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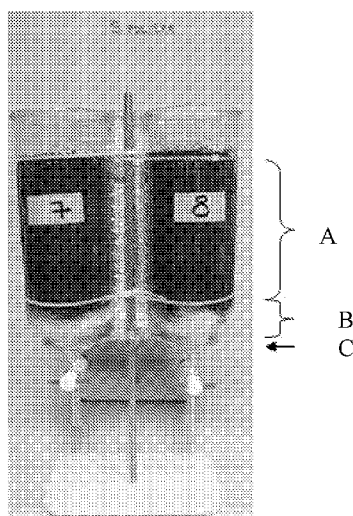


Figure 1: Equipment for the collection of leachate from soil

- A Soil thickness about 12-13 cm
- B Fibreglass
- C Blotting paper

(57) Abstract: A method to change and optimise the level of acidity and the mineral composition of a soil that has undergone salinization or changes in the optimal level of acidity as a result of natural phenomena or anthropic activities, said method comprising the treatment of the soil with an aqueous suspension of hydrophilic sulphur having peculiar features of acidity and granulometry of the suspended phase. The above treatment allows at the same time a rapid fertilisation of the soil and is a faster and more effective way of disposing of excess sulphur resulting from the processes of purification of fossil fuels.



## **METHOD FOR ADJUSTING THE IONIC FEATURES OF A SOIL AND COMPOSITION SUITABLE FOR THE PURPOSE**

### DESCRIPTION

This invention refers to a method for regulating the acidity and salinity of a soil.

More specifically, this invention refers to a method for modifying and optimising the level of acidity and the mineral composition of a soil that has experienced soil salinization or changes in the optimal level of acidity as a result of natural phenomena or anthropic activities.

Soil salinization means the phenomenon of the accumulation of salts having a greater solubility product than that of gypsum. Most of the times, the salts are sodium-based ( $\text{Na}^+$ ), and therefore salinization is recognised as one of the most dangerous soil threats, such as to produce serious consequences on the natural biological, biochemical, hydrological cycles and on erosive processes. The direct impact on the soil loss of multifunctionality translates into a reduction and alteration of the balance of ecological processes and an accentuated limitation of agricultural production, causing a substantial reduction of arable land. The increase in salinized surfaces is viewed as a socio-cultural problem, as the emergence of soils which are no longer cultivable due to soil salinity is one of the causes of the increase of migrants from the most disadvantaged areas.

Each soil has a natural content of salts, essential for plant growth, which can become excessive due to various natural and anthropic processes. Among the natural processes or "primary salinization", is the case of soils derived from evaporitic rocks (consisting of soluble salts) such as those found in the inland areas of Tuscany and Sicily. Another case of primary salinization is that of soils originating from the physicochemical alteration of rocks rich in carbonate minerals and feldspars. In wet areas, the salts released due to alterations are collected and removed by leaching soil profiles with meteoric water. On the contrary, in dry areas the above process is limited by the fact that evapotranspiration is greater than precipitation, and therefore salts tend to concentrate in the soil, often leading to surface salt efflorescence following the occurrence of capillary rise phenomena. Soil salinity can also be caused by events such as the submersion of a pre-existing soil by marine waters (especially in low-lying areas facing the seas and oceans), or may occur due to the action of marine aerosol deposition along coastal areas.

Soil salinization nowadays is mainly due to human activity ("secondary salinization"), and this is the main cause of desertification along the coasts of the Mediterranean and in large areas of the Near and Middle East. In these areas, in order to maximise agricultural production, excessive use has been made of pumping ground water to be used for irrigation, initially causing the ascent of brackish water and then salted water in aquifers that were once fresh water. Over time, the spread of this incorrect practice in arid environments or with low rainfall and characterised by a high rate of evapotranspiration, has triggered salinization phenomena even in places where they would not have occurred naturally. Another cause of salinization is the excessive fertilisation as a result of intensive farming in the presence of poor soil drainage.

Soil salinity is due to the presence of salts that are more soluble than gypsum, consisting mainly of inorganic solutes (mainly sodium, calcium and magnesium chlorides and sulphates). Depending on the degree of accumulation of the above salts, there may be different repercussions on the soil from a chemical-physical point of view as well as in terms of plant ecology. Generally, the pH in saturated paste of saline soils does not exceed 8.2 and the high content of neutral soluble salts maintains flocculated the clay fraction, which is why the soils have a well defined structure. Under the above conditions, however, the high osmotic pressure in the soil solution leads to a reduced water absorption by the roots of plants, with consequent radical stress and limitations in growth. This lower biomass production negatively affects the stability of soil aggregates and produces a decrease in soil organic carbon (SOC) due to reduced fertility and microbial and enzymatic activity. The final consequence is that dispersion of the clay fraction can occur, so that the soil becomes more prone to water and wind erosion.

Salinization does not only have environmental and ecological repercussions but, by influencing production, generates negative effects also at an economic level. In particular, it represents one of the most important threats to sustainable agriculture, especially in arid and semi-arid regions.

In order to control and, if possible, reverse the phenomenon of salinization, it is therefore imperative to resort to reclamation processes, based on multiple processes developed since ancient times. For example, to improve the features of saline soils, it is possible to leach the excess salts using irrigation water of a suitable quality. The difficulty in finding water resources has, however, stimulated over time the search for other solutions for reclamation such as the distribution of calcium chloride, acids of various kinds and gypsum. See, for example, the publication by Hilal and Abd-Elfattah, "Effects of CaCO<sub>3</sub> and clay content of alkaline soils in their response to added sulphur"; *Sulfur in Agriculture*, vol. 11 (1987), pp. 15-19. Among the

various products used, gypsum is certainly the most frequent due to its accessibility and application at low cost compared to others. However, the positive effects of gypsum are difficult to predict as they depend both on its solubility and on the movement of water along the soil profile. As an alternative, numerous experiments attest a noticeable improvement in the quality of saline and alkaline-saline soils with the use of sulphur (Hilal and Abd-Elfattah, see above) which, besides favouring an increase in crop production and quality, are able to improve soil features with positive effects on plant growth as described, for example in Zhang et al., "Study on the effect of S fertilizer application on crops and the balance of S in soil"; *Journal of Agricultural Science*, 1999, vol. 5, pp. 25-27. Sulphur, due to the biological oxidation that occurs through the intervention of soil micro-organisms, produces  $\text{H}_2\text{SO}_4$  which reacts with sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) to form sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), which is so soluble that it can be removed with water from irrigation. With the occurrence of the above reaction, at the same time there is a lowering of the soil's pH due to the release of protons ( $\text{H}^+$ ) and also the cation exchange of  $\text{Na}^+$  with  $\text{H}^+$  on the exchange complex. The application of sulphur in soils affected by salinity also counteracts the absorption by plants of toxic elements such as  $\text{Na}^+$  and  $\text{Cl}^-$ . Elemental sulphur is considered an economic and successful soil improver for saline-sodium soils, in accordance with Kubenkulov et al. (in the publication "Reclamation efficiency of elemental sulfur on the soda saline soil", in *World Applied Science Journal*, vol. 23(9) (2013), pp. 1245-1252) they used elemental sulphur from the refinery as a soil saline-sodium soil improver and obtained interesting results. In addition, literature describes the benefits of sulphur for various crops on saline-sodium soils such as corn, sunflower, rapeseed and wheat. The above is due not only to the ability of S to improve the physical and chemical conditions of the soil, but also because, lowering the pH, allows to release nutrients such as phosphorus and some micro-nutrients that would otherwise be less available. Sulphur is also considered effective in the correction of alkaline soils due to the presence of calcium carbonate (Tarek et al., 2013; Kampf et al., 2006), where S undergoes the same microbial oxidation with sulphuric acid formation, as reported by Jaggi et al. in the publication "Impacts of elemental S applied under various temperature and moisture regimes on pH and available P in acidic, neutral and alkaline soils", *Biology and Fertility of Soils*, vol. 41(1)(2005), pp. 52-58, and then reacts with the existing carbonate ( $\text{CaCO}_3$ ) to form gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). In any case, the distribution of S is recommended for soil pH values above 6.6.

The industrial production of sulphur derives today mainly from the production of mineral oil and natural gas, of which sulphur compounds, and in particular hydrogen sulphide

H<sub>2</sub>S, are undesirable impurities, which therefore require an accurate and almost total separation according to many well-known processes in the sector, such as, for example, the Claus process, which involves the partial oxidation of H<sub>2</sub>S to SO<sub>2</sub>, and the subsequent reaction of the latter with the remaining part of H<sub>2</sub>S to give elemental sulphur with a purity normally greater than 99.5%. Sulphur obtained by this process is crystalline, of an orthorhombic form and has a molecular shape substantially consisting of rings made up by neutral rings from S<sub>5</sub> to S<sub>8</sub> or even greater.

Despite the multiple industrial and agricultural uses of elemental sulphur, in particular for the production of sulphuric acid, as a fertiliser and as an anticryptogamic and plant disinfectant, currently there is a problem of overproduction and disposal due to the enormous quantity of oil and gas extracted from underground.

Furthermore, the use of elemental sulphur, usually in powder form dispersible in water or as a crystalline granulate or composite dipole component used in agriculture, is not however without drawbacks. In particular, slow oxidation and bioconversion kinetics, lasting for months or even years, which may entail, in addition to a long wait for the appearance of the desired effects, also the pollution of aquifers with elemental S or the transport of powder to unwanted areas. The obtainment of solid form dispersible S also entails the use of complex processes of grinding and sieving, in addition to the risk of flammability.

It would be desirable to be able to use sulphur in forms that would allow to overcome the aforementioned drawbacks and thus be able to widen the range of possible uses of this element.

According to the international patent application WO2005/095271 (in the Applicant's name), through the reaction of H<sub>2</sub>S e SO<sub>2</sub> in an aqueous solution at room temperature, it is possible to obtain elemental sulphur in a particular form, capable of forming diluted suspensions (S content about 1% in weight) in water without the need for emulsifying or suspending additives. The above suspensions can then be separated to obtain high purity sulphur for the known uses of the sector, including the production of sulphuric acid and use in agriculture, or they may be disposed of by direct injection into exhausted sites. No mention is made in said patent application, of the use of said suspensions, such as obtained, in agriculture, nor even of any use directly as soil improver.

The Applicant has now found that by means of said process it is possible to obtain a particular form of sulphur in aqueous suspension which has proved particularly suitable for the treatment of alkaline or saline soils, in order to make them suitable for cultivation again.

A first aim of this invention is therefore a method for modifying the chemical composition of the soil, of soil, comprising the treatment of said soil with a suitable amount of an aqueous suspension of hydrophilic sulphur with a concentration in S comprised between 0.5 and 300 g/L, preferably between 5 and 200 g/L, more preferably between 15 and 150g/L, pH comprised between 0 and 4, preferably between 0.5 and 2, said sulphur having an average granulometry of between 2 and 100  $\mu\text{m}$  (micron), measured with the "light scattering" method.

A second aim of this invention is also an aqueous suspension of hydrophilic sulphur suitable as soil improver, having the following features: concentration in S comprised between 15 and 300 g/L, preferably between 15 and 150 g/L, pH between 0 and 4, preferably between 0.5 and 2, PZC comprised between 1 and 3, said sulphur having an average particle size of between 2 and 100  $\mu\text{m}$  (micron), measured by the "light scattering" method.

For purposes of this description and of the following claims, definitions of numerical ranges always include the upper and lower limits unless otherwise specified.

In the description of the embodiments of this invention, the use of the terms "comprising" and "containing" means that the described options, for example concerning the steps of a method or process, or the components of a product or device, are not necessarily exhaustive. However, the embodiments in which the term "comprising" refers to the described options, for example concerning the steps of a method or a process or the components of a product or device, must also be considered within the scope of this invention and be interpreted as "consisting essentially of" or "consisting of", even if not explicitly stated.

For purposes of this description and of the claims that follow, percentages are always by weight, except in cases where it is not otherwise specified.

For purposes of this invention, the term "soil", as used herein in the description and claims, refers to a polymorphic granular solid composite material of natural or artificial origin, suitable, or potentially suitable for the growth of plant organisms endowed with roots.

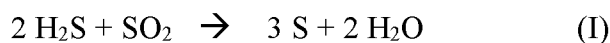
For the purposes of this invention, the term "aqueous suspension" means a suspension of a solid particulate in a liquid consisting of more than 80%, preferably over 90%, of water, which may possibly comprise other components, such as for example, suspending agents, emulsifiers, organic solvents such as alcohols, fertilisers, plant protection products and other products useful for agriculture, traces of salts such as salts contained in mineral water and groundwater.

Figure 1 represents a typical laboratory apparatus for the treatment of soil based on the method of this invention and the collection of the percolate to be analysed.

The aqueous suspension of hydrophilic sulphur suitable for the process according to this invention can be generally obtained by making sulphur dioxide and hydrogen sulphide react in an aqueous liquid medium, preferably water, to reach the desired sulphur concentrations.

A preferred method for preparing oligomeric hydrophilic sulphur suspensions suitable for the method of this invention is the process described in the aforementioned international patent application WO2005/095271 (in the Applicant's name), the contents of which have been included in this application by reference.

In particular, a gaseous stream of H<sub>2</sub>S, preferably diluted with an inert gas with concentration between 5 and 35% in terms of volume of H<sub>2</sub>S, is oxidised with air to obtain SO<sub>2</sub>, which is absorbed in water and the solution thus obtained is made to react with H<sub>2</sub>S, preferably in gaseous form, by simple contact, preferably by bubbling or another suitable method of gas distribution in the liquid, at a temperature equal to or lower than 100°C, preferably between 5°C and 40°C, more preferably at room temperature. Predominantly, the following reaction (I) of elemental sulphur formation is obtained:



while, to a lesser extent, reactions are established that lead to the formation of polythionic acids with variable chain length.

Possibly, it is possible to obtain particularly stable suspensions and with a more homogeneous distribution of the particle size, by applying ultrasounds to the liquid phase during the reaction or subsequently, as described, for example, in the aforementioned patent application WO2005/095271.

The suspensions obtained with the previous process are characterised by properties particularly suitable for use according to the method of this invention, as they contain sulphur in a very pure and finely dispersed form in water, which is therefore already prepared for distribution in the soil. Moreover, the process described to obtain them is easy to apply even on a small scale.

According to a preferred form of this invention, the hydrophilic sulphur suspension does not include suspension agents or emulsifiers and is more preferably essentially constituted by S (also in the form of polythionic acids) and water. However, if it is desired to further increase the stability of the aqueous suspension, suspension agents known to be suitable for the purpose can be added, such as, for example, 0.1% by weight of Agar-agar.

The hydrophilic S aqueous suspension in accordance with this invention preferably has a stability of at least 10 days, preferably at least 30 days, more preferably at least 60 days, where

by stability what is meant is the number of days after which the suspension produces a sediment greater than 0.5 % in volume in an Imhoff Cone, applying the method and the equipment as reported in the literature, for example in the publication by APHA, AWWA, WEF (1998): “Standard Methods for the Examination of Water and Wastewater”, XX Ed. (Washington, APHA), pages 2-54/2-59. The Applicant however, has verified that any sediments produced, even after months of racking, can be removed in a stable manner (within the meaning of what has been mentioned above) purely by mechanical stirring. Evidence of irreversible degradation of the hydrophilic S suspension as defined herein and prepared, with changes of the mean particle size and reaggregation, were observed after times greater than 1 year.

The stable aqueous suspension of hydrophilic sulphur which can be used in accordance with this invention comprises, in mixture, both neutral molecular sulphur, having the known orthorhombic crystalline structure formed by cyclic molecules predominantly of the S<sub>8</sub> formula, and sulphur with a linear structure, essentially constituted by polythionic acids having chains from 2 to 80, preferably from 3 to 60, S atoms and their ends are bonded to -SO<sub>3</sub>H groups (in the protonated form), or -SO<sub>3</sub><sup>-</sup> (in the dissociated form), which, besides favouring the stabilisation of the suspension, confer high acidity to the latter, usually having pH values (measured directly on the suspension at room temperature) ranging from 0 to 4, preferably from 0.2 to 2.0, more preferably lower than 2.0, even more preferably from 0.5 to 1.95. Preferably, said hydrophilic S suspensions comprise from 0.05 to 10.0 %, preferably from 0.1 to 5 %, by weight of polythionic acids, with respect to the total weight of the suspension.

The hydrophilic sulphur in the stable aqueous suspension of this invention is in the form of suspended particulate matter having a medium particle size, in terms of average particle diameter, ranging from 1 to 100 µm (microns), preferably between 2 and 30µm, measured with the light scattering method using a laser diffraction granulometer.

In a preferred form of this invention, the stable hydrophilic sulphur suspension shows a PZC (point of zero charge) comprised between 1 and 3, measured by potentiometric titrations with various ionic strengths, at increasing concentration of transport electrolytes, as described in *Int. J. Electrochem. Sci.*, 7 (2012) 6142 – 6153.

According to an embodiment of the method of this invention, the aqueous hydrophilic sulphur suspension is distributed on the soil to be treated by means of suitable techniques and equipment suitable for the purpose, normally used by sector operators for similar distribution operations of suspensions or aqueous suspensions such as spreaders, sprayers, etc. The choice of hydrophilic sulphur suspension quantities to be distributed on the soil and of the most suitable

application method is within the reach of the technician with normal technical knowledge, without the need for further original solutions. In particular, it is possible to choose a wide range of values, depending on the soil's saline features and acidity, concentration of the suspension, compatibility with organisms already present in the soil, desired recovery times. In accordance with the method of this present invention, the amount of said aqueous suspension is preferably selected so that the average amount of S distributed in the soil is between 10 and 500 g/m<sup>2</sup> of soil, preferably between 50 and 300, g/m<sup>2</sup> of soil, more preferably comprised between 100 and 300, g/m<sup>2</sup> of soil.

Suitable soils for the method of this invention may be all soils characterised by a saline or acidity imbalance with respect to values deemed as normally suitable or tolerable for the desired cultivation, as reported in scientific and technical-applicative publications of the agricultural sector. Particularly suitable soils are those having a pH (measured as hereinafter specified) greater than or equal to 6.5, preferably greater than or equal to 7.0, and / or a saline concentration such as to result in an electrical conductivity of the medium greater than 1.0 dS m<sup>-1</sup>, preferably greater than 2.0 dS m<sup>-1</sup>. Soil electric conductivity is measured by a conductivity meter on an aqueous extract of the soil obtained by treating 10g of soil with 250 mL of distilled water. The method of this invention can, however, be applied also to soils having acceptable values of pH and electrical conductivity, but that are unbalanced with respect to the concentration of one or more specific salts.

According to the method of this invention, surprisingly it has been discovered that the salt content of treated soils, in particular the Na, Ca, Mg, Al content, is significantly reduced in reduced times by at least 20%, preferably by at least 50%, and more preferably by at least 90%, with the same changes in concentration, with respect to the treatment itself carried out with the normal commercial elemental sulphur, in powder or as an aqueous suspension.

Surprisingly, it has also been discovered that according to this invention, the soil treatment method entails a more rapid and effective fertilisation, understood as an improvement in the growth and rooting of cropland with respect to the treatment with the same quantities of commercial granular sulphur.

This invention, in its many aspects, is now explained in greater detail by the following examples, which are shown for purely demonstrative purposes, without this being in any way considered as limiting the invention overall scope.

#### EXAMPLES

Preparative example 1: synthesis of an aqueous suspension of hydrophilic sulphur according to this invention.

A solution of sulphur dioxide and a gaseous stream containing hydrogen sulphide is made to react during an aqueous phase. The reaction product consists of highly hydrophilic sulphur, able to give stable suspensions in water for a long period. The reaction is carried out in a bench-top system, maintained at 25°C by means of a thermostatic bath, comprising a 5 L glass reactor equipped with mechanical stirring, and lines for feeding the gaseous H<sub>2</sub>S.

Two litres of an aqueous SO<sub>2</sub> solution are introduced into the reactor, with a concentration of 1 mole per litre (64.06 g/L). A gaseous mixture of H<sub>2</sub>S and nitrogen is then made to bubble at room temperature, with a volumetric concentration equal to 10% of H<sub>2</sub>S. The formation of a milky yellow lactate suspension is observed. The bubbling continues for about 24 hours, until reaching a residual concentration of SO<sub>2</sub> lower than 0.02 moles/L. Nitrogen is still bubbled for about 1 hour to remove residual H<sub>2</sub>S, possibly absorbed in the reaction mixture. At the end of the reaction a stable suspension of hydrophilic sulphur is obtained, having a pH of 1.3. A portion of 50 g of the suspension thus prepared was dried under high vacuum (10Pa), obtaining a sulphur residue weighing 4.15 g. Assuming the residue consists only of sulphur and polythionic acids, a sulphur concentration in the suspension is calculated equal to 8.02% by weight with respect to the total weight of the suspension.

The suspension of S thus obtained remained stable for at least 30 days, during which the soil treatment tests were prepared.

EXAMPLES nos. 3, 6, 9 and 12 (according to the invention) and Comparative Examples nos. 1, 2, 4, 5, 7, 8, 10 and 11.

#### Equipment preparation for soil tests

The experimental system was set up as shown in Figure 1, by means of glass columns with an internal diameter of 8 cm and a height of 1 cm, equipped with a PTFE tap, supported by sample-holding columns. In each column a percolated filtration system has been placed, composed of an absorbent paper disc with a porosity of about 20 µm with 2-3 g of glass wool on top.

#### Method for determining the pH

Liquids. The pH of the hydrophilic S suspension and eluate samples is determined by direct immersion into the liquid of an electronic pH meter probe.

Soils. The pH is the measure of the soil's reaction. A 10 g of sample for each type of soil was placed in a plastic container and deionized water was added to the soil: water ratio of 1:2.5.

The mixture was placed in a mechanical stirrer for 2 hours and allowed to stand for 30 hours to allow the deposit of the particles. To measure the soil's, electrodes (in this case semi-micro electrodes) are used, consisting of a reference electrode (Ag/AgCl) which is placed in contact with the solution to be measured, and one consisting of a thin glass bulb to separate the solution to be measured from an acid with a known, saturated AgCl concentration. The two electrodes are connected by a salt bridge consisting of a 4M KCl solution, saturated by AgCl; on the glass bulb an electric voltage is created which is proportional to the concentration of  $H^+$  of the suspension of the soil to be measured. The instrument is calibrated with reference solutions of known concentrations (pH 4, 7 and 10). Once the calibration is complete, the electrode is washed with distilled water, dried and immersed in the sample.

#### Method for determining metals in the eluate.

For the analysis of the metallic cations in the eluate collected in each test, the well-known ICP-OES (Inductively Coupled Plasma) plasma spectrophotometric method was used, on a Perkin Elmer Optima 8300 instrument, after calibration with standard solutions of known metal concentrations of Na, Mg and Ca. The samples to be measured were previously centrifuged at 7,500 rpm for 8 minutes. The results are expressed in mg/Kg.

#### Sample preparation

Samples of soil were taken with the features shown in Table 1, in five different sites. The soils were dried at room temperature and then the aggregates were broken down, either mechanically with a percussion press, or manually using a ceramic mortar with a pestle. The next step was the 2 mm sieving by mechanical sieve in order to obtain the so-called "fine soil" according to the terminology in use, i.e. the fraction conventionally considered representative and homogeneous of the sample and therefore useful for subsequent experimental tests.

The experimentation was conducted on five different soils: one volcanic, two alkaline and two alkaline-saline. The soils chosen for the experiment have been selected on the basis of specific geological and pedological features.

Soils having the features shown in table 1 have been examined.

ID	Type	Description	pH	Electrical conductivity $\sigma$ (dS m <sup>-1</sup> )
A1	Alkaline	Soil cultivated with cereals (120 m a.s.l.). Soil evolved on semi-coherent pelitic rocks of marine origin.	8.33	0.44

A2	Alkaline	Abandoned pasture partially colonised by shrubs (750 m a.s.l.). Soil evolved from calcareous rock containing various lithological layers	6.51	0.23
S1	Alkaline-saline	Bare soil (plant cover <5%) (71 m a.s.l.). Soil evolved from semi-coherent pelitic rocks of marine origin.	8.09	6.23
S2	Alkaline-saline	Former cultivated soil near the coast, currently colonised by tamarisk (about 3 m a.s.l.). Soil evolved from semi-coherent pelitic rocks of marine origin.	7.48	6.97

**Table 1** – Identification code and properties of the land (soil) examined

For each of the soils examined it was envisaged to evaluate three different treatments:

- (C) Control, comparative, with the only addition of distilled water;
- (Sp) Powdery sulphur ( $\geq 99.5\%$ , Sigma-Aldrich), comparative, irrigating with distilled water;
- (Ss) Aqueous suspension of hydrophilic sulphur, according to the invention, at 8.02% by weight with respect to the weight of the suspension, and irrigation with distilled water.

With each soil, prepared as above, a column was filled as previously described, pouring 600 g of sample prepared as above, so as to reach an average height of about 12 cm. The sample is soaked with distilled water until saturation (about 40-50 mL of water).

A sulphur quantity equal to 2 grams is then introduced from the top of the column, except for the control examples. The commercial sulphur powder of the comparative examples is introduced as such, without preliminary suspension in water. The hydrophilic sulphur suspension according to the invention is introduced in a quantity equal to 24 mL.

The column is eluted for each soil sample with distilled water, adding a portion of 50mL in about 18-30 hours and collecting the eluate until the supernatant liquid layer disappears. The same operation is repeated every 5 days for a duration of the experiment of 90 days in total, bringing together the eluates for each soil. The elements of interest were quantitatively determined on the overall collection. The soil's pH and electrical conductivity were also measured at the end of the treatment. The results are shown in the following table 2.

Example No.	Soil	Treatment	Soil pH	Features of the eluate:		
				Na (mg/Kg)	Mg (mg/Kg)	Ca (mg/Kg)
1 (comp.)	A1	C	8.46	57	10	30

2 (comp.)	A1	Sp	8.10	57	10	30
3	A1	Ss	7.98	146	107	405
4 (comp.)	A2	C	6.29	10	7	30
5 (comp.)	A2	Sp	5.72	10	7	30
6	A2	Ss	4.88	22	29	290
7 (comp.)	S1	C	7.68	1025	84	80
8 (comp.)	S1	Sp	7.67	1025	84	80
9	S1	Ss	7.58	1400	120	102
10 (comp.)	S2	C	8.22	665	42	180
11 (comp.)	S2	Sp	7.43	665	42	180
12	S2	Ss	7.37	875	87	475

Table 2 - Results of treatments

As can be seen from the data in Table 2, the eluent capacity in the presence of hydrophilic sulphur according to this invention increases significantly (even by an order of magnitude in certain cases) with respect to the use of an equal quantity of commercial sulphur in powder form.

CLAIMS

1. Method for modifying the chemical composition of a soil, comprising the treatment of said soil with a suitable amount of an aqueous suspension of hydrophilic sulphur with a concentration in S comprised between 0.5 and 300 g/L, preferably between 5 and 200 g/L, more preferably between 15 and 150 g/L, pH comprised between 0 and 4, more preferably between 0.5 and 2, said sulphur having an average granulometry of between 2 and 100  $\mu\text{m}$  (micron), measured with the "light scattering" method.
2. Method according to claim 1, wherein said treatment comprises the distribution on the soil's surface of a quantity of said hydrophilic sulphur aqueous suspension such that the average quantity of S distributed on the soil is between 10 and 500, preferably between 50 and 300,  $\text{g}/\text{m}^2$  of soil.
3. Method according to any of the claims 1 or 2, wherein said aqueous sulphur suspension comprises from 0.05 to 10.0 %, preferably from 0.1 to 5 %, by weight of polythionic acids, with respect to the total weight of the suspension.
4. Method according to any of the preceding claims, wherein said soil comprises an overall ion concentration such as to result in an electrical conductivity of the medium greater than 1.0  $\text{dS m}^{-1}$ , preferably greater than 2.0  $\text{dS m}^{-1}$ .
5. Method according to any of the previous claims, wherein said soil has a pH higher than 6.5, preferably higher than 7.0.
6. Method according to any of the preceding claims, wherein said hydrophilic sulphur suspension also comprises at least one suspension agent.
7. Aqueous suspension of hydrophilic sulphur, having the following features: concentration in S between 15 and 300 g/L, preferably between 15 and 150 g/L, pH between 0 and 4, preferably between 0.2 and 2.0, said sulphur having an average particle size between 2 and 100  $\mu\text{m}$  (microns), measured with the "light scattering" method.
8. Aqueous suspension of hydrophilic sulphur according to claim 7, having a PZC comprised between 1 and 3.
9. Aqueous suspension of hydrophilic sulphur according to claims 7 or 8, which is obtained by a process which includes making an aqueous solution of  $\text{SO}_2$  react with  $\text{H}_2\text{S}$ , at a temperature equal to or lower than  $100^\circ\text{C}$ , preferably between  $5^\circ\text{C}$  and  $40^\circ\text{C}$ .
10. Aqueous suspension of hydrophilic sulphur according to any of the preceding claims from 7 to 9, for use as soil improver.

11. Aqueous suspension of hydrophilic sulphur according to any of the preceding claims from 7 to 10, having a pH comprised between 0.5 and 1.95
12. Method according to any of the previous claims from 1 to 6, in which the treatment of the soil is carried out with an aqueous suspension of hydrophilic sulphur according to any of the claims from 7 to 9.

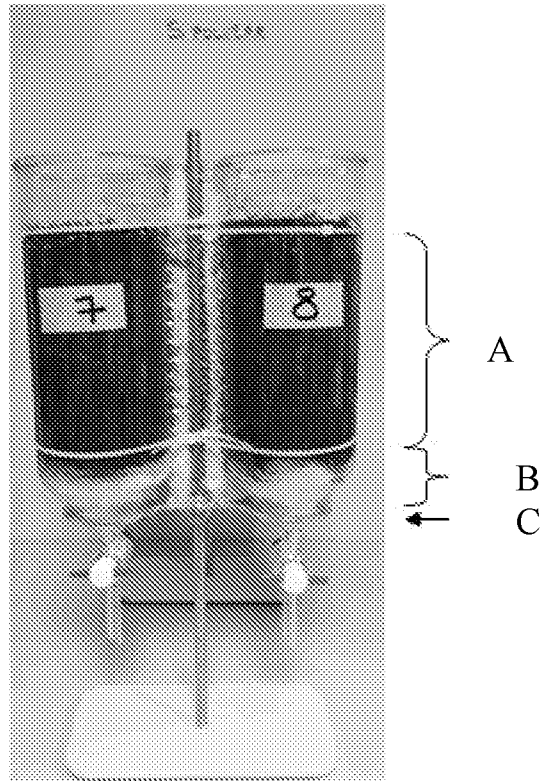


Figure 1: Equipment for the collection of leachate from soil

- A Soil thickness about 12-13 cm
- B Fibreglass
- C Blotting paper

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/IB2018/058889

**A. CLASSIFICATION OF SUBJECT MATTER**  
INV. B09C1/08  
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
C09F B09C C05D C05F C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	EP 2 629 606 A2 (CERADIS BV [NL]) 28 August 2013 (2013-08-28) paragraphs [0012] - [0013] paragraphs [0014] - [0017] claims 1,2,5,13 paragraph [0034]	1,2,4-8, 10,12 3,9,11
X A	----- WO 2005/095271 A (ENITECNOLOGIE S.P.A.) 13 October 2005 (2005-10-13) claim 14 claims 1-13 figures 1-5; examples 1-3	1-6 7-12
X A	----- GB 202 613 A (HEINRICH VOGEL) 27 December 1923 (1923-12-27) the whole document ----- -/--	7-9 10-12

Further documents are listed in the continuation of Box C.       See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  <b>28 January 2019</b>	Date of mailing of the international search report  <b>04/02/2019</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  <b>Dossin, Maxime</b>
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## INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2018/058889

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 228 490 A (SANDOZ LTD [CH]) 29 August 1990 (1990-08-29) page 1 - page 3 -----	7
A	WO 2016/097378 A1 (SHELL INT RESEARCH [NL]; SHELL OIL CO [US]) 23 June 2016 (2016-06-23) page 8, line 25 - page 9, line 11 page 13, line 15 - page 15, line 10 -----	1-12
A	WO 00/78893 A1 (ULTIMATE PRODUCTS AUST PTY LTD [AU]; STRACHAN GRAHAM GEORGE [AU]; MCDO) 28 December 2000 (2000-12-28) claims 1-17 -----	1-12
A	US 3 186 826 A (DE RENDON MARGARITA DEL MURO) 1 June 1965 (1965-06-01) claims 1-7 -----	1-12
A	EP 0 949 221 A1 (HOLLAND CHEMICAL INTERNAT N V [NL]) 13 October 1999 (1999-10-13) paragraphs [0001] - [0026] example 1 -----	1-12

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2018/058889

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2629606	A2	28-08-2013	EP 2629606 A2 28-08-2013
			ES 2634553 T3 28-09-2017
			WO 2012053894 A2 26-04-2012
-----			
WO 2005095271	A	13-10-2005	
GB 202613	A	27-12-1923	FR 565547 A 29-01-1924
			GB 202613 A 27-12-1923
			NL 13770 C 28-01-2019
-----			
GB 2228490	A	29-08-1990	BR 9000852 A 05-02-1991
			CH 684514G A3 14-10-1994
			CN 1045115 A 05-09-1990
			DE 4004222 A1 30-08-1990
			ES 2026748 A6 01-05-1992
			FR 2643380 A1 24-08-1990
			GB 2228490 A 29-08-1990
			HK 70495 A 19-05-1995
			IT 1240771 B 17-12-1993
			JP H02248467 A 04-10-1990
			RU 2044751 C1 27-09-1995
			US 4992078 A 12-02-1991
-----			
WO 2016097378	A1	23-06-2016	CA 2971078 A1 23-06-2016
			CN 107001165 A 01-08-2017
			EA 201791407 A1 31-10-2017
			EP 3233760 A1 25-10-2017
			US 2017327430 A1 16-11-2017
			WO 2016097378 A1 23-06-2016
-----			
WO 0078893	A1	28-12-2000	US 6752850 B1 22-06-2004
			WO 0078893 A1 28-12-2000
-----			
US 3186826	A	01-06-1965	NONE
-----			
EP 0949221	A1	13-10-1999	DE 69917831 D1 15-07-2004
			DK 0949221 T3 25-10-2004
			EP 0949221 A1 13-10-1999
			NL 1008820 C2 07-10-1999
-----			