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Arthur ZEIGLER Seawater Fertilizer ("Sea-Crop")

<http://www.sea-crop.com/index.html>

SEA-CROP

SEA-CROP is an extension of the life's work of pioneer scientist Dr. Maynard Murray.

His ground-breaking book "Sea Energy Agriculture" is well known and loved by many.

Over a century of well documented research has shown that seawater can have profound effects on both plant and animal life as long as sodium chloride is not over-applied.

In the late nineteenth century [Dr. Rene Quinton](#) did experiments showing that seawater could be used to replace blood in animals and he went on to develop a seawater extract that was used for transfusions in place of blood plasma during World War One.

During the twentieth century Dr. Maynard Murray spent decades doing agricultural research with both plants and animals to demonstrate the many benefits that can be obtained by using both seawater and seawater concentrates.

In the twenty-first century Ambrosia Technology, LLC has continued research based on the work of these pioneers and has developed the product Sea-Crop. Sea-Crop is a concentrate that contains all of the wonderful goodness of seawater in concentrated form but with the sodium chloride 95% reduced.

It is believed that the 89 elements in seawater working together with its contained organic content are responsible for its well documented positive effects.

Leaves and raspberries from ordinary raspberry plant on left and the plant on the right was treated with SEA-CROP for 3 consecutive years. The 6 berries from the treated plant weighed 20.66 gm and the 6 berries from the control weighed 8.53 gm.

SEA-CROP is a catalytic trigger that releases nature's energy to give the full benefit of soil microflora symbiosis.

General Observations:

In all applications the root system of the treated plants was increased.

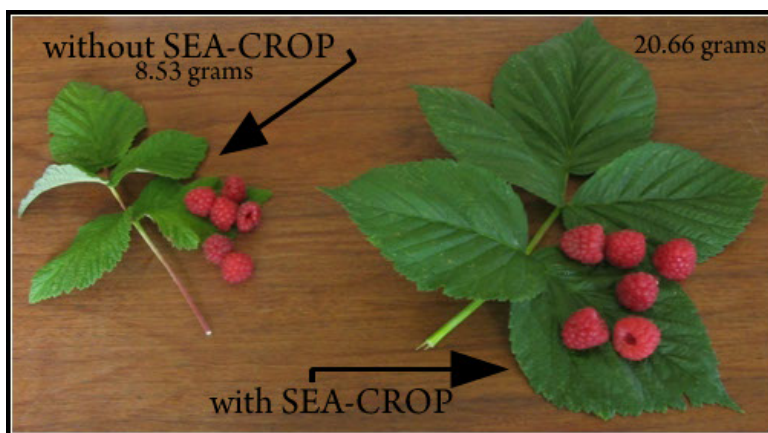
In all instances soil tilth and microbial populations were enhanced.

In all cases Sea-Crop improved the health and vigor of the treated plants.

Using Sea-Crop on transplants of crucifers, melons and peppers decreased the incidence of transplant loss by at least 50%.

In all applications the size, weight and shelf life of fruits and vegetables was increased.

[Click to enlarge]



US7261912 A METHOD OF PRODUCING USEFUL PRODUCTS FROM SEAWATER AND SIMILAR BRINES

Inventor: ZEIGLER Arthur

A process is provided for the recovery of useful products, including fertilizers and nutritional supplements, from the organic matter and minerals contained in seawater and other brines. The dissolved organic carbon-based chemicals and suspended particulate carbon-based organic matter are co-precipitated together with the contained magnesium and/or calcium, along with incidental trace minerals, entrained water and water of hydration. Caustic soda (NaOH) and other alkali base or alkaline earth bases and/or carbon dioxide (CO₂) are added to the brine until pH of 10.75 to 11.0 is achieved. The settled or non-dry filtered or centrifuged precipitate is utilized as a slurry and the supernatant brine is discarded.

Background of the Invention

0001 This invention relates generally to the fields of chemical extraction, fertilizers and nutritional supplements and more specifically to a METHOD OF PRODUCING USEFUL PRODUCTS FROM SEAWATER AND SIMILAR BRINES.

0002 For thousands of years mankind has utilized the minerals and vegetable products of the oceans for both food and fertilizer.

0003 Even to this day sea salt is prized for its trace mineral content and kelp products are used as both food and fertilizer in many parts of the world.

0004 The present invention bonds both dissolved carbon-based organic chemicals and suspended carbon-based organic particles to hydroxide precipitates of marine minerals.

0005 They are bonded ionically, mechanically, electrostatically or otherwise.

0006 For the bulk of dissolved organic carbon in the ocean, chemical structure and basic biochemical parameters are largely unknown.

0007 Fulvic acid which is ubiquitous at low concentrations in all parts of the ocean consists of many thousands of different organic substances of both marine derived and terrigenous origin.

0008 Not only are the compositions of these substances largely unknown, so are their physical properties.

0009 It is known that some of these substances, especially exopolysaccharides, are capable of spontaneous polymerization with the production of jelly-like layers covering several square miles.

0010 Dimethylsulfoniopropionate, a substance produced by phytoplankton for osmotic control, is generated in such quantities that some of its decomposition products are considered to have a major effect on planetary weather. It is known to have a kosmotropic effect on water molecules.

0011 Other of the dissolved organic substances organize water molecules into liquid and solid phase clathrates and quasiclathrates.

0012 A new class of highly abundant, nonliving organic marine particles has recently been recognized.

0013 These colloidal particles consist primarily of exopolymers released as exudates by phytoplankton and bacteria. These exopolymer particles have been found to be present in seawater ranging up to 5,000 particles per ml and varying in size from 3 to 100 nanometers.

0014 They are characterized as containing large amounts of water which has been organized by the organic matter. It is postulated that this ability of dissolved and particulate organic matter in the oceans to organize and add structure to water molecules is, at least in part, responsible for the observable and measurable biological effects of the present invention on plant, animal and human life.

0015 In the past, minerals have been extracted from seawater for fertilizer and nutritional supplementation or the organic chemicals have been extracted separately for the same purpose.

0016 To the best of the inventors knowledge, no one has previously, intentionally extracted the two together for the synergistic effect which they have in combination when used as a slurry.

0017 **U.S. Patent #3,374,081** is a method of separating minerals from seawater which are suitable

for use as fertilizers and animal feeds. It employs added proteinaceous materials to precipitate minerals as chelated complexes.

The methods employed and precipitates obtained are of very different nature than those of the present invention.

0018 **U.S. Patent #2,606,839** employs methods similar to the current invention for the purpose of producing a pure sodium chloride product.

The patent shows no awareness of the valuable nature of the byproduct for the applications claimed by the present invention.

0019 **U.S. Patent #3,071,457** describes a method of evaporating seawater to dryness for application of the resultant solids as fertilizer.

This product very successfully increased crop yields but required application rates of 550 to 2,200 pounds of sea solids per acre.

The first paragraph of this patent states that it relates only to the inorganic salts contained in seawater.

0020 **U.S. Patent #2,404,550** uses methods similar to the current invention but uses them for the purpose of extraction and purification of mineral salts from the waters of the Great Salt Lake. One of its aims is the separation and exclusion of organic content from the final product. Testing of the present invention has demonstrated that purified minerals extracted from brines do not have the desired effects.

0021 **U.S. Patent #2,934,419** uses methods similar to the current invention but differs in two very important respects. No mention is made of organic content and the mineral precipitates are dried. Testing of the current invention has shown that if the precipitates are dried they can no longer significantly stimulate plant growth.

0022 **U.S. Patent #4,634,533** uses methods similar to the current invention to recover useful products such as fertilizer, animal feed supplements and mineral salts from brines. It differs in two important respects.

It makes no mention of the organic chemical constituents of the brine.

It requires the addition of a phosphorous source in order to have the claimed benefit as a fertilizer.

0023 **U.S. Patent #4,015,971** has the object of producing fertilizers from seawater containing "microelements and active organic substances".

This is accomplished by adding bivalent iron ions to the seawater so that the organic substances are co-precipitated with the iron hydroxides. It does not utilize the contained magnesium and calcium brine constituents as does the present invention. The patent claims

5% to 10% increased crop yields with application rates of .5 to 3 kg of dried solids per hectare.

On this basis it is both less effective and less economical than the present invention.

0024 **U.S. Patent #5,074,901** is a method for producing a liquor from seawater by achieving a 90% reduction of the original volume through evaporation.

Although the patent states that this Liquor, when diluted, will function as a fertilizer, its nature is very different from the liquor produced by the current invention.

0025 **U.S. Patent #6,147,229** describes a method of producing magnesium fulvate from humus material.

It involves digesting the humus in a solution of sodium hydroxide, then acidifying to precipitate humates followed by the addition of magnesium hydroxide to the supernatant in order to precipitate magnesium fulvate.

The current invention extracts magnesium fulvate from seawater in a single step by the addition of sodium hydroxide, which precipitates the contained magnesium as hydroxide that in turn precipitates the contained fulvates as magnesium fulvate.

0026 These prior usages have not recognized the benefits, economies and synergies that can be achieved by using the magnesium and/or calcium constituents of the sea water and similar brines to co-precipitate and recover in usable form, the organic chemical and particulate organic content of said brines. Furthermore, they did not recognize that the resultant precipitates are most bioactive in slurry form. That they did not do so indicates that such usage is unobvious.

Brief Summary of the Invention

0027 The primary object of the invention is to extract, from seawater and similar brines, its dissolved, carbon-based, organic chemicals and particulate carbon-based organic matter together with the contained bivalent minerals and incidental trace minerals, entrained water and water of hydration, so that these substances may be applied to beneficial use.

0028 Another objective of the invention is to produce from seawater and similar brines an economical and efficacious fertilizer and plant growth stimulant which would contain microelements and active organic substances.

0029 Another objective of the invention is to produce a nutritional supplement from seawater and similar brines that will promote health and growth in animals and humans.

0030 An advantage of the invention is that it will produce magnesium fulvate from seawater and similar brines in a single chemical operation.

0031 Other objects and advantages will become apparent from the following descriptions, taken in connection with the accompanying drawing, Figure 1, wherein by way of illustration and example, an embodiment of the present invention is disclosed.

0032 In accordance with a preferred embodiment of the invention, there is disclosed a method of co-precipitating the carbon-based organic chemicals and carbon-based particulate matter contained in seawater and similar brines together with its constituent, bivalent magnesium and/or calcium and incidental trace minerals, entrained water and water of hydration.

0033 In accordance with a preferred embodiment of the invention, there is disclosed a method for producing from seawater and similar brines, an economical and efficacious fertilizer and plant growth stimulant, which utilizes both the organic substances and constituent bivalent minerals which may be co-precipitated from said brines together with trace minerals, water of hydration and entrained waters.

0034 In accordance with a preferred embodiment of the invention, there is disclosed a method for producing from seawater and similar brines, a health and growth promoting nutritional supplement,

which utilizes both the organic substances and constituent bivalent minerals which may be co-precipitated from said brines along with trace minerals, water of hydration and entrained waters.

Detailed Description of the Preferred Embodiments

0035 Detailed descriptions of the preferred embodiment are provided herein. It is to be understood, however, that the present invention may be embodied in various forms. Therefore, specific details enclosed herein are not to be interpreted as limiting, but rather as a basis for the claims and as a representative basis for teaching one skilled in the art to employ the present invention in virtually any appropriately detailed system, structure or manner.

0036 As illustrated in the drawing Figure 1, the seawater 10 is treated in a reaction vessel 11, with caustic soda (NaOH), or any other base or alkaline earth base that yields hydroxyl ions on hydrolysis. The caustic soda is indicated in the drawing as being fed through line 12, to the reaction vessel, 11. The concentration of the caustic soda is such that the number of hydroxyl ions added from line 12 is chemically equivalent to the total concentration of the magnesium ions present in the seawater from the source, 10. As a practical application, caustic soda is added until a pH of 10.75 to 11.0 is achieved. Soda ash (Na₂CO₃) or any other alkali carbonate or alkaline earth carbonate is added to the seawater in reaction vessel 11, in such concentration that the carbonate ions are chemically equivalent to the calcium ions present in the seawater. The soda ash is schematically indicated on the drawing as being added to the reaction vessel 11, through line 14, and such addition may be simultaneously with, or at different times from, the addition of the caustic soda. Preferably, the seawater with the caustic soda and soda ash added thereto is agitated in the reaction vessel 11, to complete the dissolving and reaction of the chemicals.

0037 A precipitation occurs within a few minutes after the addition of chemicals to the reaction vessel 11, from lines 12 and 14 and such precipitate is for the most part, magnesium hydroxide and calcium carbonate. The surface area of such magnesium hydroxide precipitates is tremendous, largely due to the fact that it precipitates out in very small particles. The calcium carbonate precipitate also has a very large surface area. The magnesium hydroxide and calcium carbonate precipitates absorb trace elements in the seawater on their large surface areas and thereby trace elements are also separated from the seawater. Fulvates are precipitated as magnesium fulvate. Most importantly, substantially all of the dissolved organic carbon-based chemicals and particulate carbon-based organic matter are co-precipitated together with the magnesium hydroxide and calcium carbonate and bonded to their surface either mechanically, ionically or electrostatically. They can thus be separated from the seawater together with their waters of hydration.

0038 Another preferred embodiment of the invention, which will achieve the same result as the preceding description, would be as illustrated in Figure 1, to treat the seawater 10, in reaction vessel 11, with caustic soda or any other base or alkaline earth base that yields hydroxyl ions on hydrolysis. The caustic soda (NaOH) is indicated in the drawing as being fed through line 12, to the reaction vessel 11. The concentration of the caustic soda is such that the number of hydroxyl ions added from line 12, is chemically equivalent to the total concentration of the magnesium ions present in the seawater from the source, 10. As a practical application, caustic soda is added until a pH of 10.75 to 11.0 is achieved. Next, the liquor in reaction vessel 11, is agitated and carbon dioxide gas is introduced through supply pipe 15, in an amount sufficient to precipitate all of the contained calcium as calcium carbonate.

0039 Another preferred embodiment of the invention, which will extract and recover all of the organic carbon contained in the seawater, would be as illustrated in Figure 1, to treat the seawater 10, in reaction vessel 11, with caustic soda (NaOH) as indicated in the drawing as being supplied through line 12 to the reaction vessel 11. The concentration of the caustic soda is such that the number of hydroxyl ions added from line 12, is chemically equivalent to the total concentration of magnesium ions present in the seawater from the source, 10. Potassium hydroxide is also added, as

indicated in Figure 1, through supply line 13. The KOH is supplied in sufficient quantity to convert all of the calcium contained in the liquor being treated in reaction vessel 11, into calcium hydroxide. As a practical application, but not limited to this example, the sodium hydroxide can be supplied, together with the potassium hydroxide, in a ratio of 95% sodium hydroxide to 5% potassium hydroxide. This blend is supplied to the reaction vessel 11, until a pH of 10.75 to 11.0 is achieved.

0040 All of the examples given as preferred embodiment will achieve substantially the same results, as far as co-precipitating together with the magnesium and calcium, substantially all of the dissolved carbon-based chemicals and carbon-based particulate organic matter contained in the seawater feed illustrated as 10, in Figure 1.

0041 Once the precipitation is achieved in the reaction vessel 11 by the chosen method, the liquor is allowed to stand quietly for a period of time so that the precipitates may settle. In a preferred embodiment of the invention as illustrated in Figure 1, the liquor is allowed to rest in settling tank 16, for 48 hours and the supernatant solution, 17, is then decanted and discarded. The settled precipitates are the valuable product illustrated in Figure 1, as 18, the slurry product.

0042 Seed germination tests done by the inventor have shown that if the slurry is allowed to dry out, it loses its potency even if rehydrated. Other tests have shown that it is the presence of the organic content together with the bivalent marine minerals which make the slurry product effective. A slurry of pure magnesium and/or calcium hydroxide will not produce the beneficial effects on plant and animal life that the slurry produced by the present invention does.

0043 If it is desired to alter the characteristics of the slurry product identified as 18 in Figure 1, minerals or other substances with the desired attributes may be added before and/or after precipitation. For example, bivalent iron could be added to feed 10 and it would be precipitated along with the other minerals as hydroxide. For special applications, any number of minerals or other substances can be added before and/or after precipitation to give desired characteristics to the slurry product.

0044 In a preferred embodiment of the invention, the precipitates will contain from 10 to 50 grams per liter of total suspended solids, although other proportions may be achieved if so desired.

0045 The slurry is stored in opaque containers away from direct sunlight and strong electromagnetic fields, which may cause the loss of potency.

0046 As a fertilizer and plant growth stimulant, in a preferred embodiment the slurry is added to the growth medium at the rate of one or more gallons per acre.

0047 In another preferred embodiment of a fertilizer prepared under this invention, the slurry product illustrated in Figure 1, as 18, and containing 20 grams of total suspended solids per liter, would be diluted with 999 parts of water so that the final solution contains .1% of the slurry, illustrated as 18. To this solution, any soluble nitrate fertilizer may be added at its recommended rate. The resultant solution may be added directly to the growth medium or applied as a foliar spray.

0048 Wheat treated in this manner has yielded 36% more grain by weight than the control, which received the nitrate fertilizer only, in this test the slurry 18, was applied at the rate of one gallon per acre. Similar results have been achieved with a variety of row and orchard crops. Typical results with fruit include increased size, increased sugar content, increased overall yield and better keeping quality. 0049 If it is desired to alter the characteristics of the agricultural slurry product, minerals or other substances with the desired attributes may be added before and/or after precipitation. For example, bivalent iron could be added to feed 10 and it would be precipitated along with the other minerals as hydroxide. Ionic zinc is an example of a mineral that might be added after precipitation. For special applications, any number of minerals or other substances can be added before and/or

after precipitation to give desired characteristics to the agricultural slurry product.

0050 As a preferred embodiment of a nutritional supplement for animals prepared from the slurry product identified as 18 in Figure 1, the slurry product containing 20 grams of total suspended solids per liter is added to the drinking water or feed so that the daily dosage is one tenth to one half milliliter per kilogram of body weight.

0051 The daily dose of this preparation is used to describe a daily dose for a primate having a body weight of 70 kgs, unless otherwise stated.

0052 hi animal testing conducted by the inventor, the above formula was used at the rate of .4 milliliters per kg of body weight per day to supplement the diet of white mice for a period of thirty days, after which they were subjected to forced swim testing. During the test period of 30 days the control population, consisting of 10 mice that did not receive the supplement, experienced a 30% mortality while the test population, consisting of 30 mice that received the supplementation, experienced no mortalities.

0053 When subjected to swim testing, the mice that had received the supplementation were able to endure for a period averaging 3.23 times greater than the control population.

The groups which had received the supplementation had a 3.8 % greater body weight at the termination of the test than did the control population.

0054 In a preferred embodiment of this invention to prepare a nutritional supplement for humans, the seawater feed illustrated as 10 in Figure 1, would be filtered before being placed in the reaction vessel 11, in order to remove any extraneous material. The final slurry product 18 would undergo additional processing to become the food grade slurry product identified in Figure 1 as 19. The slurry would be rinsed by diluting to five times its volume with fresh water and allowed to settle. This is illustrated in Figure 1 with the fresh water shown as being supplied by line 20.

0055 After 48 hours the supernatant would be discarded as shown in Figure 1 by line 21 and sodium chloride would be added at the rate of one gram per liter and this is illustrated in Figure 1 as being supplied by line 23. The resultant liquor may be further sterilized before bottling by boiling for 10 minutes and, after boiling and being allowed to cool, an addition of 35% hydrogen peroxide is made at the rate of 2 milliliters per gallon of liquor. The H₂O₂ is shown in Figure 1 as being supplied by line 22. Total suspended solids in the food grade slurry will vary between 7 and 20 grams per liter and may be otherwise concentrated or diluted.

0056 This liquor may be used as a beverage or added to food to promote health and vigor, hi a preferred embodiment of packaging, after bottling, the food grade slurry would be over-packed in metalized plastic film or anti-static protective bags such as is used for shipment of computer parts. Alternatively a metalized bottle could be used or metal foil could be utilized as an outer cover. These measures allow the product to be stored and shipped without loss of potency.

0057 If it is desired to alter the characteristics of the food slurry product identified as 19 in Figure 1, minerals or other substances with the desired attributes may be added before and/or after precipitation. For example, bivalent iron could be added to feed 10 and it would be precipitated along with the other minerals as hydroxide. For special applications, any number of minerals or other substances can be added before and/or after precipitation to give desired characteristics to the slurry product. Ionic cobalt and iodine are examples of minerals that might be added after precipitation.

0058 With respect to all methods disclosed herein, all steps, procedures or processes may be considered to be done without regard to the priority unless specified, or dictated by necessity or

force of logic. The identification of steps or products in any priority is done only for the purpose of introducing them and distinguishing them from one another, unless otherwise dictated by necessity or force of logic.

0059 The foregoing is offered primarily for purposes of illustration. It will be readily apparent to those skilled in the art that the proportions, material, formulation procedures, administration protocols and other parameters of this invention may be further modified or substituted in various ways without departing from the spirit and scope of the invention.

0060 While the invention has been described in connection with a preferred embodiment, it is not intended to limit the scope of the invention to the particular form set forth, but on the contrary, it is intended to cover such alternative, modifications, and equivalents as may be included within the spirit and scope of the invention as defined by the appended claims. Table 1 Experimental Proofs

Our agricultural research has established the following data:

1. Seeds treated with the invention and germinated in a closed container consumed 118% more oxygen in the first 24 hours than did the control. This test of aerobic cellular respiration shows that independent of all other factors, cellular respiration of the plant is increased.
2. Yeast introduced to the invention in sugar water and placed in a sealed container generated one third more CO₂ in the first 24 hours than the untreated control. This test of anaerobic cellular respiration shows that independent of what is happening in the plant; increased cellular respiration will take place in microorganisms in treated soil.
3. Treated soil in which wheat was germinated and grown out for 20 days was analyzed by a soil laboratory. The test showed that the invention gave an increase of total bacterial biomass 32% greater than fertilizer alone did. The test also showed that the treated soil had an increase of total fungal biomass. The increase over baseline was 264% greater with the invention than fertilizer alone achieved.
4. Brix refractometer testing of the sap from all of the various species being trialed has shown at least a 30% greater content of dissolved solids, primarily sugars, in the sap of the treated plants when compared to the controls. This can only be achieved through increased photosynthesis.

Taken together the data indicate the following:

- A. All species of plants, when treated with the invention, will gain the benefit of more energy through increased cellular respiration and increased photosynthesis.
- B. Soil health and vitality of the treated soil will be greatly increased due to greater microorganism growth and content.
- C. As a consequence of points A. and B., those species of plants that have a symbiotic relationship with mycorrhizal fungi should experience increased yields in direct proportion to each species degree of dependence upon the mycorrhizal relationship.

This hypothesis is validated by the following test data: Potato trials indicate Table 1 Experimental Proofs

achievable yield increases in the vicinity of 100% over and above what fertilizer alone can produce. Wheat trials show increases of 25% to 45%. Other species show a similar pattern.

The fungi obtain carbohydrates and growth factors from the roots of the plants. As the invention

increases these carbohydrates in the sap by over 30%, and at the same time increases the cellular respiration of the soil microorganisms, a previously unattainable synergy is achieved. This accounts for much of the enhanced yields and plant health that we have observed.

Animal Testing

The method:

Four week old white mice were obtained and split into two populations. The control population consisted of ten mice and the other group consisted of thirty mice.

All populations were given measured amounts of the same food and measured amounts of water daily. The mice in the test population were also each given five drops of the formula in their water every day for thirty days.

During the first week of the test there was a 30% mortality for the control population but no deaths occurred in the group receiving supplementation with the invention.

Termination:

At the end of 30 days the mice were subjected to forced swim testing to the point of terminal exhaustion and death.

The Results:

1. The control group, that had not received supplementation, endured for an average of 257 minutes, or 4 hours and 17 minutes.
2. The test population, that had received the invention endured for an average of 830 minutes, or 13 hours and 49 minutes.

Observations:

The test population, that received supplementation exhibited more stamina than the control group by enduring the forced swim testing for a much greater duration.

Conclusions:

Supplementation with the invention as performed in this study greatly enhances stamina.

Referenced Patents:

US4015971

Method of producing fertilizers from sea-like waters

The present invention relates to the production of fertilizers for agriculture and, more specifically to fertilizers produced from sea-like waters. The term "sea-like waters" means any natural water featuring chlorine factors of individual components and elements of the water which are characteristic of ocean water. The chlorine factor is calculated from the formula: $\text{Kel} = \% \text{el} \cdot \text{times} \cdot 100 / \% \text{Cl}$, where $\% \text{el}$ is the percentage of a component, elements; $\% \text{Cl}$ is the percentage of chloride ions.

Known in the art are fertilizers produced from sea water. These fertilizers may be exemplified by, for example, potassium salts. Potassium salts are prepared from sea water by addition of phosphate

ions to water containing potassium and magnesium, increasing its pH to 7.5-9.5 by means of an ammonium-free base, and separation of a residue the water by filtration, decantation or centrifugation. Potassium salt is separated from the resulting residue of a double salt of potassium-magnesium according to the reaction:



where A is an anion (cf. U.S. Pat. No. 3,195,978).

Another process (U.S. Pat. No. 3,382,038) contemplates recovery of potassium from sea water by the addition of an alkali to increase its pH to 10.5-12 and elevation of the water temperature from 25 DEG to 100 DEG C. Potassium along with other components is precipitated. Finally, potassium may be recovered from sea water by contact with a naturally-occurring zeolite, viz-glaucanite, from which it is partially removed by treating with a solution of an ammonium salt the thus-regenerated zeolite or glaucanite is again contacted with sea water, followed by treating with a solution of an ammonium salt to produce a potassium salt (U.S. Pat. No. 3,497,314). Potassium salts pertain to the class of microfertilizers and it is necessary to introduce into soil several hundred kilograms of said salts per one hectare. If potassium is recovered from sea water by the above-said processes, losses of such valuable components as ions of ammonium, phosphate-ions, caustic soda are possible as a result of increasing the pH of sea water. Moreover, said salts neither contain microelements and organic substances. Potassium salts recovered from sea water correspond to similar fertilizers, in their efficiency and purpose, produced in various countries from salt deposits on dry land. The only advantage of the above-mentioned fertilizers is that they may be produced by any country with an access to sea water. The main disadvantage of potassium fertilizers produced from sea water resides in a relatively high loss of ammonium and phosphorus ions and a high alkali consumption, whereby production of potassium fertilizers from sea water is limited.

It is an object of the present invention to produce fertilizers from sea water which would contain microelements and active organic substances.

Another object of the present invention is to select such a composition of the fertilizers which would selectively stimulate the growth and evolution of agricultural plants.

Still another object of the present invention is to provide such a composition of the fertilizers which could be used in combination with other type fertilizers.

A further object of the present invention is to provide such a method of producing fertilizers from sea water which would be easily reproduced on a commercial scale on the basis of cheap and readily-available raw materials.

The method of producing fertilizers, according to the present invention comprises introduction, into the sea-like water, of ions of bivalent iron in an amount within the range of from 10 to 100 mg of iron per liter of said water at a pH = 5 to 9; therewith, bivalent iron ions are oxidized and transformed into trivalent iron ions with the formation of iron hydroxide; sorption of microelements and organic substances being present in said water by iron hydroxide at said pH values without sorption of sodium chloride; separation of the resulting precipitate; drying of the separated precipitate to the air-dry state containing predominantly iron in an amount of from 23.4 to 31.5%, total carbon 2.3 to 3.0%, total amount of microelements 0.1 to 0.3%.

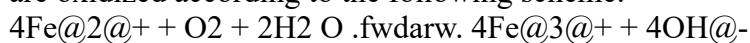
As has been mentioned hereinbefore, concentration of hydrogen ions in sea water should be within the pH range of from 5 to 9. If the pH of water is below 5, then the rate of oxidation of Fe^{2+} ions into Fe^{3+} becomes strongly retarded and the fertilizer yield becomes substantially reduced, while at a pH of water above 9 the resulting product becomes diluted with potassium and magnesium hydroxides, wherefore its effectiveness, as a fertilizer, is substantially lowered.

When iron is added to sea water in an amount of less than 10 mg Fe/l, it is necessary to separate too large amounts of water from the precipitate and the fertilizer production cost is substantially increased; if iron is introduced into sea water in an amount of more than 100 mg Fe/l, the resulting product has a small content of organic substances, wherefore its efficiency is reduced.

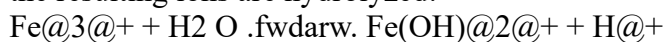
As a source of bivalent iron ions it is advisable to use ferrous salts both in a solid and liquid state. It is preferred, however, to spent solutions from etching ferrous metals with hydrochloric acid; these solutions are available in considerable amounts from plants of mechanical engineering and ship-building industries. Said solutions are toxic production wastes and great sums of money are allocated to eliminate them, wherefore the use of spent etching solutions for the production of fertilizers is economically efficient and, furthermore, large areas of land and sea are not polluted and, hence, environment pollution is reduced.

Solutions from etching of ferrous metals usually contain 120-160 g of iron per liter of a solution and 30 to 60 g/l of hydrochloric acid; occasionally in such solutions there may be present corrosion inhibitors in an amount of from 0.8 to 1.2% such as a product of copolymerization of urotropin and aniline. Our investigations in vegetation tests under field conditions have shown that corrosion inhibitors being present in the fertilizer do not exert any noticeable effect on the fertilizer efficiency.

In the practice of the present invention, the method according thereto is effected as follows. Sea water is poured into a vessel and ferrous chloride is introduced thereinto in the form of a solid salt, aqueous solution, or spent etching solution at a rate of 10 to 100 mg Fe/l of water. The pH of the water is maintained within the range of from 5 to 9. Ions of bivalent iron introduced into sea water are oxidized according to the following scheme:



the resulting ions are hydrolyzed:



with the formation of hydroxide $\text{Fe}(\text{OH})^{2+} = \text{H}_2\text{O} \rightarrow [\text{Fe}(\text{OH})_2]^{+} + \text{H}^+$, containing active positively charged centers capable of recovering, according to the ion-exchange mechanism, valuable metals such as copper, zinc, molybdenum as well as amine complexes and other components from sea water. The resulting precipitates of ferrous hydroxide possess a particular property, i.e. they result in no sorption of sodium ions. This phenomenon is favorable for the fertilizer quality as will be shown hereinbelow. Sorption time is 0.1 to 6.0 hours. Solid particles of iron hydroxide with co-precipitated thereon microelements and organic substances are separated from sea water by decantation with subsequent filtration of the precipitate. The filtered precipitate contains about 70% of water.

This precipitate is dried to the air-dry state, i.e. such a state when the precipitate contains an equilibric amount of humidity under normal conditions. To this end, the precipitate is poured over the ground and dried under environmental conditions or in special drying chambers at a temperature of from 0 DEG to 50 DEG C. When dried at a temperature of above 50 DEG C, the fertilizer may have its activity lost, wherefore the use of such temperatures is not advisable. As a result of these operations, a fertilizer of the above-mentioned composition is obtained.

The present invention has the following advantages: the process of its preparation is rather simple and commercially efficient sources of the starting material, i.e. sea-like waters, are practically unlimited and each country has vast resources of ferrous salts. Taking into account the fact of utilization, with equal success, of waste products containing ferrous salts, economic efficiency is substantially increased. In addition, the method of the present invention contributes to preventing pollution of the environment with poisonous production wastes. The fertilizer according to the present invention has an additional advantage residing in that it steadily increases the yield capacity of numerous agricultural plants by at least 5-10% at an insignificant rate of 0.5 to 3 kg of one

hectare. Another feature of the present invention resides in its ability to stimulate the growth of grape vines and increasing the yield capacity of not only pulse plants but other type plants as well.

For a better understanding of the present invention some specific Examples illustrating the method of producing fertilizers as well as the use of the thus-produced fertilizers in with respect to particular agricultural plants.

EXAMPLE 1

Into a pool there was poured Black Sea water with a salinity of 1.83% and composition (percentage of the salt mass): NaCl--77.29; KCl--2.11; MgCl₂ -- 8.92; MgSO₄ -- 6.33; MgBr₂ -- 0.20; CaSO₄ -- 3.64; Ca(HCO₃)₂ -- 1.52.

the water also contained 3.5 mg/1 organic substances, 3.10@-@6 g Cu/1, 4.10@-@6 g Mo/1, 8.10@-@6 g Zn/1. It was added with a spent solution from etching of iron containing 120 g/1 of Fe, 30 g/1 of HCl, and 1% of an inhibitor. Concentration of hydrogen ions in the solution was adjusted to a predetermined value by means of a 36% hydrochloric acid or solid soda; the solution was mixed by means of air bubbling. After settling of the solution for 24 hours, water was decanted. The resulting precipitate was filtered through a dense tissue and dried in the air at a temperature within the range of from 20 DEG to 35 DEG C.

Conditions of the process and results obtained are given, for six texts in Table 1 hereinbelow.

Table 1

Chemical characteristics of the products obtained in tests a, b, c, d, e are given in Table 2.

Table 2

It may be seen from Table 2 that the fertilizers produced at a higher concentration of hydrogen ions in the solution contain greater amounts of organic substances, while at a lower concentration of hydrogen ions in the solution fertilizers with a greater content of microelements are produced.

It has been found that a pH within the range of from 6.9 to 7.2 was the most advantageous for the process. This pH range was selected due to the fact that practically no hydrochloric acid or sodium carbonate need to be added to the sea water, whereby fertilizers with a minimal production cost could be obtained.

Vegetation tests of the fertilizers for growth and development of various agricultural plants have shown a high efficiency thereof.

EXAMPLE 2

Effect of the fertilizers produced from sea water in tests a and d was determined in vegetation field experiments according to the following scheme:

1. Control - seeds not treated with the fertilizers
2. Seeds treated with the fertilizes
3. Fertilizers were introduced into soil.

The tests were performed on soils of Ukraine and Moldavia. In vegetation experiments the effect of a pre-seeding treatment of seeds as well as the soil dressing effect on the productivity of sugar beet and corn were studied. Seeds of sugar beet and corn were treated at the rate of 0.125 kg of the fertilizer per 100 kg of seeds of corn and 1.0 kg. of the fertilizer per 100 kg. of seeds of sugar beet. The solid was dressed, for sugar beet, at the rate of 1.5 kg of the fertilizers, and for corn at the rate of 0.5 kg of the fertilizers per 10 kg of commercial fertilizer mixture based on nitrogen, phosphorus

and potassium (referred to hereinafter as NPK for the sake of brevity). Each experiment was repeated 5 times. Soil humidity in the experiments was 70% of the total moisture-absorbing capacity of the soil. The results of the vegetation tests of sugar beet and corn are given in Table 3 hereinbelow.

Table 3

It follows from Table 3 that the use of the fertilizer according to the present invention increases the total mass of beet, its sugar content, reduces the content of harmful nitrogen. For corn there is an increase in total mass and grain. According to the visual observations, beets to which the fertilizers of the present invention were used in combination with pre-seeding enrichment of seeds and with its introducing into soil, showed a more developed leaf surface.

EXAMPLE 3

In 1972 under field conditions the influence of pre-seeding enrichment of seeds with the fertilizer of the present invention on yield and sugar content on podzolic soils was studied. Meteorological conditions of that year were unfavorable for sugar beet. In the beginning of the vegetation period there was an insufficient amount of humidity in the soil, poor precipitation, while at the end of the period there was an abundant precipitation which made the soil more dense thus impairing its aeration.

According to the data provided by the meteorological station of the region where the experiments were performed, stock of humidity in a one-meter soil layer was 22 mm during the test period at the relative humidity of air of 62%. Only in July and August in a meter soil layer the stock of humidity increased to 104-176 mm at a relative humidity of air 70-75% while in September there was a drought again.

Efficiency of the fertilizers under these conditions is shown in Table 4.

Table 4 illustrates unquestionable improvement of said characteristics by using the fertilizer according to the present invention.

Table 4

It should be noted that the fertilizer introduced into soil is located in places of root spreading. This phenomenon was noticed both in laboratory and nature; it probably exerts a favorable action on the plant growth.

EXAMPLE 4

The fertilizer of the present invention produced in test d was tested during a two years' period for soil dressing of two strains of grapes "Risling" "Rkatsiteli" and cabbage "Mozharskaja". Dressing was effected by means of a 1% aqueous solution of the fertilizer suspension simultaneously with nitrous fertilizers in the amount of 400 l of the suspension per one hectare. The soil for cabbage was dressed with a 0.5% aqueous solution of the fertilizer suspension in the amount of 400 l per one hectare. The test results are given in Table 5.

Table 5

As seen from the data of this Table, the use of the fertilizer of the present invention increases the yield of grapes and, to some extent, its sugar content; yield of cabbage is substantially increased.

In addition to said plants, we have performed vegetation and field tests of the fertilizer of the

present invention on such plants as pea and millet. These test also provide the efficiency of the fertilizers according to the present invention, since the results of four field tests on gray podzol soils and grassland chernozems showed an increased, by 21-62 c/ha, yield of sugar beet, improved sugar content by 0.4-0.8%; sugar output was increased by 4.7-5.0 c/ha.

Soil dressing with the fertilizer of the present invention along with NPK, as determined by the results of one experiment on gray polzol soils, increased the yield of sugar beet roots by 51 c/ha with simultaneous increase in the root sugar content by 1.1%.

The yield of corn silage mass in one experiment on solonetz-chestnut soils was increased, as compared to the control value, by 40 c/ha and yield of corn grain - by 4.4 c/ha.

The yield of corn silage mass in three experiments on calcareous-chestnut, solonetz-chestnut and grassland-chernozemic soils was increased by 20 to 40 c/ha.

The yield of winter wheat in two experiments on gray podzol and calcareous-chestnut soils was increased by 3.0-3.6 c/ha; yield of corn grain under the same conditions as for wheat was increased by 3.7 c/ha.

The yield of millet, according to the data of a two-years' test period, on grassland-chernozems was increased by 6.8-8.8 c/ha.

US4634533

Method of converting brines to useful products

SOMERVILLE, R., et al.

A process is provided for the recovery of one or more useful products including fertilizer, animal feed supplements, iron oxide, magnesia, salt, purified brine, and purified water from brines. The source of the brines can be oil and gas field wastes, seawater or effluent from a seawater desalination plant, or other inland brine sources. Iron and magnesium are initially precipitated from the brine. Then phosphoric acid is added to the brine followed by an alkaline agent to produce precipitates useful as fertilizer and animal feed supplements. The remaining salt in the brine may then be removed and recovered along with purified water.

BACKGROUND OF THE INVENTION

This invention relates to a process for converting brines into useful products, and more particularly to converting saline waters such as oil and gas field brine wastes, seawater or effluent from a seawater desalination plant, or other inland saline waters into animal feed supplements, fertilizer, salt, purified brine and purified water.

Oil and gas field operations generate waste products in the production and handling of crude oil and natural gas. These waste products include drilling mud pit waters and oil and gas field brines. The quantities of brines produced in oil and gas fields can be substantial, with brine fractions accounting for from 4 to 96 percent of the total liquid volume produced. Brines from other inland or seawater sources also present disposal problems.

Various method of disposal of these brines have been attempted including solar evaporation, thermal evaporation, controlled release of brines into surface water, and injection of brines into subterranean formations. However, in areas of high annual rainfall and/or high relative humidity, such as much of the midwestern and eastern portions of the United States, solar evaporation becomes impractical.

Moreover, with increasing state and federal regulatory pressures, diversion of large volumes of brine into surface waters is not an environmentally acceptable solution.

While evaporation as a means of recovering fresh water from these saline sources has been attempted, the presence in such brines of a large proportion of divalent metal chlorides such as calcium and magnesium chloride have greatly complicated recovery efforts. These metal chlorides are highly corrosive to process equipment surfaces and deposit hard to remove mineral scales. This scale deposition becomes an even greater problem when the brines are heated.

Presently, brine treatment using dissolved air flotation methods to remove suspended oil, followed by deep well injection of the brine is regarded by the United States Environmental Protection Agency as the best practicable technology for disposal. However, deep well injection is expensive, difficult to design to a given level of capacity, and requires careful conditioning of the brine prior to injection. Also, deep well injection of brines may present a contamination hazard to fresh water aquifers. Economies of scale favor deep well injection systems having capacities of millions of gallons of brines per month. However, in oil and gas fields in the midwestern and eastern United States where less brine wastes are produced than in western oil fields, and where the oil and gas fields themselves are smaller, deep well injection may not, in many instances, be an economically feasible disposal alternative.

Some attempts have been made in the past to separate useful byproducts from brines or other industrial waste waters. For example, Miller, U.S. Pat. No. 3,374,081, teaches a method of precipitating minerals from saline waters using lignin compounds, proteinaceous compounds, and tannins. The saline waters are initially concentrated by evaporation and the resultant salt precipitate removed. Then an organic precipitating agent such as a lignin or tannin is added to form an organic fertilizer containing other inorganic minerals.

Baldassari, U.S. Pat. No. 4,069,033, teaches the extraction of fertilizer salts and organic substances from a variety of industrial waste waters including sugar mill, distillery, and fermentation wastes. Baldassari teaches the use of strong acids or bases to form precipitates from such waste waters which precipitates are taught to be useful as fertilizers. However, neither of these particular procedures is believed to have gained widespread use.

Accordingly, the need exists for a cost effective and environmentally acceptable method for the disposal of oil and gas field waste brines and other saline water sources.

SUMMARY OF THE INVENTION

The present invention provides for the recovery of valuable products such as animal feed supplements, fertilizers, magnesia, iron oxide, salt, purified brine, and purified water from saline water sources such as oil and gas field waste brines and seawater. These products are useful materials having economic value.

According to one aspect of the present invention, a method is provided in which an oxidizing agent is initially added to the brine to remove iron from the brine as a precipitate. An alkaline agent is then added to the brine to adjust the pH of the brine to the range of 7.5 to 9.0 to cause magnesium ions present in the brine to precipitate and be removed. Sufficiently phosphoric acid is then added to the brine to provide a substantially stoichiometric ratio of phosphoric acid to divalent cations, principally calcium, in the brine. An alkaline agent is then added to the brine to form calcium phosphate precipitates which are useful as an animal feed supplements or fertilizers.

Optionally, the remaining dissolved salts in the brine solution, which is now substantially free of divalent metal compounds, can be readily separated and recovered by the use of a vapor compression evaporator crystallizer or multiple effect evaporator crystallizer. The recovered salt is

principally sodium chloride. This salt is a highly purified product which is useful for practically all commercial purposes. The water which is recovered from the separation process is substantially free of dissolved solids and deleterious metal cations and can be disposed of directly or can be sold as purified water to industrial and commercial concerns.

Accordingly, it is an object of the present invention to provide a process for the recovery of one or more useful products including animal feed supplements, fertilizer, iron oxides, magnesia, salt, purified brine, and purified water from brines. This and other objects and advantages of the invention will be apparent from the following detailed description, the accompanying drawing, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The single drawing FIGURE illustrates, in the form of a schematic diagram, the process of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the practice of the present invention, and with reference to the drawing FIGURE, a saline water source such as an oil field waste brine, seawater, or other inland saline water is initially stored in a large pit, tank, or storage chamber 10. The pit, tank, or storage chamber 10 is preferably lined or otherwise formed to be substantially water tight. If an oil or gas field waste brine is used as the saline water source, it may be necessary to remove traces of oil which are present in the brine. Typically, there is approximately one-half pint of oil per barrel of brine as received from oil field operations. This oil removal is accomplished through the use of a surface skimmer 12 which collects oil floating on the surface of the brine and pumps it via line 14 and pump 16 to an oil storage tank 18.

Additionally, further oil may be removed from the brine in a separation device such as heater treater 20 after removal of the brine from pit 10 via line 22 and pump 24. Heater treater 20 typically comprises a holding tank or the like which provides undisturbed residence time for separation of the oil and brine. Heat is supplied to heater treater 20 to accelerate the separation process, and, optionally, chemicals may be added to heater treater 20 which further enhance separation.

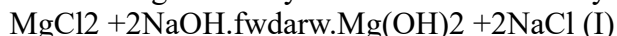
The brine is then filtered to remove suspended solids by pumping it via line 26 through filter 28. Filter 28 may be any suitable filtration device and is preferably a vacuum drum or plate and frame type filter. Such filtration devices are commercially available from a number of sources.

After filtration, the brine is sent to tank 30 where an oxidizing agent is added to the brine to convert any ferrous ions present in the brine to the ferric state. Suitable oxidizing agents include hydrogen peroxide, or ozone. Preferably, this oxidizing reaction is carried out at an acidic pH. Depending on the pH of the brine entering tank 30, the pH of the solution may be adjusted by the addition of an acid or base to bring it within the optimum range. An additional advantage of the oxidation step of the process is that it will destroy any traces of organic materials which may be present in the brine.

After oxidization, an alkaline agent is added to tank 30 to raise the pH of the brine to about 7.0 and cause all iron ions present therein to precipitate as iron oxides. The brine is then sent to a suitable filter 32 where the iron oxide precipitate is removed. The brine is then pumped via pump 34 to a further holding tank 36.

At this point in the process, magnesium is removed from the brine. The presence of magnesium ions in the brine at a later point in the process will result in the production of products having a lower economic value. Additionally, purified magnesium compounds have economic value. Magnesium is typically present in the brine as magnesium chloride which can be reacted with an alkaline material

to form magnesium hydroxide as illustrated by equations I and II below:



To remove magnesium, the brine is pumped via pump 38 to reactor 40. A sufficient amount of an alkaline agent to adjust the pH of the brine to the range of 7.5 to 9.0 is added to reactor 40. A pH meter (not shown) may be used to monitor the pH of the brine solution. After reaction, the brine may be sent to a thickener or settling tank 42 where the precipitated magnesium hydroxide would be concentrated. The precipitate is then filtered in filter 44, washed free of soluble salts, and either dried or calcined in dryer 46. The magnesia product is useful in making refractory bricks and magnesium metal as well as an additive for cosmetics, pharmaceuticals, and insulation.

As shown by equations I and II above, the alkaline agent may be either calcium hydroxide (hydrated lime), hydrated lime from burned dolomite, or sodium hydroxide. If burned dolomite is used, the magnesium content of the dolomite is recovered with the magnesium hydroxide precipitate. Sodium and/or calcium cations, which replace the magnesium ions in solution, are recovered later in the process as explained below.

The clear brine solution from settling tank or thickener 42 and/or filtrated from filter 44 is then sent to a work tank 48 which serves as a holding tank for the brine prior to reaction with phosphoric acid. The brine in work tank 48 may be periodically sampled and analyzed at analysis station 50 to determine the concentration of divalent calcium and other metal cations contained therein. This analysis is then utilized to meter the proper amount of phosphoric acid into the brine from phosphoric acid source 52 and metering pump 54. Preferably, the amount of phosphoric acid added is in a substantially stoichiometric ratio to the concentration of divalent metal cations, principally calcium, in the brine, resulting in a chemical reaction which causes substantially all of the divalent metal cations in the brine to be removed as a precipitate as more fully explained below. The addition of a substantially stoichiometric amount of phosphoric acid to the brine will lower the pH of the brine to less than 2.0. The flow rate of the brine into reactor 56 may be controlled by pump 58 and flow rate valve 60, and is monitored periodically by flow rate indicator 62.

A preferred source of phosphoric acid is agricultural grade phosphoric acid containing 75% orthophosphoric acid (54% when reported as phosphorous pentoxide). The brine and phosphoric acid are thoroughly agitated in reactor 56 to form a reaction mixture. Any suitable agitation device may be utilized including a stirred tank reactor or motionless mixing device.

To the reaction mixture, an alkaline agent is added to adjust the pH of the mixture to the range of 1.8 to 2.9. A metering pump and pH meter may be used to control the addition of alkaline agent. As the alkaline agent, either soda ash (Na_2CO_3), caustic soda (NaOH), potassium hydroxide, or potassium carbonate are preferred. The addition of an alkaline agent causes the precipitation of a mixture of fertilizer salts including principally dicalcium phosphate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). Additionally, most trace impurities in the brine such as strontium, iron, aluminum, fluorine, and the like, will also be precipitated at this stage as complex mineral salts. This is because other ions will react with the phosphoric acid at pH's lower than that which calcium will react. This first stage of precipitation may not be necessary where impurity levels in the brine are sufficiently low.

Such precipitated compounds are separated from the brine solution by filtration, such as by belt filter 64. The precipitate is then dried in dryer 66. The dried precipitate is a citrate soluble fertilizer material having an approximate NPK analysis of 0-40-0.

The reaction mixture is then taken to a further agitated reactor 68 where more alkaline reagent is added to bring the pH of the reaction mixture to the range of 3.5 to 6.0. This causes essentially complete precipitation of all remaining dicalcium phosphate from the brine solution. Because of the

preliminary precipitation step, the dicalcium phosphate precipitated at this stage of the process is quite pure as is useful as a premium grade animal feed supplement. The precipitated dicalcium phosphate is removed via belt filter 70 and then dried in dryer 72.

By controlling the pH of the brine solution after the addition of phosphoric acid, the ratio of calcium phosphates precipitated at each stage (reactors 56 and 68) may be controlled. If impurity levels are sufficient to warrant a two-stage precipitation then, preferably, a minimum amount of calcium phosphates is initially precipitated with the major portion being precipitated in reactor 68. In practice, this ratio is about 10-30% in the first stage and 70-90% in the second stage.

Additionally, the total amount of calcium phosphates produced by the process may be modified somewhat by the selection of alkaline agents at various stages of the process. The use of calcium hydroxide as an alkaline agent at earlier stages of the recovery process will place more calcium cations into solution for later precipitation. In this manner, the process of the present invention is flexible to market conditions for the need for more or less calcium phosphate products. Additionally, while the preferred process has been described above, it is within the scope of the invention to add phosphoric acid and alkaline agent to the brine to precipitate calcium phosphates in a single stage procedure or a procedure with two or more successive states.

The remaining brine is now substantially free of all divalent metal cations. The brine is pumped from storage tank 74 by pump 76 to an optional evaporation system 78. It may be desirable to adjust the pH of the brine in storage tank 75 to minimize corrosion problems in the evaporation equipment, and this may be accomplished by further addition of an alkaline agent such as sodium hydroxide to the brine. The brine itself is a useful product which can be used as a raw material for chlor-alkali plants. Optionally, it may be evaporated to recover crystallized salt.

Evaporation system 78 is preferably a forced circulation evaporator-crystallizer with vapor recompression. Such systems are commercially available. The evaporation system provides both a pure crystallized salt and purified process water.

The recovered salt is principally sodium chloride. Potassium, lithium, and any remaining calcium and magnesium cations are concentrated in the bitterns produced by the evaporation process and may be recycled back to the beginning of the process. The recovered salt is a highly purified product which can be marketed for practically all commercial uses.

The recovered water from evaporation system 78 is itself highly pure and contains less than 1 mg/l of total solids and an absence of deleterious anions and divalent metal cations. The water can be used as process and wash water in the process of the present invention, can be discharged directly to rivers, lakes, and streams with no environmental harm, or alternatively may be sold to industries having large purified water requirements.

While the methods herein described constitute preferred embodiments of this invention, it is to be understood that the invention is not limited to these precise methods and that changes may be made without departing from the scope of the invention, which is defined in the appended claims.

US5074901

Composition derived from sea water for the treatment of vegetation and its method of production

There is disclosed a LIQUOR useful as a natural herbicide and also, when diluted with water, useful as a plant micronutrient.

O does not guarantee that they are complete, up-to-date or fit for specific purposes.

The present invention relates to a LIQUOR, a method for making the same, and its use as a herbicide and/or a plant micronutrient, depending on dilution.

BACKGROUND OF THE INVENTION

Sea solids useful as fertilizer are known from **U.S. Pat. No. 3,071,457** to Murray. In addition, the use of nutrient sea solids in hydroponic farming is disclosed in Murray's U.S. Pat. No. 3,250,606. According to the teachings of these patents, precipitated sea solids are harvested and used as a plant nutrient or fertilizer.

On the other hand, **U.S. Pat. No. 3,770,410** discloses the production of potassium polyphosphates from a phosphoric acid sludge by heating the sludge to eliminate most of the water and then adding a salt mixture thereto to make a fertilizer.

Soilless culture of plants using sea water which is chemically modified with non-natural substances to change its composition is disclosed in **U.S. Pat. No. 2,713,741**. **U.S. Pat. No. 3,640,695** and **U.S. Pat. No. 3,332,767** disclose processes for converting mineralized water into irrigation water, by distillation and similar treatment.

U.S. Pat. No. 2,934,419 deals with the conversion of sea water into a solid fertilizer. **U.S. Pat. No. 2,663,628** discloses a method of making a lignin fertilizer base using a cooking liquor as a component thereof. **U.S. Pat. Nos. 4,450,001; 4,334,910; 4,382,013; 4,508,559; and 4,125,392** disclose similar compositions to regulate plant growth.

All of these known methods and their products fall into one of two categories. Firstly, sea solids are precipitated, removed and used as such. Secondly, the water of the starting material is distilled and used as fresh water. In the first instance, the resultant product is nothing more than a mixture of chemicals derived from sea water; in the second instance, the resultant product is pure water.

None of the prior art disclose the use of a LIQUOR containing water and salts, in which the ratios of the mineral salts to each other and to the remaining water are different from the ratios of such salts in the initial natural sea water. The resultant LIQUOR thus naturally altered from its initial state functions per se as a natural herbicide and also, in dilute aqueous concentrations, as a natural micronutrient. As used herein, the term "LIQUOR" defines the resultant product in which the ratios of salt are modified as disclosed and is to be distinguished from natural sea water as well as from a merely concentrated solution.

As will be explained hereinafter, the undiluted LIQUOR of the present invention is a swift, highly effective natural herbicide even when used in small amounts and may be applied directly to offending and deleterious growths without affecting any surrounding desirable vegetation. On the other hand, when highly diluted with fresh water, the LIQUOR of the present invention provides a totally unexpected and unobviously effective nutrient, by means of which the growth of desirable vegetation is enhanced and increased with rapidity and substantive benefit to the size, taste, appearance and the like of the vegetation. A further unexpected and unobvious result lies in the fact that the LIQUOR acts as a preservative in that the fruit of such vegetation lasts for a longer time after being picked. Thus, having a longer shelf life and transport life.

The noted benefits and advantages of the invention will be apparent from the following disclosure.

SUMMARY OF THE INVENTION

According to the present invention, natural sea water is subjected to conditions suitable to evaporate

a portion of the water therefrom and simultaneously to precipitate a portion of the mineral salts dissolved therein so that the amount of such mineral salts remaining in the resulting LIQUOR differs from the amount of mineral salts contained in the natural sea water in proportion both to itself and to the remaining water. Thus, after the precipitate is removed, the resultant LIQUOR is not a mere concentrate of the natural sea water, but an unexpected mixture of water and salt capable of being used per se as a natural herbicide or diluted sufficiently with fresh water as a natural micronutrient.

More specifically, the present invention provides a method comprising the steps of subjecting a quantity of natural sea water to evaporation for a period of time sufficient to drive off a substantial portion of its water content and to precipitate a portion of the mineral salts dissolved in such natural sea water, thereby forming a LIQUOR containing dissolved mineral salts in ratios to each other and to the water different from those in the initial sea water; separating the remaining LIQUOR from the precipitated solid material (mineral salts); and recovering the LIQUOR.

Still further, in accordance with the present invention, deleterious vegetation can be destroyed or eradicated by applying to the same the LIQUOR described above in an amount effective to accomplish such result. On the other hand, when the above described LIQUOR is diluted sufficiently with fresh water, it may be applied to vegetation as a natural plant micronutrient when utilized in an amount effective to enhance in a significant and unobvious manner, the growth, appearance, and the like of the plant to which it is applied.

DESCRIPTION OF THE INVENTION

In general, the production of LIQUOR according to the present invention can be simply performed by allowing natural sea water to rest in a shallow pan or the like until a quantity of the water evaporates and a layer of precipitate scum is produced on the surface of the remaining natural sea water. The precipitate is then removed, the remaining natural sea water decanted, and the resultant used as the LIQUOR.

For example, shallow pans are filled to the brim with natural sea water and allowed to stand under conditions so that the dissolved mineral salts appear as a precipitate on the surface of the remaining natural sea water. Such precipitate is separated from the remaining natural sea water, which comprises the LIQUOR and can be decanted and bottled. The LIQUOR may first be filtered to remove any large particles and similar contaminants. In general, a quantity of about 5680 ml. of such initial natural sea water in two pans (e.g. shallow 3 quart, 13.times.9.times.2 inches) is reduced to about 230 ml. (an actual reduction of between 90% to 95% of volume) to provide the LIQUOR. This LIQUOR contains approximately 26% by weight of dissolved mineral salts in comparison to about 3.5% of mineral salts dissolved in the natural sea water, and has a substantially neutral pH.

The process may be enhanced by allowing the natural sea water to be moderately heated, with a gas or electric heater to elevate its temperature to induce evaporation, but not to boil the same. Also, the natural sea water may be placed in a vacuum environment to increase the rate of evaporation.

Because of the relatively constant rate of evaporation induced by the low heat, or the ambient external heat and the different rates of precipitation of the mineral salts contained in the natural sea water, the remaining LIQUOR contains dissolved mineral salts in ratios to each other, different from those in the original natural sea water. Such LIQUOR comprises a natural herbicide per se and exerts a herbicidal effect on vegetation when applied thereto in an amount effective to eradicate undesired or unwanted specimens.

While natural sea waters throughout the world vary somewhat in the amount of dissolved mineral salts, there is a relative similarity among them. New York sea water is generally typical of ocean waters. The analysis of sea water is well established, as evidenced by the data set forth on Pages 176

and 177 of "The Oceans" (1942) by Sverdrup, Johnson, and Fleming.

A LIQUOR made from New York sea water in accordance with the present invention has the following analysis with respect to the mineral salts dissolved therein:

ppm.(mg./l.)
Nitrate <1.0
Sodium 2141.69
Aluminum 0.21
Cadium <0.01
Chromium Total 0.02
Chromium Hexavalent<0.01
Copper 0.31
Iron 0.37
Nickel 0.02
Lead 0.05
Silver 0.19
Zinc <0.01
Manganese 0.05
Chloride 2373.2
Sulfate 4.11
Fluoride 0.26
Calcium 6.45
Barium 0.07
Magnesium 1.69
Ammonia 0.15

and had a pH of 6.87.

The present LIQUOR is effective, undiluted, as a natural herbicide, as already indicated. It has also been found that the addition of a slight amount of fresh water to the LIQUOR does not reduce its effectiveness as a herbicide. A small amount of a wetting agent may be used to enhance the spread of the same. This LIQUOR may be applied directly to the root system and/or to the leaf system of the plant or vegetation to be killed by spraying or other suitable means.

As previously mentioned, the LIQUOR is also useful as a plant nutrient when it is highly diluted with fresh water. Broadly, the LIQUOR should be present in an aqueous diluent in an amount at least sufficient to have a micronutrient effect on plant life, i.e., up to about 3800 parts of fresh water to 1 part of LIQUOR by volume. In general, however, the LIQUOR is present in the aqueous diluent in a concentration of about 0.5 ml. to about 1.0 ml. per gallon to be useful as a plant nutrient. It has been found that for fruit plants the lower range of concentration is best, while for green leaf plants and the like, the upper range of concentration (i.e. 1.0 ml. per gallon) is generally preferred. Application of such diluted LIQUOR may be made to the root and/or the leaf systems by spraying or otherwise as desired.

EXAMPLES OF USE

In order to illustrate the present invention more fully, the following examples are set forth. In the examples all values with respect to amounts and ratios are the same as those set forth above, unless otherwise indicated.

Example I As a Herbicide

Dandelion plants in a New York suburb were treated by spraying the base of the plants with undiluted LIQUOR. The spray was made to wet the soil but not to saturate it. Within one day signs of morbidity were observed; and within three days the dandelions were dead.

Such LIQUOR was similarly applied to weeds known as Nut Grass and "Torpedo grass" in Lake Worth, Florida, with similar results.

The foregoing procedures were respectively repeated 5 to 10 times over a period of several days on similar patches of dandelions and Torpedo grass, nut grass, crab grass and the like.

In each instance, the present LIQUOR herbicide was selective and attacked only those plants to which it was applied and did not spread or leach outwardly and cause harm to any surrounding desired vegetation.

It must be noted that the LIQUOR is made from a product of nature and does not injure or affect the aquifer as previously known commercial herbicides or pesticides do. It is made from a natural product and does not have a carcinogenic background.

Example II As A Nutrient

The LIQUOR was diluted in a ratio of 1 ml. to 1 gallon of fresh tap water, the diluted solution being applied to tomato and strawberry plants on commercial farms in Lake Worth, Florida during the months of January through April. The plants were only a part of the entire field of plants and were located in a partially shaded area. The diluted LIQUOR was applied by spraying directly to the leaf portions of the plants and to the soil surrounding the plants.

Within several days it became obvious that the plants exhibited improved color and strength. The plants grew more rapidly than plants not so treated. The treated crop was larger in size and weight and better resisted insect blight; and the fruit, when harvested, were sweeter and tasted better than those not so treated. This occurred notwithstanding the partial shade and the winter growth season. The results, i.e., fruit of this experiment were taste tested in comparison to non-treated fruit (control) by an impartial panel. Of the persons responding, about 70% liked the experimental tomato best, and only 25% liked the control tomato best, while the rest could not differentiate between the experimental fruit or the control.

An unexpected and unanticipated result was observed during recent tests with strawberries. A large number of the control strawberries displayed extensive mold formation and softening and had to be discarded nine to eleven days after picking even when kept under refrigerated conditions. On the other hand, strawberries treated with the LIQUOR of the present invention lasted over 3 weeks and few if any, were lost to mold, etc. Therefore, a natural preservative feature is apparent from the present invention.

The present invention presents many other advantages. For example, the LIQUOR is made from readily available natural starting materials; and the method for making the same is simple and straightforward, requiring no special expensive equipment or the use of non-material chemical components. Moreover, the LIQUOR so prepared can be readily made useful as a plant nutrient by simple dilution with water or the like; and whether used as a herbicide or a plant nutrient, the LIQUOR may be applied in any convenient manner. Numerous other advantages of the invention will be readily apparent to those skilled in the art.

It is to be understood that numerous modifications and variations of this invention may be made without departing from the spirit and scope of the invention, and consequently this invention should

not be limited to the described embodiments except as defined in the appended claims.

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