

March 19, 1963

R. C. SABINS

3,082,160

ELECTROLYTIC METHOD

Filed Sept. 15, 1958

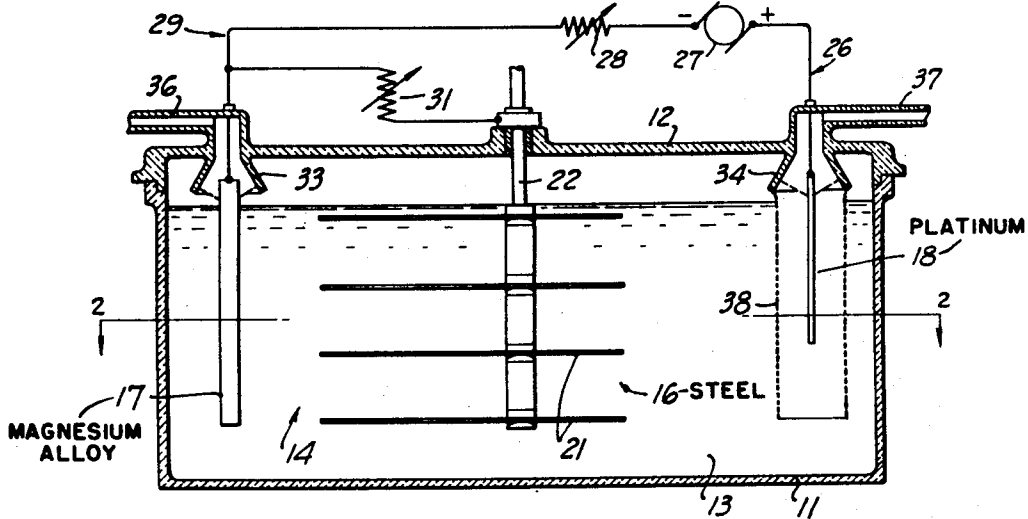
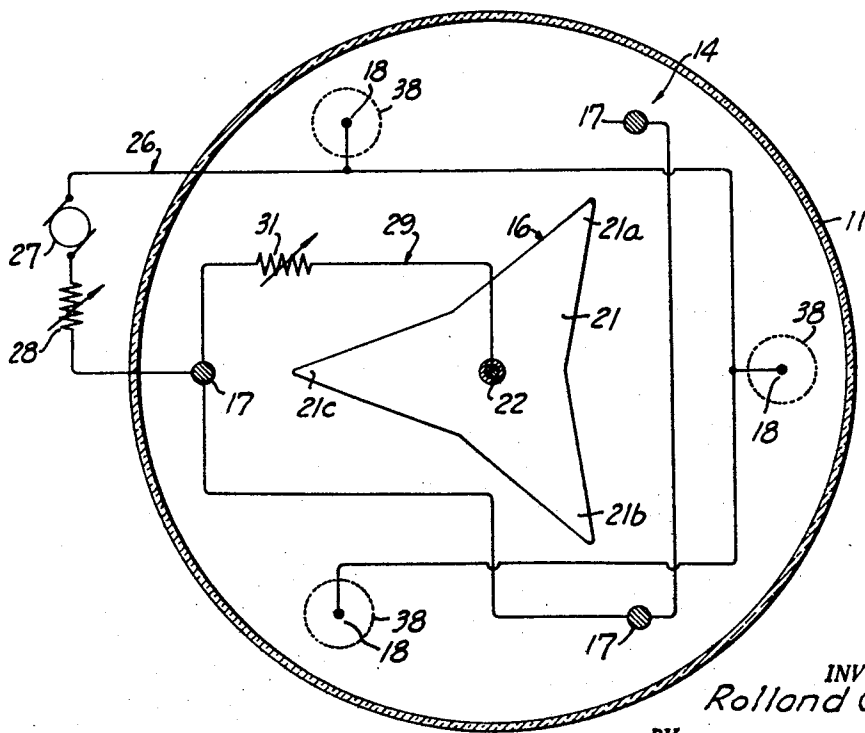


FIG. 1.

FIG. 2.



INVENTOR.
Rolland C. Sabins

BY *Felix J. Slocum*
ATTORNEYS

ATTORNEYS

1

3,082,160

ELECTROLYTIC METHOD

Rolland C. Sabins, 522 Catalina Blvd., San Diego, Calif.

Filed Sept. 15, 1958, Ser. No. 760,971

1 Claim. (Cl. 204—96)

This invention relates generally to an electrolytic apparatus and method and more particularly to an electrolytic apparatus and method for removing substances in solution from the electrolyte.

This application is a continuation in part of my co-pending application Serial No. 586,969, now Patent No. 2,903,405, and my co-pending application Serial No. 645,353, filed March 11, 1957, now abandoned, and which was a continuation of the aforementioned application Serial No. 586,969, now Patent No. 2,867,913 entitled "Electrolytic Cell Employing a Cathode, Anode, and a Cathode-Anode-Electrode."

Electrolytic cells have long been in use in conjunction with various processes. Such cells, however, normally have consisted of an anode and a cathode or a plurality of anodes and cathodes connected in parallel. With certain processes in which conventional electrolytic cells are used, it has been found that large amounts of power are required for removing substances in solution from the electrolyte. It is readily apparent, therefore, that there is a need for an electrolytic cell which can be utilized for removing substances from solution from the electrolyte with low amounts of energy.

In general, it is an object of the present invention to provide an electrolytic apparatus and method which can be utilized for removing substances in solution from electrolytes or, in other words for causing decomposition of the electrolyte.

Another object of the invention is to provide an electrolytic apparatus and method of the above character which is particularly adapted for removing substances from sea water.

Another object of the invention is to provide an electrolytic apparatus and method of the above character which can be utilized for the removal of minerals and the like from water to reduce the hardness of the water.

Another object of the invention is to provide an electrolytic apparatus and method of the above character which can be utilized for the treatment and reclamation of waste water.

Another object of the invention is to provide an electrolytic apparatus and method of the above character which can be utilized for the treatment of sewage.

Another object of the invention is to provide a method and apparatus of the above character which does not require ion migration through substantial distances.

Another object of the invention is to provide an apparatus and method of the above character which has reduced energy requirements.

Another object of the invention is to provide an electrolytic apparatus which is particularly adapted for removing dissolved substances from an electrolyte.

Additional objects and features of the invention will appear from the following description in which the preferred embodiment of the invention has been set forth in detail in conjunction with the accompanying drawing.

Referring to the drawing:

FIGURE 1 is a cross-sectional view taken along the line 1—1 of FIGURE 2 showing electrolytic apparatus with certain parts schematically illustrated incorporating the present invention and which can be utilized in performing my method.

FIGURE 2 is a cross-sectional view taken along the line 2—2 of FIGURE 1.

In general, the present invention consists of an electro-

2

lytic apparatus which has a particularly novel construction. The electrolytic cell consists of three separate electrodes which are immersed in the electrolyte. Circuit means including a D.-C. power supply is provided for impressing a current flow between the first and second electrodes so that the first electrode serves as an anode and the second electrode serves as a cathode with respect to the first electrode. Additional circuit means is provided for connecting the second electrode to the third electrode so that the second electrode serves as an anode with respect to the third electrode. Means is provided for adjusting the current flow through both of the circuit means so that desired polarization levels are maintained on the electrodes. It has been found that an electrolytic cell which will be referred to as a tri-electrode cell, has many commercial applications particularly in the fields of removing dissolved substances from electrolytes.

In describing in detail one procedure for carrying out the invention, reference will be made to the use of sea water as an electrolyte and the removal of substances therefrom. The composition of sea water is generally as follows:

Table I.—Composition of Sea Water

[In grams per liter of sp. gr.=1.024]

NaCl	27.319
MgCl ₂	4.176
MgSO ₄	1.668
MgBr ₂	0.076
CaSO ₄	1.268
Ca(HCO ₃) ₂	0.178
K ₂ SO ₄	0.869
B ₂ O ₃	0.029
SiO ₂	0.008
Iron and alumina, R ₂ O ₃	0.022

In the treatment of sea water in its natural condition in accordance with the present invention, it is desirable to utilize an electrolytic apparatus or cell such as that illustrated partially in schematic form in FIGURES 1 and 2 of the drawing.

Such an electrolytic cell consists of a tank 11, provided with a cover 12 both of which are formed of suitable insulating material such as clear plastic. The tank is filled with sea water 13 to the level shown. A plurality of electrodes 14 which form a part of the electrolytic cell are immersed or submerged in the electrolyte or sea water 13. Three different types of electrodes 14 are utilized within the electrolytic cell. They are the cathode 16, cathode-anode 17 and the anode 18. These electrodes can be formed of any suitable material and in any desired manner. For example, the cathodes 16 as shown can be formed of a plurality of horizontal vertically spaced star-shaped steel plates 21 mounted on a rod 22, each of which is provided with three points 21a, 21b and 21c, spaced 120° apart.

The cathode 16 is centrally disposed within the tank 11 and is oriented in such a manner that the points 21a, 21b and 21c are directed toward the cathode-anodes 17. The cathode-anodes 17 can also be of any desired shape and formed of any suitable material. For example, as shown, they can be in the form of magnesium alloy rods. The anodes 18 were spaced between the cathode-anodes 17 and can be formed of a suitable material such as platinum wire.

Circuit means 26 including a D.-C. power supply 27 is connected between the anodes 18 and the cathode-anodes 17 to impress a current flow between the same. It will be noted that all of the anodes 18 and all the cathode-anodes 17 are connected in parallel to the D.-C. power supply 27. The circuit means 26 also includes

a potentiometer 28 for adjusting the rate of current flow through the circuit means 26. Circuit means 29 is provided for connecting the cathode-anodes 17 to the cathode 16, and includes a potentiometer 31 for varying the current flow in this circuit. The potentiometers 28 and 31 serve to vary the polarization levels on the electrodes as hereinafter described.

Cone-like members 33 and 34 are formed on the cover 12 and overlie the anodes 18 and the cathode-anodes 17. These cone-like members are connected to lead-out pipes 36 and 37. Skirts 38 of suitable material such as asbestos cloth are secured to the lower ends of the cone-like members 34 and encompass or surround the platinum anodes 18 for a purpose hereinafter described.

In operation of the electrolytic apparatus or cell, in one specific embodiment a D.-C. power supply 27 of seven volts was utilized. The potentiometers 28 and 31 were adjusted so that the magnesium alloy cathode-anodes had a polarization level of 3300 millivolts with respect to a silver-silver chloride half cell and the cathode 16 had a polarization level of 1100 millivolts with respect to a silver-silver chloride half cell.

In practicing my method as soon as the cathode-anodes 17 and the cathode 16 have been approximately adjusted to the above polarization levels, the sea water within the tank 11 immediately will begin to cloud up which is caused by a flocking of magnesium hydroxide. Within approximately 30 minutes a large quantity of magnesium hydroxide will have formed and will have settled to the bottom of the tank.

By way of example, one electrolytic cell utilized for carrying out my method consisted of a tank 11 which held approximately 20 gallons of water. The steel star-shaped plates 21 were formed of 20 gauge steel and provided a cathode surface area of approximately 20 square feet. The magnesium anodes were approximately $\frac{3}{4}$ inch in diameter and had a length of 10 inches. The platinum anodes 18 were formed of 14 gauge wire approximately 6 inches in length. With this apparatus, a current flow of 5 amperes was impressed through the circuit means 26.

Using sea water from the San Diego Bay, the following results were obtained with this apparatus:

Table II

	Analysis of Seawater Before Treatment	Analysis of Seawater After Treatment
Total Hardness (CaCO ₃)	6,200	800
Calcium Hardness (CaCO ₃)	1,000	800
Magnesium Hardness (CaCO ₃)	5,200	0
Alkalinity P (CaCO ₃)	0	3,800
Alkalinity M (CaCO ₃)	160	6,000
Caustic Alkalinity (OH ⁻) (CaCO ₃)	123	0
Free Carbon Dioxide (CO ₂) (CaCO ₃)	18,000	8,800
Chlorides (Cl)	3,840	3,100
Sulphates (SO ₄)	41,000	38,000
Total Dissolved Solids (conductivity)		
Iron (Fe)		
Manganese (Mn)		
Silica (SiO ₂)	7.4	12.9
pH	none	none
Turbidity	clear	clear
Color	0	815
Hydroxide (OH ⁻)		

The units used in the above water analysis are expressed in parts per million. The hardness is expressed in a conventional manner, that is, in terms of the dissolved calcium and magnesium salts calculated as a calcium carbonate equivalent CaCO₃.

The above analysis also indicates that the total hardness (scale forming elements) in the sea water was reduced by 87%. Seventy-six (76) pounds of chlorine gas were recovered per 1,000 gallons of sea water and twenty-four (24) pounds of magnesium hydroxide (Mg(OH)₂) in relatively pure form were also obtained per 1,000 gallons of sea water.

During the time the process was carried out, it was found that large amounts of hydrogen gas were also released from the sea water at the magnesium anodes 17. The hydrogen was carried away by the cone-shaped members 33 and into the pipe 36. The chlorine was released at the platinum anode 18 and was collected by the conical members 34 and led away by the pipes 37.

During operation of the electrolytic cell, it was found that it was difficult to prevent hydrochloric acid from forming within the electrolytic cell which tended to decrease the rate of flocking of the magnesium hydroxide. The formation of this hydrochloric acid was eliminated by the placement of the asbestos skirts 38 around the platinum anodes 18. As is well known to those skilled in the art, asbestos cloth is not adversely affected by the chlorine.

It was found that the flocks which formed within the cell and precipitated to the bottom of the tank was a relatively pure magnesium hydroxide. The above analysis of the sea water discloses that practically all of the magnesium ions had been removed from the sea water by treatment with my process.

It is apparent from the foregoing that the magnesium hydroxide is removed from the sea water with a very small amount of power e.g. for removing the magnesium hydroxide from approximately 20 gallons of water, 17.5 watt hours were consumed.

It is believed that the low power requirement can be explained by the fact that my electrolytic apparatus or cell contains an electrode, the cathode-anodes 17, which serves as a cathode and as an anode and thus serves to attract both positive ions and negative ions which are normally cations and anions respectively. Thus in a sea water solution, the magnesium ions which are cations and the hydroxide ions which are anions are both attracted to the cathode-anodes 17 to permit the discharge of their ions at the cathode-anode electrode and to permit ready formation of magnesium hydroxide in this area. In conventional electrolytic cells, the ions must generally migrate through long distances in the electrolyte in the electrolytic cell. In addition, the magnesium ions would be attracted to one electrode and the other hydroxide ions would be attracted to the opposite electrode which generally would be far removed from each other and, therefore, inhibiting the formation of magnesium hydroxide.

It is believed by the utilization of other polarization levels on the cathode and the cathode anode, other substances can be removed from the sea water. However, additional experimentation will be required to establish this belief.

It is readily apparent to one skilled in the art that my method and process is also adapted for a continuous flow process as well as a batch process. For example, in moving streams of sea water, it could be passed through a plurality of electrolytic cells after which the magnesium hydroxide could be readily removed by screening. The screened magnesium hydroxide may then be dehydrated. The magnesium hydroxide may be used for any desired purpose such as for the production of magnesium in a manner well known to those skilled in the art.

As hereinbefore explained, various elements may be used for the electrodes 17. However, when a magnesium alloy is used as a cathode-anode, care must be taken so that the polarization level of the magnesium is high enough to prevent dissolution of the magnesium in the sea water. It has been found that a steel cathode in a cell of the type shown in the drawing normally has a potential level of approximately 630 millivolts with reference to a silver-silver chloride half cell, that the magnesium alloy has a potential of 1590 millivolts and that the platinum anode has a reverse potential of minus 850 millivolts. Platinum, of which the anode is formed, is a

5

relatively inert material which is low in the electrochemical series with respect to magnesium.

In order to provide for continuous operation of the electrolytic cell, it is desirable to raise the polarization level of the cathode 16 as well as that of the cathode-anode 17. Thus, to prevent the corrosion of the cathode 16 in the sea water, a potential of over 890 millivolts should be maintained. And, similarly, magnesium, to prevent it from passing into the solution should have a polarization level of 2105 millivolts.

It has been found that the use of the tri-electrode cell is particularly advantageous in removing elements of hardness from sea water and also from fresh water. Thus, after treatment in the tri-electrode cell, the water will have a much lower mineral content.

It also has been found that the use of the tri-electrode cell or system is particularly advantageous in the treatment of sewage. Heat is given off at the anode which serves as a secondary digester for the sewage. Also, migration of ions through the sewage breaks down the entrapped gases in the sewage and thereby liberates sulfides, chlorides and/or other organic acids. This has a particular advantage in that it decreases the chlorine required for sewage treatment and also in that it reduces the quantity of the solids.

By way of example, one electrode, cell or system utilized for treatment of sewage utilized 1.7 amperes of 12 volt direct current in which a steel cathode was maintained at a polarization of 1500 millivolts with respect to a silver-silver chloride half cell and the magnesium cathode-anode at a polarization level of 4000 millivolts. At the end of four hours, it was found that the temperature of the sludge around the platinum anode had been raised from a temperature of 75° F. to 118° F. With a tank having a depth of 4 feet, it was found that at the end of 4 hours, 4 inches of solids had settled to the bottom of the tank and that after 12 hours, 6 inches of solids had settled to the bottom of the tank and that after 16 hours, the amount of solids had increased to approximately 10 inches. In a tank having similar depth which contained no tri-electrode cell, it was found that with the same sewage, only 4 inches of solids had collected at the bottom of the tank after the end of the test period. From this it is readily apparent that the tri-electrode cell facilitates the separation of the solids from the sewage and thereby facilitates treatment of the sewage. The organic gases liberated during treatment with the tri-electrode can be utilized for fuel.

6

It is apparent from the foregoing that I have provided a novel type of electrolytic cell which is particularly adapted for the treatment of electrolytes to remove substances therefrom. It can be used for removing desired substances from the electrolyte such as magnesium hydroxide from sea water. It also can be utilized for removing minerals and the like from sea water and fresh water to reduce the hardness of the water.

I claim:

- 10 A method for electrolytically removing magnesium hydroxide from sea water by precipitation, impressing a current flow from an external source of direct current between a platinum anode and a magnesium electrode, permitting current flow between the magnesium electrode
- 15 and a steel cathode and regulating the current flow between the anode and the magnesium electrode and between the magnesium electrode and the cathode so that the polarization level on the magnesium electrode is approximately 3300 millivolts and the polarization level on
- 20 the cathode is approximately 1100 millivolts.

References Cited in the file of this patent

UNITED STATES PATENTS

25	398,101	Webster	Feb. 19, 1889
	641,438	Darling	Jan. 16, 1900
	1,252,654	Betts	Jan. 8, 1918
	1,312,756	Stover	Aug. 12, 1919
	1,371,698	Linder	Mar. 15, 1921
30	1,414,423	Langer	May 2, 1922
	1,526,644	Pinney	Feb. 17, 1925
	1,541,947	Hartman et al.	June 16, 1925
	1,567,791	Duhme	Dec. 25, 1925
	1,837,355	Burns et al.	Dec. 22, 1931
35	2,128,548	White	Aug. 30, 1938
	2,158,269	Bowman et al.	May 16, 1939
	2,316,917	Wallace	Apr. 20, 1943
	2,341,356	Briggs	Feb. 8, 1944
40	2,490,730	Dublier	Dec. 6, 1949
	2,696,466	Beaver	Dec. 7, 1954
	2,752,306	Juda et al.	June 26, 1956
	2,903,405	Sabins	Sept. 8, 1959

FOREIGN PATENTS

45	492,347	Great Britain	Sept. 19, 1938
	738,520	Great Britain	Oct. 12, 1955