7.5YR 8/2) and white 10YR 8/1 for other anhydrite samples (IDs 2-5). In-situ color of anhydrite in soil profile can be seen in Figure 3. The impurities decrease commercial value of any material, as significant efforts are required to clean the material to an acceptable level for a specific use.

3.4.3. Solution chemistry and mineral formation

The results of the solution chemistry are shown in Table 3, which clearly illustrates that ionic composition of all samples is dominated by cations (calcium > sodium > magnesium > potassium (Ca > Na > Mg > K) and anions (sulfates > chlorides > bicarbonates ($SO_4 > Cl > HCO_3$). Soluble carbonates were undetectable. Appreciable quantities of Na and Cl have been found, this is due to sea water intrusion into the study area, and being high solubility of halite than anhydrite, halite (NaCl) occurs as an impurity, however, total quantity of anhydrite is significantly higher than halite in anhydrite deposit, which is also confirmed through mineral composition by x ray diffraction (Table 5).



Figure 3: Visual observation of relatively pure anhydrite layer (site number 3)

The crystallization of salts from saline solutions through evaporation depends upon several factors including variation in solubility of minerals, the concentration of salts in solution, the concentration and type of anions and cations in the solution, the temperature and the nature of previously crystallized salts which serve as reactions products, and the pressure. The type of salt mineral that may be present can be predicted from thermodynamic considerations or by the use of mineral stability diagrams for MgSO₄-Na₂SO₄ in a saturated solution of NaCl [14]. The minerals are formed in reverse order of their solubilities, i.e., the least soluble will precipitate first and highly soluble the last. It can be speculated that sulfate minerals of calcium (anhydrite) will crystallize first and then halite (NaCl) in the last due to high solubility. Earlier, it has been explained that anhydrite when react with water at temperature below 42°C will convert to gypsum (CaSO₄.2H₂O), from this we can conclude that where anhydrite is found as dominant over gypsum, the temperature of crystallization of main mass is above 42°C [9]. It has been further stated that anhydrite also has poikilitic intergrowth with halite (NaCl) [9]. Joze [15] found that temperature of Abu Dhabi coastal lands surfaces has been reported to reach 60°C or more in summer. As a consequence, evaporation is intensive and the salinity of the near shore areas can reach to 70%. Based on above it can firmly be concluded that increased salinity in the coastal lands of Abu Dhabi Emirate due to sea water intrusion and high temperature decreases the temperature at which gypsum can transform to anhydrite, thus appearing to favor anhydrite formation, although the exact mechanism(s) of anhydrite formation in evaporites may still require further investigation. Two types of anhydrite have been reported [15,16], the primary (occurs inland and appears as nodules and contorted layers), secondary (cottage cheese texture formed through secondary replacement of gypsum), in the present study the secondary type was found.

Sample ID	pН	EC μS/cm	Na	K	Ca	Mg	CO ₃	HCO ₃	Cl	SO ₄
Sample 1D	pm	EC µS/CIII				_[/]	1			
1	7.10	1640	9.56	nd	12.50	1.95	nd	0.85	6.25	16.91
2	7.05	2000	13.04	nd	16.40	1.80	nd	0.60	5.75	24.89
3	6.73	2180	12.17	nd	19.75	2.80	nd	0.65	5.50	28.57
4	7.00	2080	11.30	nd	16.50	1.95	nd	0.65	6.00	23.10
5	7 51	2040	9.56	nd	17 10	4 60	nd	0.95	5.50	24 81

Table 3: Solution chemistry of anhydrite deposits

nd = non detectable

3.4.4. Purity of the anhydrite material

It is essential to establish purity of the anhydrite deposits to establish the commercial value. The purity was determined by dissolving a small quantity in enough deionized water to dissolve all material and finally anhydrite was quantified in all the samples (Table 4).

Table 4: Percent anhydrite in five samples

Sample ID	Percent purity
1	51
2	98
3	91
4	81
5	77

Table 4 clearly illustrates four samples exceeds commercial value (70%) of anhydrite, one sample shows some impurities, leading to lower anhydrite contents. The closer material gypsum qualifies for agricultural grade (mined) when it is 70% pure. The studied anhydrite material is in much better quality than the mined ones. However, further detailed investigation is required in other parts of the Emirate where anhydrite may be occurring, and their commercial value to be evaluated. Cost of mining the anhydrite should also be determined, prior to making the decision to exploit the resource for commercial purposes, as well as impact on the environment, which should not compromised.

3.4.5. Mineralogical composition of anhydrite samples

The XRD patterns of five anhydrite samples revealed dominance of anhydrite over other minerals. The results are summarized in Table 5. An x-ray diffractogram of sample number 3 is presented in Figure 4. The results correlate with solution chemistry data where sample ID 1 is found to be relatively impure compared with other samples. The impurity is determined as plagioclase, quartz, dolomite and magnesite, which have very low solubility, and therefore render the sample having low commercial value.

Table 5: Mineral association in anhydrite samples

Sample ID Major minerals		Minor minerals		
1	Anhydrite	Halite, plagioclase, quartz, dolomite, magnesite		
2	Anhydrite	-		
3	Anhydrite	Halite		
4	Anhydrite	Halite, quartz		
5	Anhydrite	Calcite		

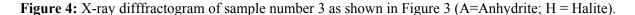
4. Conclusions

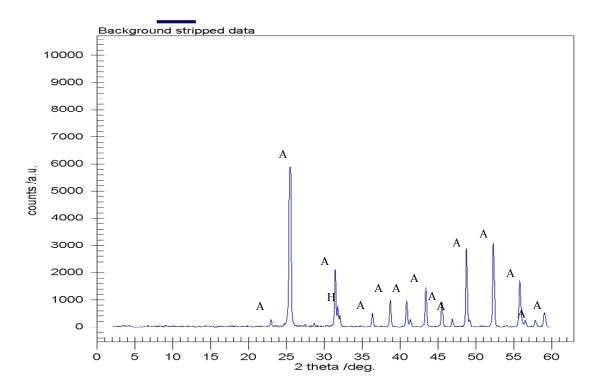
The paper presents breakthrough in soil information to international soil science community in the form of new discovery of anhydrite soil in the coastal lands of Abu Dhabi Emirate. The discovery is

anhydritic subsurface diagnostic horizon; 2) addition of anhydritic mineralogy class and; 3) addition of Anhydritic Aquisalids (soil subgroup) in Order Aridisols. In addition to new soil information, the anhydrite deposits are evaluated for their physical, chemical, purity and mineralogical characteristics and used as a base to evaluate commercial value of the anhydrite for commercial uses. Present study concludes that the anhydrite material has a potential for commercial use, however, it contains some impurities in the firm of evaporites and other minerals. Four out of five samples have purity ranging from 73 to 98% as required for a commercial product (> 70%), only one sample showed 51% purity which have impurities such as quartz, plagioclase, dolomite, and magnesite. It is also concluded that high temperature of crystallization in Abu Dhabi coastal lands and high salinity are main cause to favor anhydrite formation over gypsum even when coexist with water table.

5. Acknowledgement

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