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(54) Title: METHOD AND APPARATUS FOR THE DECONTAMINATION OF PRODUCTS CONTAINING HEAVY METAL

(57) Abstract

According to the invention, by using the electro-kinetic principle for a method for the cleaning of materials contaminated with heavy metals, and whereby use is made of an apparatus comprising two charge-selective ion-exchange membranes with different charges combined with an inner and an outer electrolyte solution chamber which are separated from the membranes which serve a blocking function, a surprisingly good degree of utilization is achieved, particularly in relation to the current consumption, and at the same time the precipitation of the heavy metals is so effective that they can be reused. There is hereby achieved a hitherto-unknown degree of profitableness compared with known methods of cleaning.

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METHOD AND APPARATUS FOR THE DECONTAMINATION OF PRODUCTS CONTAINING HEAVY METAL.

Background of the invention

The invention relates to a method for the removal of heavy metals from soil, mud, sludge and the like by the electro-kinetic process, whereby electric current is used to drive the heavy metals towards electrodes where they can be concentrated in an electrolyte solution from which they can be removed, an apparatus for the execution of said method and the use hereof.

The need for cleaning soil and areas which are polluted with heavy metals is great and increasing in step with the recognition of the risks which these contaminated areas constitute in both the short and the long view for the environment.

Cleaning, however, is a very complicated and costly process. This means that in the most threatened areas the contaminated earth or sludge must be removed and deposited under controlled conditions for the safety of the surrounding environment.

In other words, the polluted material is isolated and thus the problem of cleaning is postponed until later.

Consequently, there is a great need for a method of cleaning which is suitable for the removal of heavy metals.

Efforts have been made with a so-called electro-kinetic method, whereby electric current is used to drive the heavy metals which exist in the earth in the form of ions towards electrodes where the metal can be concentrated and thereafter removed.

In practice, two electrodes are placed in separate chambers at a suitable distance in the earth. The positive heavy metal ions hereby move towards the negative electrode and the negative heavy metal ions towards the positive electrode.

However, there is a difference in the mobility or the movement of the ions which stem from the electrode process and the heavy metal ions which are bound in the earth. The ions from the electrode process are the least bound and are herewith of the easiest movability.

There thus arises the problem that a considerable part of the process current will be used to convey ions from the one electrode chamber to the other, so that only a smaller part of the power is utilized in the removal of the heavy metals in the earth.

This means that this known method is not particularly effective and, moreover, uneconomic in relation to the costs involved in the removal and the depositing of earth contaminated with heavy metals, which in turn means that the method has not been taken into practical use.

Advantages of the invention

According to the invention, by using a method whereby the earth is separated from electrodes in chambers, and that there is placed a cation-exchange membrane to prevent anions from the negative electrode chamber from seeping out into the earth and at the same time permit the passage of positive heavy metal ions from the earth and out in the negative electrode chamber, and also placing a second ion exchange membrane to prevent the passage of cations from the positive electrode chamber into the earth and at the

same time permit the passage of heavy metal ions from the earth to seep out in the positive electrode chamber, there is achieved the advantage that the ions from the electrode chamber do not pass out into the earth, but remain in the electrolyte solution. The energy is hereby utilized in a far more efficient manner, i.e. solely for the transport of the earth-bound ions to the electrodes, and not for the transport of ions between the electrodes.

According to the invention, it hereby becomes possible to clean products contaminated with heavy metals with a consumption of energy which is particularly competitive with other forms of cleaning, and at the same time to ensure a considerable degree of cleaning effect and herewith the possibility of achieving a degree of cleaning which is surprisingly high.

By using the apparatus according to claim 2 comprising an electrode in an electrolyte solution in a chamber separated from a second electrolyte solution in a second chamber by means of ion-exchange membranes, and separating this second electrode chamber from the earth by means of other ion-exchange membranes, an electrode unit which functions satisfactorily is achieved in a surprisingly simple manner.

As disclosed in claim 3, an optimum effect of the electrode is ensured by isolating the electrolyte solution in the electrode chamber from the remaining electrolyte solution.

As disclosed in claim 4, by using a circulating electrolyte solution, this can be pumped to a separate electrode chamber where the heavy metals can be deposited and removed from the electrolyte solution.

Finally, it is expedient, as disclosed in claim 5, to use the method and the apparatus for the cleaning of earth,

sludge and the like, either alone and/or in connection with a biological cleaning of the earth.

Description of the example embodiments

The following is a more detailed description of an example of the apparatus for the execution of the cleaning method.

The apparatus, which comprises an electrode etc., is configured as a unit which innermost comprises an electrode element which is connected to a power supply which, for example, is negative.

Around the electrode element there is arranged a closed chamber which is filled with an electrolyte solution of a commonly-known kind, such as a sodium-nitrate solution, which is electrically conductive.

In or on the side walls of the chamber there is mounted an ion exchange membrane which is charge selective. In the example described, it is positive. The membrane can be made of any suitable supportive and chemically resistant material which is not electrically conductive.

The chamber wall can be configured of membrane material, merely providing that this is of adequate strength. The material used can be known cellular ceramic materials and the like.

The charge-selective ion-exchange membranes are in contact with an additional electrolyte solution which extends around the outer wall of the electrode chamber, said solution extending in a closed chamber which constitutes the exterior of the unit.

It should be noted that the electrolyte solution around the

electrode is separated from the circulating solution.

The outer chamber is outermost defined by additional charge-selective ion-exchange membranes, which in the example described are negatively charged.

Similarly, these membranes can also be configured to form the outer wall.

During operation, the unit is submerged in the product which is required to be cleaned, and which can be earth or the like such as sludge, sediments, cleaning residuals etc., which are contaminated with heavy metals.

The unit can be in liquid connection with a collection vessel for circulating electrolyte solution. During operation, the heavy-metal ions will be concentrated in the solution in the unit, and by passing electrodes which are placed in the vessel, and in the described example with each its charge, the ions upon passing these electrodes will be precipitated. In this manner the metals can be removed, and the solution can be recirculated to the unit.

The following is a description of the method:

When the units are placed in the product which is required to be cleaned, the power supply and the electrolyte solution are established as described earlier.

There is thus established a plant which functions as an electro-kinetic heavy-metal cleaning method for heavy metals.

The contaminated product is separated from the electrode chambers in such a manner that the cation-exchange membrane

prevents anions from the negative electrode chamber from seeping out in the contaminated product, which can be earth, but at the same time allows the positive heavy-metal ions to pass from the product, the earth, out in the negative electrode chamber.

At the same time, the anion-exchange membrane prevents cations from the positive electrodes from passing into the product, the earth, but allows the passage of negative heavy-metal ions from the product to seep into the positive electrode chamber in the unit.

There is hereby ensured the best possible utilization of the current, which makes the method and the means particularly competitive when compared with other known methods of cleaning.

To this can be added that the precipitation of the heavy metals which occurs is so effective that these can be reused and hereby contribute in a positive manner to the profitability of the plant.

The method and the apparatus according to the invention can therefore with advantage be used directly in the contaminated product such as earth, sludge, sedimentations in tanks and the like.

In this connection is should be noted that the units can be provided with several separate electrolyte solutions and ion-selective membranes, hereby enabling a selective cleaning of specific metal ions to be achieved.

Finally, the method can be used in connection with other methods of cleaning, e.g. in connection with a biological cleaning, where the heat developed by the method is utilized to further the biological cleaning process.

C L A I M S

1. Method for the cleaning of earth, sludge and the like containing heavy metals by use of the electro-kinetic method, whereby electric current is used to drive the heavy metals towards electrodes where they can be concentrated in an electrolyte solution and thereafter removed, c h a r a c t e r i z e d in that the earth is separated from electrodes in chambers, and in that a cation-exchange membrane is used to prevent anions from the negative electrode chamber from seeping out into the earth and at the same time allow passage of positive heavy-metal ions from the earth and out in the negative electrode chamber, and also that a second ion-exchange membrane is used to prevent passage of cations from the positive electrode chamber into the earth and at the same time allow passage of heavy-metal ions from the earth to seep out into the positive electrode chamber.

2. Apparatus for the execution of the method according to claim 1, c h a r a c t e r i z e d in that the electrode is placed in an electrolyte solution in a chamber, said chamber being separated from a second electrolyte solution chamber by means of charge-selective ion-exchange membranes, and in that the second electrolyte solution chamber is separated from the earth by means of other charge-selective ion-exchange membranes.

3. Apparatus according to claim 2, c h a r a c t e r i z e d in that the electrolyte solution in the chamber with the electrode is isolated from the electrolyte solution in the second chamber.

4. Apparatus according to claims 2 and 3, c h a r a c t e r i z e d in that the electrolyte solution in the second chamber can be led out to a collection vessel with

electrodes for the separation of the heavy metals, after which the electrolyte solution can be recirculated to the chamber.

5. Use of the method according to claim 1 and the apparatus according to claims 2-4, c h a r a c t e r i z e d in that the method and the apparatus are used alone and/or supplemented with a biological cleaning process.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/DK 95/00209

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: B09C 1/00, A62D 3/00
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)

IPC6: A62D, B09B, B09C

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

SE,DK,FI,NO classes as above

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

DIALOG: CLAIMS, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9101392 A1 (IONEX ET AL), 7 February 1991 (07.02.91), claims 1,17,28,35-41, abstract --	1
A	US 5190628 A (JANE P. BIBLER), 2 March 1993 (02.03.93), claim 1, abstract --	1
P,A	WO 9511095 A1 (EA TECHNOLOGY LIMITED), 27 April 1995 (27.04.95), figure 6, abstract --	1,4
A	US 5074986 A (RONALD F. PROBSTEIN ET AL), 24 December 1991 (24.12.91), abstract --	1

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

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Information on patent family members

28/08/95

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A1- 9101392	07/02/91	AU-A- 6425190	22/02/91
		CA-A- 2064224	22/01/91
		EP-A,A- 0483286	06/05/92
		US-A- 5262024	16/11/93
		US-A- 5405509	11/04/95
US-A- 5190628	02/03/93	NONE	
WO-A1- 9511095	27/04/95	NONE	
US-A- 5074986	24/12/91	NONE	