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ABSTRACT

A process for extracting magnesium hydroxide and/or calcium carbonate from sea-water, brine or other water containing minerals is carried out using apparatus comprising an electrolysis cell having a cathode chamber (1) and an anode chamber (2) separated by a membrane (3), a cathode (4) and an anode (5) in the respective chambers (1,2) in close proximity to the membrane (3), a port (6) for charging salt water into the cathode chamber (1) and a port (7) for discharging spent electrolyte therefrom, a port (8) for charging salt water or a fresh water solution of a chloride-free salt into the anode chamber (2) and optionally another or the same port for discharging it therefrom, means (10) for dislodging accreted material from the cathode (1), and means (11) for conveying accreted material from the cathode chamber (1).

Fig. 1

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- 1 -

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A METHOD AND APPARATUS FOR THE EXTRACTION OF MAGNESIUM
HYDROXIDE AND/OR CALCIUM CARBONATE FROM SALT WATER OR BRINE

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This invention relates to the extraction of magnesium hydroxide and/or calcium carbonate from sea water, brine or solutions containing minerals, with gases also being produced.

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Magnesium hydroxide is required in substantial quantities for industrial use, principally in the pulp, paper and refractory industries for example. It is used in the refining of sugar and in the processing of uranium. Medicinally it is important as an antacid (milk of magnesium) and as a laxative. Chemically pure magnesium hydroxide shipped and used in the U.S.A. alone in 1987 amounted to 263,187 short tons with a value of U.S. Dollars 52,578,000. The cost of one short ton of magnesium hydroxide (National Formulary powder), freight equalized, was U.S. Dollars 1,560.00 at the end of 1987, while imports for consumption of crude and processed magnesite by the U.S.A. totalled 223,555 short tons in 1987 with a value of U.S. Dollars 43,539,000 (Mineral Yearbook, Vol I, Metals and Minerals, U.S. Dept. of the Interior, Washington, D.C., 1987, pp.595-601).

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- 2 -

Sea water represents a large source of magnesium hydroxide. It is known to precipitate magnesium hydroxide from sea water by increasing its alkalinity through addition of dolomitic or slaked lime. However, no attempts have been made to harvest magnesium hydroxide from sea water, brine, or other solutions containing minerals, using electrolysis on an industrial scale.

After oxygen, hydrogen, chlorine, and sodium, magnesium is the fifth most abundant element of sea water. One cubic mile contains 6,125,000 tons of magnesium (Life Nature Library, The Sea, The Matchless Phenomenon of the Sea, Leonard Engel and the editors of Time - Life Books, New York, 1972, p. 11). Thus, 660 - 3000 cubic meters of sea water will have to be processed in one hour to yield one ton of magnesium contained in the compound magnesium hydroxide.

Calcium carbonate is potentially a valuable "sink" for carbon whose presence in the environment contributes greatly to the "greenhouse" effect. The binding of carbon present in sea water into calcium carbonate on an industrial scale could contribute significantly to a reduction in environmental carbon levels, thus mitigating global warming.

In 1981 the present inventor obtained U.S. Patent 4,246,075 for mineral accretion of large surface structures, building components and elements. By establishing a direct electrical current between electrodes in an electrolyte such as sea water, calcium carbonates, magnesium hydroxides, and hydrogen were produced at the cathode, while at the anode, oxygen and chlorine were produced. The electrochemical accretion of minerals was utilised to construct large surface area (i.e. greater than 100 square feet) structures, building components and elements of a hard, strong material (i.e. 1000-8000 P.S.I. compression strength). To make a large surface area structure, building component or element of hard, strong material, a preshaped form of electrically conductive material was disposed in a volume of electrolyte, such as sea water, to serve as a cathode, one or more anodes were disposed in proximity to the form, and a direct electrical current was established between the electrodes for a period of time sufficient to accrete a solid covering of material on the form.

- 3 -

Figure 8 of the drawings in U.S. 4,246,075 showed the application of mineral accretion technology to the construction of an ocean thermal energy conversion plant. The drawings showed self-cleaning cathodes in the $Mg(OH)_2$ chamber. The description at
5 column 6, lines 51-55 referred to Figure 8 and stated that, aside from converting ocean thermal energy into electricity, the plant could also produce chlorine, hydrogen, ammonia, $Mg(OH)_2$ (Brucite) as a by-product of the electrolysis process used to provide uplift of cold water in the deep water pipes. Through the application of heat,
10 Brucite could be directly reduced to the mineral Periclase (MgO). Thus the plant might produce refractory magnesia at potentially competitive cost. However, these proposals have not been put into practice on an industrial scale.

15 U.S. Patents 4,440,605 and 4,461,684 of the present inventor described the application of similar mineral accretion technology in the repair of reinforced concrete structures and in protection against biodegradation.

20 J 61,177,385-A of Mitsui Engineering & Shipbuilding describes production of magnesium hydroxide by electrodeposition from high salt content water e.g. brine from sea water distillation. Using a high current density and a low temperature, magnesium hydroxide having a low calcium carbonate content can be obtained. Figure 2 shows a
25 continuous belt which apparently also acts as the cathode on which the magnesium hydroxide is deposited and then conveyed out of the cell.

SU 1,193,177-A Khasanov et. al. describes a method of
30 extracting magnesium hydroxide by electrolysis of water containing minerals (e.g. subterranean water) as starting materials in a diaphragm cell with the starting material supplied to the anode and cathode compartments of the cell, the electrolysis being carried out at a cathode current density of $0.4-0.8 \text{ A/dm}^2$, a voltage of 8-10V
35 and a pH value in the cathode compartment of 10.5-11. It is claimed that these conditions result in 100% extraction of Mg containing no Ca and Sr impurities. However the specification indicates that this process has only been carried out in a glass beaker with the anode

- 4 -

and cathode compartments separated with the aid of a 50mg capacity Schott crucible. No process or apparatus for harvesting the magnesium hydroxide is described.

5 K. Menzel "Elektrochemische Abscheidung von mineralischen Substanzen aus Meerwasser" in "Naturliche Konstruktionen - Mitteilungen des SFB 230, Heft 1 - Aus den Teilprojekten/ Sonderforschungsbereich 230" University Stuttgart/University
10 Tübingen, 1988 describes the covering of wire mesh electrodes with "self repairing" mineral coatings in sea water by means of electrical current. The mechanisms of precipitation and the electrochemical conditions for obtaining growing solid layers are discussed and experimentally studied. In the experiments, in order to avoid
15 production of chlorine gas at the anode, a chloride-free anode electrolyte (KOH solution) is used. The anode space is separated from the cathode electrolyte by a porous fritted glass filter (1 micrometre pore diameter) or a ceramic diaphragm. The experimental results obtained are valuable background material for the present invention and are incorporated herein by reference. However the
20 description relates to deposition of magnesium hydroxide and calcium carbonate in layers for building purposes, and not to harvesting of these minerals.

The present invention provides a process for extracting
25 magnesium hydroxide and/or calcium carbonate from sea-water, brine or other water containing minerals (hereafter called "salt water") by the steps of:

charging salt water into a cathode chamber of a 2-chamber
30 electrolysis cell,

charging salt water or a fresh water solution of a chloride-free salt into the anode chamber of the cell, the anode and cathode chambers being separated by a membrane,
35

establishing a direct current between the cathode and anode at a current density appropriate to produce a high pH in the salt water electrolyte in the cathode chamber, so that magnesium hydroxide

- 5 -

and/or calcium carbonate precipitates from the salt water solution and accretes on the cathode,

5 dislodging the accreted material from the cathode, and conveying the accreted material from the cathode chamber.

Preferably the accreted material is dislodged from the cathode by scraping and/or brushing.

10 The term "membrane" as used herein includes an ion-permeable membrane, a diaphragm or other cell-division means as known to those skilled in the art for electrochemical processes. Preferably the membrane is an ion-exchange membrane or ion-selective membrane as known for membrane cells.

15 Preferably also the process includes the step of moving the cathode away from the membrane as accreted material builds up on the cathode to maintain a close separation between the membrane and the effective cathode surface. Furthermore the process also preferably
20 includes moving the cathode away from the membrane to a wider separation to facilitate the step of dislodging accreted material from the cathode.

Operational variables such as temperature, pH, salinity, and
25 rate of flow-through of catholyte, are preferably monitored by sensors whose output is fed to a computer unit which adjusts the relevant parameters and current density when necessary in order to maintain predetermined conditions. Preferably, sensors are located in the cathode chamber in order to monitor these parameters. The
30 sensor/microprocessor assembly while facilitating automatic manipulation of the process also provides a recorded history of each operation.

In one aspect, the present invention provides a process for
35 removing carbon from sea water by precipitating calcium carbonate in an electrolysis cell and conveying the precipitated material therefrom. In one optional feature, the process includes charging carbon dioxide into the electrolyte in the cathode chamber so that at

- 6 -

least part of the carbon content thereof may be bound into calcium carbonate accreted on the cathode. This step can be used to remove CO₂, which is a waste product from fossil fuel combustion, from the carbon cycle. The carbon dioxide may, if desired, be charged into
5 the electrolyte before it enters the cathode chamber.

The electrolysis process increases the pH of the catholyte until precipitation of calcium carbonate is induced. As the catholyte becomes more alkaline, magnesium hydroxide as well as
10 calcium carbonate is precipitated. The pH can be increased to the level where magnesium hydroxide alone is precipitated. The pH of the catholyte is determined by the current density applied between the electrodes, resulting in varying Mg(OH)₂/CaCO₃ ratios in the accreted materials.

15

Preferably the process also includes the step of collecting hydrogen gas produced in the cathode chamber and oxygen gas and/or chlorine gas produced in the anode chamber. If the anode electrolyte is a fresh water solution of a chloride-free salt the gas produced at
20 the anode will be oxygen, which is preferable as compared to the chlorine/oxygen mixture produced from a salt water electrolyte at the anode. The chloride-free salt is preferably potassium hydroxide but may be another salt such as sodium hydroxide. If the anolyte is salt water additional salts may be added to increase conductivity of the
25 electrolyte. Preferably also the process includes discharging the salt water electrolyte from the cathode chamber and passing it through a heat exchanger to heat salt water being charged into the cathode chamber. In another preferred process step, the discharged salt water electrolyte is contacted with an ion exchanger to transfer
30 hydroxyl ions to the electrolyte being charged to the cathode chamber.

According to another aspect, the present invention provides apparatus for extracting magnesium hydroxide and/or calcium carbonate from salt water comprising:

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an electrolysis cell having a cathode chamber and an anode chamber separated by a membrane,

- 7 -

a cathode and an anode in the respective chambers in close proximity to the membrane,

5 a port for charging salt water into the cathode chamber and a port for discharging spent electrolyte therefrom,

10 a port for charging sea water or a fresh water solution of a chloride-free salt into the anode chamber and optionally the same or another port for discharging it therefrom,

means for dislodging accreted material from the cathode, and means for conveying accreted material from the cathode chamber.

15 Preferably the means for dislodging accreted material from the cathode comprises scraper and/or brush means.

20 The anode may suitably be at a distance of 1-20mm from the membrane, while the cathode may suitably be at a distance of 1-50mm from the membrane.

In the preferred embodiment the apparatus also includes means for propelling the cathode away from and towards the membrane so as to adjust the separation between them. This propelling means operates:

25

a) to move the cathode progressively away from the membrane as accreted material builds up on the cathode, while maintaining a close proximity between the membrane and the surface of accreted material which forms the effective cathode surface, and

30

b) to move the cathode to a wider separation (i.e. >50mm) from the membrane to permit passage of the dislodging means between them and to prevent clogging of dislodged minerals.

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The preferred embodiment also includes means for monitoring and manipulating operation variables such as temperature, pH, salinity and flow rates. This may be facilitated using sensors in the cathode chamber linked to a microprocessor which controls the

- 8 -

operating conditions to adjust the appropriate parameters.

According to one preferred feature, adjustable baffles are provided in the cathode chamber to direct flow-through and convection
5 currents of the electrolyte. In another preferred feature one or more transducers are provided in the cathode chamber or on the walls thereof to emit sonic frequencies within said chamber. Furthermore, one or more transducers or other vibrating means may be provided in the vicinity of or attached to the anode to reduce build-up of oxygen
10 and/or chlorine bubbles on the anode surface.

Generally the accretion area of the cathode is substantially flat. In the preferred embodiment the cathode has an indented or grated surface. Preferably the cathode comprises a series of tubular
15 units preferably arranged principally vertically in a line (although they may alternatively be disposed horizontally or diagonally), of semi-circular cross section in each of which the substantially flat portion is electrically conductive and the arcuate portion is of thermally insulating material, the units being arranged so that the
20 flat conductive portions are facing the membrane. More particularly, each tubular unit defines a housing for heating means such as an electrical heating element and thermally-conducting (but electrically insulating) fluid. The heating means may be used to increase the temperature of the electrolyte at the cathode surface in order to
25 increase the rate of precipitation of the desired minerals. An electrolyte temperature in the range 3°C to 98°C is preferred. Heat exchange means may be provided to transfer heat from outgoing electrolyte to incoming electrolyte, so that cold salt water can be used as the raw material without undue expense. On the other hand
30 when tropical water is used as the raw material, heating means and/or heat exchange means may be unnecessary. The tubular units may suitably be mounted in a frame with spacers between the individual tubular units, the frame being connected to the means for propelling the cathode away from and towards the membrane.

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Electrical energy requirements can be minimised by applying extremely close spacing between the electrodes and the membrane, using highly conductive electrode materials, and working at the

- 9 -

lowest possible voltage in tropical water or hot brine. It is preferred to use energy from renewable sources. In regions with plentiful electrical energy generation, electrolysis of cold salt water can be carried out economically.

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A substantial number of electrolysis cells may be combined to form an electrolysis plant.

The following detailed description of an illustrative
10 embodiment refers to the accompanying drawings, in which:

Figure 1 is a diagrammatic vertical cross-section of apparatus according to the invention;

15 Figure 2 is a diagram of means for conveying accreted material out of the cathode chamber, viewed at right angles to Figure 1;

Figure 3 is a horizontal cross section of a fragment of the apparatus, showing part of the anode, membrane and cathode, with
20 material accreted on the cathode;

Figure 4 is a horizontal cross section similar to Figure 3 but showing the cathode assembly in disengaged position and the dislodging means in use;

25

Figure 5 is a vertical section of a fragment of a cathode unit.

As shown in the drawings, the electrodeposition apparatus comprises an anode chamber (2) which extends lengthwise of the
30 apparatus, and a cathode chamber (1) which is located in front, behind and below the anode chamber. The two chambers are separated by an ion permeable membrane (3) of known type. The respective electrodes are connected to a variable D.C. source (not shown). Anodes (5) are located at the front and rear of the anode chamber (2)
35 separated by a small distance from the membrane (3) with the cathodes (4) at a small adjustable distance from the opposite side of the membrane. "Small distance" in the case of the anode is taken to mean the smallest possible distance between anode and membrane which

- 10 -

allows free and continuous flow of electrolyte between said members under the influence of any convection current or other force acting on the electrolyte within the anode chamber. This distance is typically in the range between 1-20mm. In the case of the cathode a "small adjustable distance" is taken to have a similar meaning to that for the anode chamber with allowance made for the accretion of product (9) (see Figure 3) on the cathode surface (nearest the membrane) and for the fact that a scraping device/apparatus (10) (see Figure 4) must travel between the cathode and membrane in order to "harvest" the accreted material (9). A means (12) is provided whereby the cathode is propelled slowly away from the membrane during the accretion process, typically maintaining a distance of 1-50mm between the membrane and the cathode or, as the accretion proceeds, the outer surface of the accreted product which functions as the effective cathode surface. The same means (12) are used so that the cathode can be further separated from the membrane so as to allow the scraper to pass between said members while removing the accreted layers from the cathode.

As shown in Figure 3, the cathode unit (4) comprises a series of essentially hollow tubes (32) with a semi-circular cross section arranged principally vertically in a line. The conducting portion (15) of each cathode unit while substantially flat has a grated or indented surface (16) (comparable to a metal file) with cavities therein. The scraper (10) on the other hand does not possess projections which extend into these cavities. As a result, upon scraping the accreted material (9) off the cathode some of the minerals remain in the cavities. This is considered advantageous because it facilitates nucleation of further accretion layers.

30

The cathode is heated internally in the following manner:

The tubular shell (semi-circular cross section) of the cathode (32) comprises a substantially flat conducting cathodic portion (15), typically of a highly conductive metal such as silver or copper, and a rounded thermally insulating section (17). This shell houses a centrally located heating wire (19) which imparts heat to the cathodic portion (15) by means of a thermally conducting (but

- 11 -

electrically non-conducting) fluid such as an oil (18).

5 The rear portions of the cathode units i.e. the thermally insulating sections (17) are fixed to a rigid frame (20) which has a means (12) of propelling the said units laterally towards and away from the membrane (3). The means (12) suitably comprises a threaded shaft (12a) which engages a threaded aperture in the frame (20), the shaft (12a) being rotated in either direction by a motor (12b). This is in order to facilitate maintaining the gap (33) between cathode or
10 the effective cathode surface (i.e. the outer accreted layer (9)) and the membrane at a reasonably constant value during accretion; and expansion of the cathode/membrane gap after accretion for scraper access. The gap (33) is exaggerated in Figure 3 for the sake of clarity.

15

In addition to being fixed to the rigid frame (20) the position of the individual units relative to each other is stabilised by the presence of "spacers" (21). This is achieved by the interaction of a guide rail (22) on the spacer with a groove (23) in the cathodic
20 shell. The spacers are located intermittently up the height of the cathode unit, with gaps between them to allow circulation of electrolyte. Each of the panels (33) of cathode units shown in Figure 2 may include 20-30 cathode units per panel (i.e. 10-15 of the pairs of cathode units shown in Figure 3). The panels (35) are
25 modular components of the electrolysis cell.

The anode (5) advantageously comprises a highly conductive material such as platinum, platinum-clad metals, or titanium/mixed-metal oxides preferably in a form which maximises surface area
30 such as the Raney form (e.g. Raney Ti). One or several transducers (28) may be present in the anodic chamber in order to dislodge from the anode surface oxygen or Cl_2 bubbles, which can have an insulating effect and reduce effective current densities (or voltages). Dislodging gas bubbles therefore improves efficiency.

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The membrane (3) located between the two electrodes (4, 5) consists of a material of selective permeability which allows the passage of ions between the two chambers, but isolates the

- 12 -

electrolytes and the evolving gases. It is preferably an ion exchange membrane but may be a diaphragm of known type or a ceramic or glass material with a pore size suitably of the order of 1 micrometre.

5

The scraper (10) comprises a horizontal plastic beam or edge tool, or a guided wire, which can be propelled up and down the full height (vertically) of the cathode along two screw threaded shafts driven by one or more motors, or in another such-like manner. When
10 the cathode is in a suitable position this vertical motion of the scraper dislodges the accreted product material (9) from the face (16) of the cathode and the material falls onto conveyor belt (11). This conveyor belt (11) runs the length of the cathodic chamber (1) and emerges from the top of one end of said chamber (see figure 2).
15 A brush/cleaning means (26) removes the product from the conveyor belt (11) and it is stored in a storage vessel (34). The belt is advantageously porous to allow discharge of the spent electrolyte while retaining the accreted material. Provision is made to collect any product material remaining in the discharged electrolyte by
20 filtering said electrolyte on discharge from the cathodic chamber through the lower discharge port (7).

Sensors (30) are present in the cathode chamber capable of measuring parameters such as temperature, salinity and pH. This
25 information is fed into a microprocessor which adjusts the relevant process conditions such as heat input, rate of through flow and current density when necessary in order to maintain the conditions predetermined by the operator.

30 A series of adjustable baffles (24, 25) within the cathodic chamber (1) serve to direct the flow of electrolyte from its intake port (6) through to its outlet (7a) in such a manner that maximum contact of fresh electrolyte with the cathode occurs.

35 Figure 2 shows the generally horizontal baffles (24) adjustable to impart a wave like motion to the electrolyte as it flows through the chamber.

- 13 -

Figure 5 shows one of a series of adjustable baffles (25), generally vertical by comparison with (24), mounted on the rigid frame (20) between the tubular cathode units (32) to direct the upward flowing electrolyte to gaps between the spacers (21) so that the electrolyte reaches the cathode surface (16). In combination the two types of baffles cause the electrolyte to follow a spiral route through the chamber, creating turbulent conditions.

A further feature of the present invention which can be shown to increase productivity rates and efficiency is the "activation" of the accretion process by passing sound waves (of the frequencies 4 - 18,000 Hz) through the electrolyte. A transducer or series of transducers (29) are located on the walls of the cathodic chamber for this purpose.

15

A method of operation of the apparatus of the present invention is described below:

In one embodiment of the process of the invention, a fresh water potassium hydroxide solution (10-50% by weight KOH) is charged into the anodic chamber (2) through a port (8) and seawater, brine or the like previously heated and filtered to remove unwanted debris, is charged into the adjacent cathodic chamber (1) through the appropriate port (6) at the end of the chamber (see Figure 2). A potential difference [0.6-3.4V] is established between the two electrodes (4, 5) and a current density of 0.8-48 A/m² of cathode surface is maintained. The current density may be used to alter the pH of the electrolyte which is a crucial factor in determining the final composition of the material deposited at the cathode. The critical pH value for precipitation of magnesium hydroxide in sea water is 9.7, for calcium carbonate it is 8.7 at [Mg⁺⁺] = 5.2x10⁻³ Mol/l, [Ca⁺⁺] = 10⁻² Mol/l, (see Menzel, op. cit.).

According to the present invention it is preferable to maintain the minimum separation between the electrodes in order to operate at low voltages and currents thereby increasing the efficiency of the process. The anode (15) is fixed at a distance typically 1-20mm from the membrane. The cathode (14) differs in this respect in that it is

- 14 -

connected to a means (12) providing for an adjustable separation between the membrane and the cathode surface (16) or the membrane and the outermost layer of accreted material (9) on the cathode (the effective cathode surface).

5

During the accretion process the separation between the membrane and the outer accreted layer is maintained (at 1-50mm) automatically (by means (12) under computer control) as the layer grows. This ensures that at all times the salt water electrolyte is able to circulate between the membrane and cathode.

10

At regular intervals after a suitable amount of product material has been allowed to build up on the cathode, it may be harvested according to the present invention in the following manner:

15

The cathode is propelled further away from the membrane by the means (12). It is positioned so that the vertical movement of the scraper (10) has the effect of dislodging the accreted product from the cathode surface. On falling to the bottom of the cathodic chamber the product material is removed from said chamber by means of a conveyor belt (11) which protrudes from the chamber at one end (see Figure 2).

20

The harvesting process may be carried out while the chamber is full and active or when the electrolyte has been removed. In the former case a continuous steady flow of seawater is maintained through the cathodic chamber with the port (7) only partially open and the electrolyte discharged through said port filtered and then recycled and utilised to supplement the fresh electrolyte. Alternatively the mode of operation is such that while accretion is taking place a continuous flow of fresh electrolyte is established through the cathode chamber but at this stage the conveyor belt is stationary and the lower discharge port (7) is in the closed position. Means (27) are provided to seal the area around the conveyor belt so as to prevent excess loss of electrolyte. Naturally some electrolyte will pass below the conveyor belt since the belt itself is designed to be of a porous nature. When accretion has ceased, the cathode assembly is withdrawn from the vicinity of the

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membrane by means (12) and the scraper is engaged to dislodge the accreted material from the cathode. The conveyor belt (11) is activated, removing the product material from the chamber. Only then is the port (7) opened so that any material passing through the
5 conveyor belt may be collected on filtering the discharged electrolyte. The port (7) is then closed, the conveyor belt deactivated and the cycle is repeated upon filling the chamber with fresh seawater. The adjustable baffles (24, 25) serve to control the flow-through and convection current in the cathode compartment which
10 ensures uniform and efficient use of electrolyte.

Further to the main aim of the present invention to extract $Mg(OH)_2$, $CaCO_3$ and mixtures thereof, H_2 and O_2 gases are also evolved as by-products of water electrolysis. Provisions are made so
15 that these gases are collected through ports (13), (14) upon their evolution. In this regard some vibrating means, mechanical, sonic (by means of a transducer) or the like is used to dislodge O_2 or bubbles from the anode surface.

20 In an alternative embodiment, salt water optionally with an additional salt content such as KOH is used as the electrolyte in the anode chamber, in which case Cl_2 is also evolved and collected through ports (13). This Cl_2/O_2 mixture may be subsequently separated into the component gases.

25 The spent seawater electrolyte from the cathodic chamber exits said chamber through appropriate ports (7 or 7a) and it is then passed through a series of units for heat exchange, hydroxyl exchange, degassing of H_2 , and filtering for additional accreted
30 material; prior to being discharged. This maximises yields and minimises energy loss. Energy recovered from the heat exchange process is used to heat fresh incoming electrolyte and hydroxide ions recovered by hydroxyl exchange are used to supplement the incoming catholyte. The whole accretion unit is thermally insulated with
35 heavy thermal insulation (31) to minimise heat loss to the surroundings. Figure 1 shows the insulation (31) at the front of the unit only because this unit is intended to be one of the series of such units installed behind one another. Further insulation would

- 16 -

then be provided at the rear of the rearmost unit.

The composition of the accreted material is determined by the pH of the electrolyte, since $\text{Mg}(\text{OH})_2$ and CaCO_3 precipitate out of solution at different pH values. The pH of the electrolyte is influenced by the current density between the electrodes and varying the current changes the $\text{Mg}(\text{OH})_2$: CaCO_3 ratio. Hence $\text{Mg}(\text{OH})_2$, CaCO_3 or mixtures thereof may be produced by the apparatus of this invention using slight variations of the operating conditions. According to the present invention the preferred operating conditions are as follows:

	Voltage	0.6-3.4V
	Cathode Current density	0.8-48 A/m ²
15	Temperature	3-98°C

The catholyte pH should be within the range 8.5-12.5, preferably 9.0-11.5, more preferably 9.5-11.0 and particularly 10-11.

The critical value for precipitation of $\text{Mg}(\text{OH})_2$ is 9.7, for CaCO_3 it is 8.7.

It will be appreciated that a specific combination taken from within the above ranges will be required to obtain the correct desired composition of deposited material.

It should be noted that "low" current densities leading to "slower" accretion rates (longer accretion times) produce Brucite in its harder crystalline form as opposed to its softer, soapy form which is deposited more rapidly at higher current density.

CLAIMS

1. A process for extracting magnesium hydroxide and/or calcium
5 carbonate from sea-water, brine or other water containing minerals
(hereafter called "salt water") by the steps of:
- charging salt water into a cathode chamber of a 2-chamber
electrolysis cell,
10
- charging salt water or a fresh water solution of a
chloride-free salt into the anode chamber of the cell, the anode and
cathode chambers being separated by a membrane,
- 15 establishing a direct current between the cathode and anode at
a current density appropriate to produce a high pH in the salt water
electrolyte in the cathode chamber, so that magnesium hydroxide
and/or calcium carbonate precipitates from the salt water solution
and accretes on the cathode,
20
- dislodging the accreted material from the cathode, and
- conveying the accreted material from the cathode chamber.
- 25 2. A process according to Claim 1 wherein the accreted material is
dislodged from the cathode by scraping and/or brushing.
3. A process according to Claim 1 which includes the step of
moving the cathode away from the membrane as accreted material builds
30 up on the cathode to maintain a close separation between the membrane
and the effective cathode surface.
4. A process according to Claim 3 which includes moving the
cathode away from the membrane to a wider separation to facilitate
35 the step of dislodging accreted material from the cathode.
5. A process according to Claim 1 which includes charging carbon
dioxide into the catholyte before entry into or in the cathode

- 18 -

chamber so that at least part of the carbon content thereof may be bound into calcium carbonate accreted on the cathode.

5 6. A process according to Claim 1 which includes the step of collecting hydrogen gas produced in the cathode chamber and oxygen gas, or oxygen and chlorine gas, produced in the anode chamber, depending on the anode electrolyte used.

10 7. A process according to Claim 1 which includes discharging the salt water electrolyte from the cathode chamber and passing it through a heat exchanger to heat salt water being charged to the cathode chamber.

15 8. A process according to Claim 1 wherein the discharged salt water electrolyte is contacted with an ion exchanger to transfer hydroxyl ions to the fresh electrolyte being charged to the cathode chamber.

20 9. Apparatus for extracting magnesium hydroxide and/or calcium carbonate from salt water comprising:

an electrolysis cell having a cathode chamber and an anode chamber separated by a membrane,

25 a cathode and an anode in the respective chambers in close proximity to the membrane,

a port for charging salt water into the cathode chamber and a port for discharging spent electrolyte therefrom,

30

a port for charging salt water or a fresh water solution of a chloride-free salt into the anode chamber and optionally another or the same port for discharging it therefrom,

35 means for dislodging accreted material from the cathode, and means for conveying accreted material from the cathode chamber.

10. Apparatus according to Claim 9 wherein the means for dislodging

- 19 -

accreted material from the cathode comprises scraper and/or brush means.

11. Apparatus according to Claim 9 which includes means for
5 propelling the cathode away from and towards the membrane so as to
adjust the separation between them, this propelling means operating:

a) to move the cathode progressively away from the membrane as
10 accreted material builds up on the cathode, while maintaining a
close separation between the membrane and the effective cathode
surface, and

b) to move the cathode to a wider separation from the membrane to
15 permit passage of the dislodging means between them.

12. Apparatus according to Claim 9 wherein adjustable baffles are
provided in the cathode chamber to direct convection currents and
transfer flow through of the electrolyte.

13. Apparatus according to Claim 9 wherein one or more transducers
20 are provided in the cathode chamber or on the walls thereof to emit
sonic frequencies within said chamber.

14. Apparatus according to Claim 9 wherein one or more transducers
25 or other vibrating means are provided in the vicinity of or attached
to the anode to reduce build-up of oxygen or chlorine bubbles on the
anode surface.

15. Apparatus according to Claim 9 wherein the cathode has an
30 indented or grated surface.

16. Apparatus according to Claim 9 wherein the cathode comprises a
series of tubular units of semi-circular cross section in each of
which the substantially flat portion is electrically conductive and
35 the arcuate portion is of thermally insulating material, the units
being arranged so that the flat conductive portions are facing the
membrane.

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17. Apparatus according to Claim 16 wherein each tubular unit defines a housing for heating means such as an electrical heating element and a thermally-conducting but electrically insulating fluid.
- 5 18. Apparatus according to Claim 16 wherein the tubular units are mounted in a frame with spacers between the individual tubular units, the frame being connected to the means for propelling the cathode away from and towards the membrane.
- 10 19. Apparatus according to Claim 9 having sensors in the cathode chamber and optionally also in the anode chamber for sensing parameters such as temperature, pH, salinity, and rate of flow-through of electrolyte.
- 15 20. Apparatus according to Claim 9 wherein the output from the sensors is fed to a computer for controlling process conditions.
21. Apparatus for extracting magnesium hydroxide and/or calcium carbonate from salt water, substantially as described herein with
20 reference to and as shown in the accompanying drawings.
22. A process for extracting magnesium hydroxide and/or calcium carbonate from salt water, substantially as described herein.

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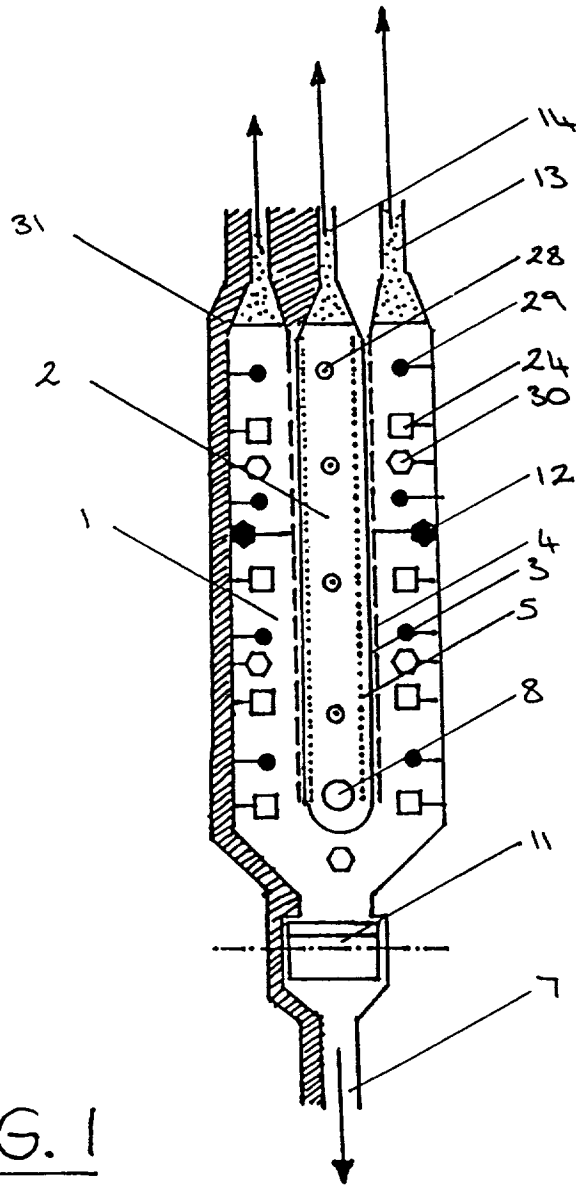


FIG. 1

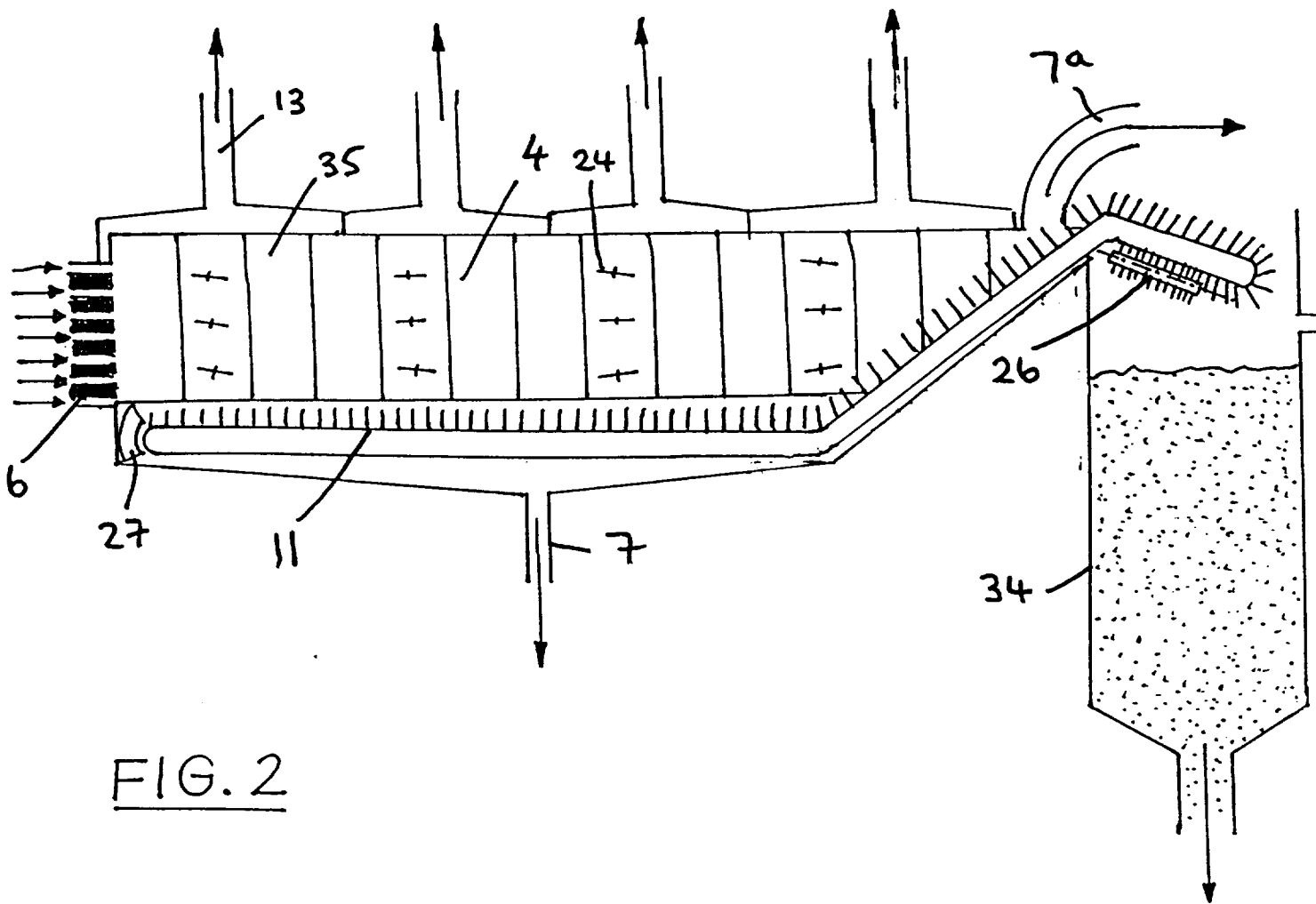
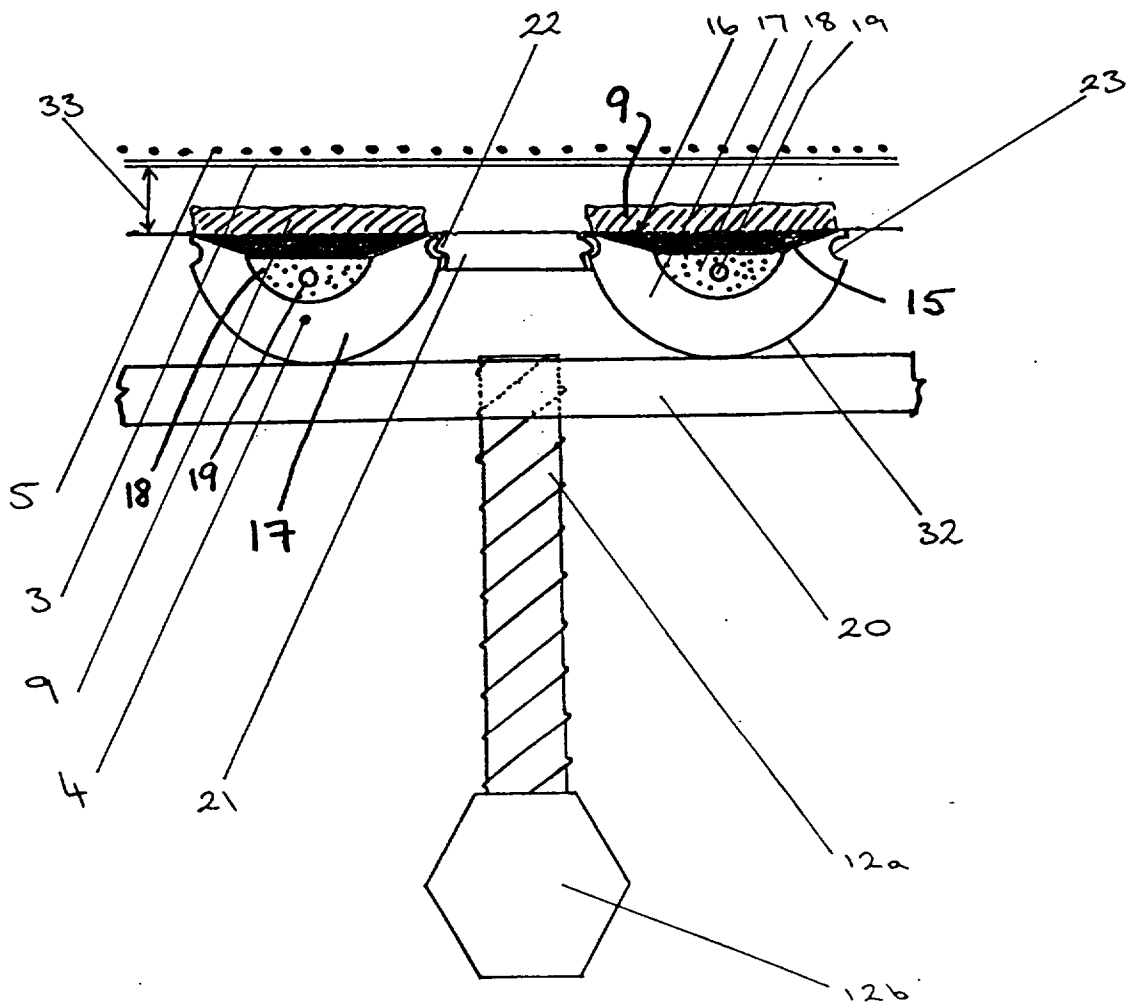
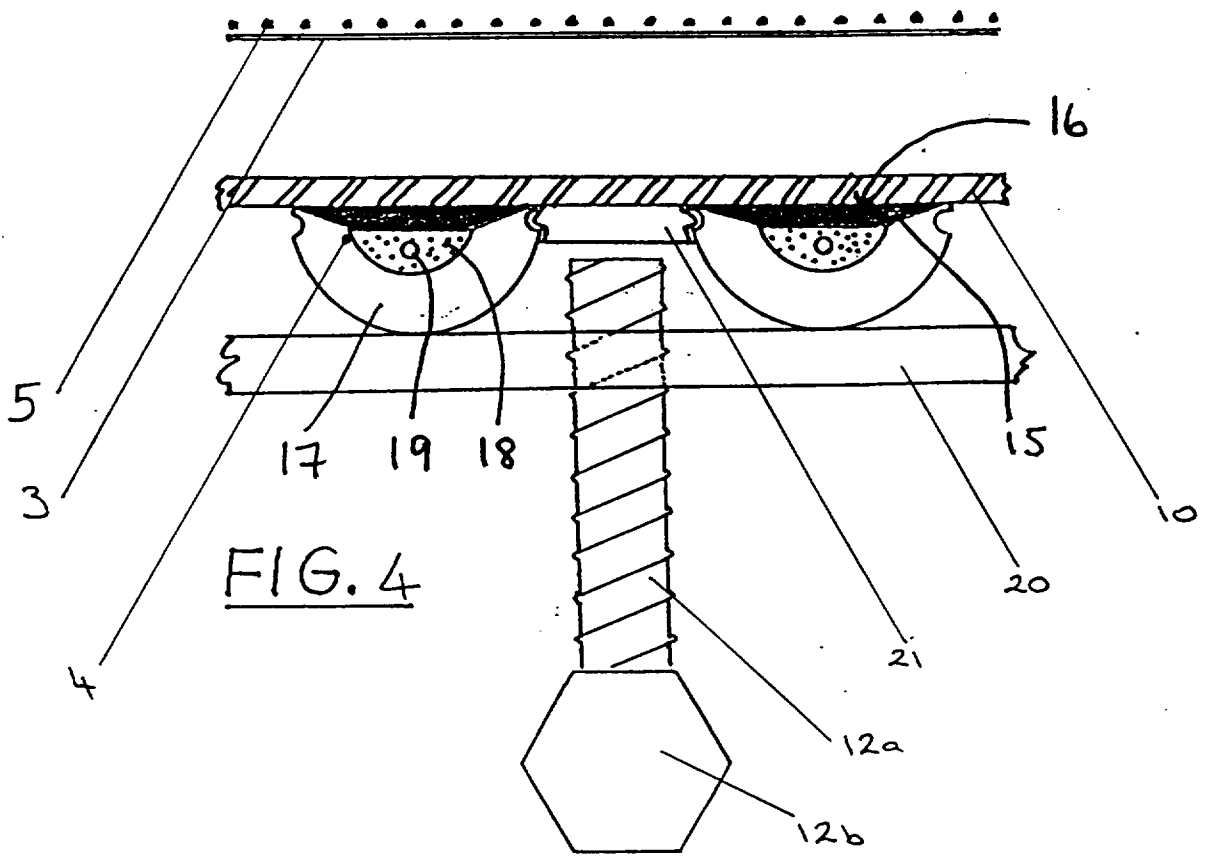


FIG. 3





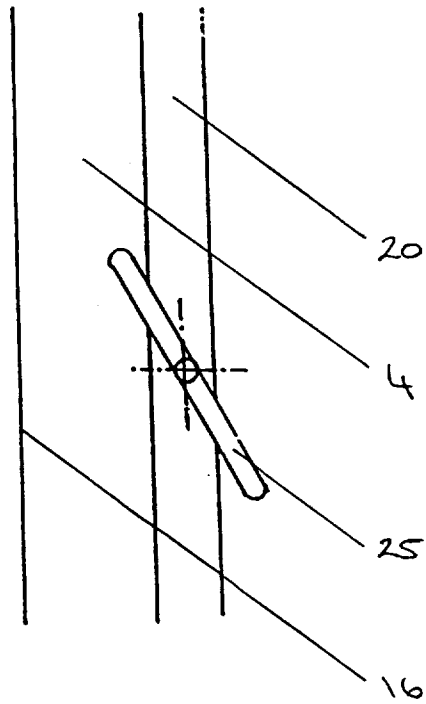


FIG. 5