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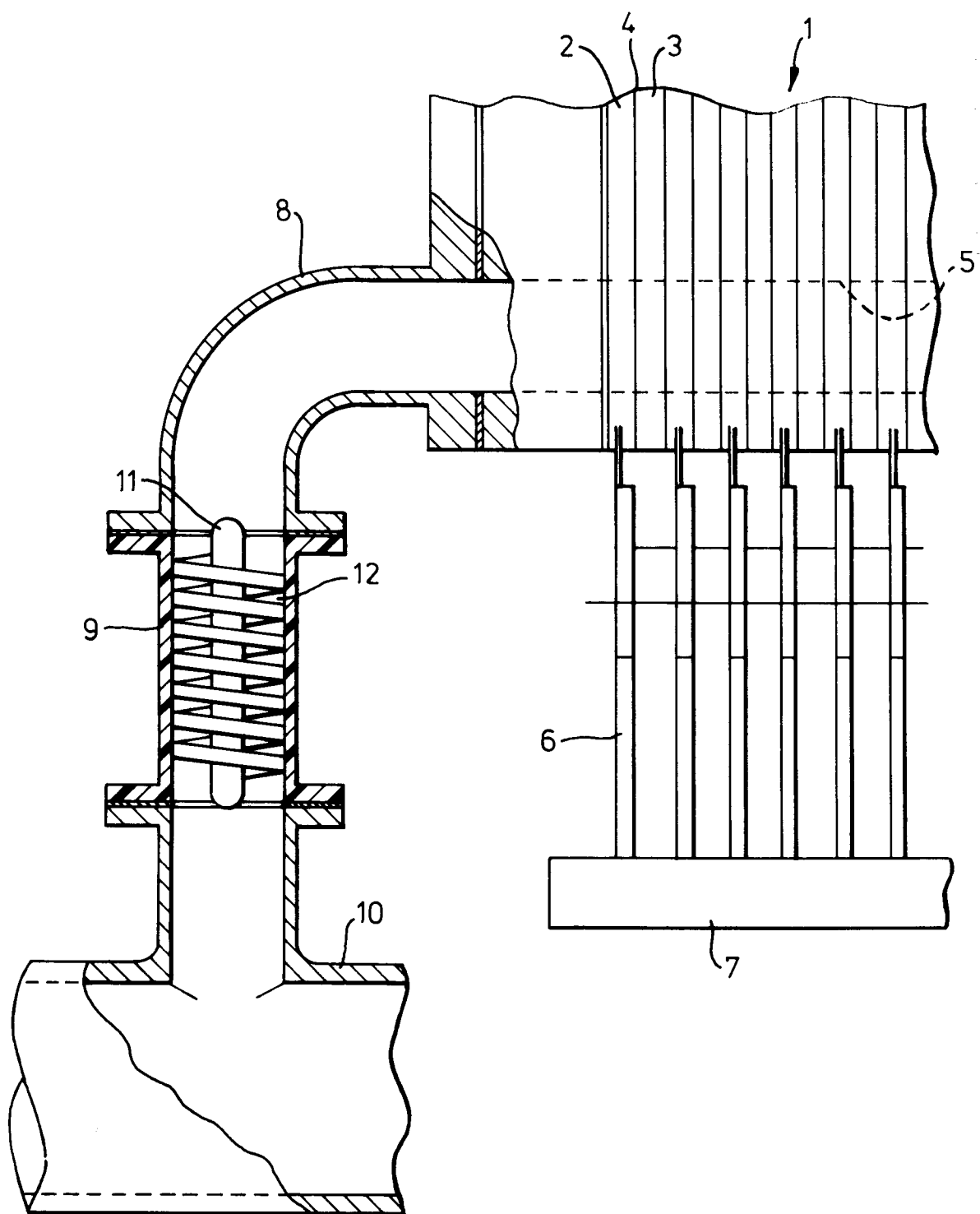
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Electrolytic cell and control of current leakage.

Current leakage in an electrolytic cell comprising at least one electrode compartment and a pipe through which electrolyte may be charged to the electrode compartment and a pipe (8),(9) through which liquid products of electrolysis may be discharged from the electrode compartment is controlled by providing an insert (11) within at least one of the pipes.

The insert (11) has an outer surface which is in register with the inner wall of the pipe, and at least one of the inner wall of the pipe and/or the outer surface of the insert comprises a circumferential groove (12) which provides a channel through which electrolyte may be charged to or liquid product of electrolysis may be removed from the electrode compartment.



This invention relates to an electrolytic cell and to the control of current leakage in an electrolytic cell. Control of current leakage in an electrolytic cell is important in order to minimise the loss of power and corrosion in the cell which is caused by such current leakage.

The production of chemical products by the electrolysis of solutions of ionisable chemical compounds, hereinafter generally referred to as electrolytes, is widely practised in industry.

For example, the electrolysis of an aqueous solution of an alkali metal halide to produce halogen and an aqueous solution of an alkali metal hydroxide or an aqueous solution of an alkali metal halate, e.g. by the electrolysis of an aqueous solution of sodium chloride, is practised industrially on a vast scale throughout the world.

Electrolytic cells for the production of chlorine and aqueous alkali metal hydroxide solution by the electrolysis of aqueous sodium chloride solutions generally are of three basic types, mercury cells, diaphragm cells, and membrane cells. In a mercury cell an aqueous sodium chloride solution is charged to a cell comprising a flowing mercury cathode and anodes which may be of graphite but which in modern practice are generally made of a film-forming metal, e.g. titanium, having an electro-conducting electrocatalytically active coating thereon, and sodium ions and chloride ions are liberated in the electrolysis, chlorine and a sodium amalgam being removed from the cell. Aqueous sodium hydroxide solution is produced by reacting the sodium amalgam with water in a so-called denuder and the depleted amalgam is returned to the electrolytic cell. A diaphragm cell comprises anodes and cathodes separated by hydraulically permeable diaphragms, for example, asbestos diaphragms, to form separate anode and cathode compartments, and the aqueous sodium chloride solution is charged to the anode compartments of the cell where it is electrolysed, chlorine is removed from the anode compartments, and an aqueous solution of sodium hydroxide containing sodium chloride is removed from the cathode compartments of the cell. A membrane cell comprises anodes and cathodes separated by hydraulically impermeable ion perm-selective membranes to form separate anode and cathode compartments, and the aqueous sodium chloride solution is charged to the anode compartments of the cell where it is electrolysed, chlorine is removed from the anode compartments, and an aqueous sodium hydroxide solution is removed from the cathode compartments of the cell. An electrolytic cell for the production of aqueous sodium chlorate solution does not comprise a diaphragm or membrane and the sodium hydroxide and chlorine produced by electrolysis are allowed to react in the electrolytic cell.

During use of such electrolytic cells an electrolyte, for example aqueous sodium chloride solution, is

charged from a reservoir of electrolyte at earth potential to the cell which is at a different electrical potential. The liquid products of electrolysis, for example, an aqueous solution containing sodium hydroxide or an aqueous solution containing sodium chlorate, are discharged from the cell to a reservoir at earth potential designed to receive the liquid products and there is a difference in electrical potential between the electrolytic cell and the product reservoir. Because of these differences in electrical potential there may be a leakage of current between the electrolytic cell and the reservoir from which the electrolyte is charged to the cell, and between the electrolytic cell and the reservoir to which the liquid products of electrolysis are discharged from the cell. The leakage of current occurs particularly where a continuous stream of electrolyte is charged to the electrolytic cell and/or where a continuous stream of the liquid products of electrolysis are discharged from the cell, the continuous streams providing a pathway for leakage of current. Whilst the leakage of current may be significant it may not of itself be a particularly serious loss of electrical energy when compared with the overall electrical energy required to carry out the electrolysis. However, the current leakage may lead to serious corrosion problems in the electrolytic cell. In particular it may lead to corrosion in those parts of the cell through which the electrolyte is charged to the cell and through which the liquid products of electrolysis are discharged from the cell, for example, at the metallic ports through which electrolyte or liquid products of electrolysis are charged to or from the electrode compartments of the cell, or at those parts of the electrodes adjacent to the ports. Furthermore, leakage of current may also be caused by differences in voltage to earth between electrolytic cells in a line of cells, eg in a bipolar electrolytic cell, with the result that corrosion may occur, for example in pipework connecting such cells and through which liquor flows.

Leakage of current, which may be an anodic current or a cathodic current, and the associated corrosion problem, is particularly severe in an installation comprising a large number of individual electrolytic cells to which electrical current is supplied in series, for example in a bipolar installation comprising a large number of membrane or diaphragm cells arranged in series. In such an installation certain of the cells, and in particular those at or near the ends of the series, will be at a high potential relative to earth, that is at a high positive or negative potential depending on the position of a particular cell in the series. For example, in a diaphragm cell installation for the electrolysis of aqueous sodium chloride solution comprising 100 individual cells arranged in series there may be a potential difference of as much as 200 volts between the cells at or near the ends of the series and earth. Thus the leakage of current, and the associated corrosion problem, may be particularly severe in the elec-

trolytic cells at or near the ends of such a series.

Various prior proposals have been made to decrease the extent of this current leakage and to reduce the extent of the associated corrosion problem.

For example, in Japanese patent publication No 53061591 an electrolytic cell for the electrolysis of alkali metal chloride solution is described in which it is proposed to discharge the liquor from the cell in a discontinuous manner by forming the liquor into droplets in a device comprising a plurality of small diameter tubes or rods. In Japanese patent publication No. 53061592 it has been proposed to provide electrodes in a liquor discharging pipe in order to reduce the difference in electrical voltage at the outlet to less than 10 volts and thereby to suppress corrosion. In British Patent No. 1523045 it has been proposed to so choose the lengths and diameters of the electrolyte feed and discharge pipes as to limit the current leakage per cell to not more than 4% of the electrolysis current per cell. Limitation of leakage currents by choosing high length/diameter (L/D) electrolyte feed and discharge pipes is a commonly practised method of limiting current leakage.

In US Patent No. 4048045 there is described a target anode which is said to control selectively the current leakage from an anode to an anolyte discharge manifold. The US Patent describes an electrolytic cell having a passageway which connects an anode compartment and an anolyte discharge manifold, and positioned in the passageway is an electrical conductor which connects the anode with the anolyte in the discharge manifold. The conductor which is positioned within the passageway acts as a target anode and inhibits corrosion damage of the anode to which it is electrically connected.

The present invention relates to an electrolytic cell which is provided with means to control current leakage which means is of the type which comprises electrolyte feed and/or liquid product discharge pipes which have a high ratio of length/diameter, that is a high L/D ratio. However, the feed and discharge pipes may themselves be relatively short yet they may have a high ratio of L/D and the current leakage control means of the invention is particularly compact and simple to install in an electrolytic cell.

According to the present invention there is provided an electrolytic cell which comprises at least one electrode compartment and a pipe through which electrolyte may be charged to the electrode compartment and a pipe through which liquid products of electrolysis may be discharged from the electrode compartment, in which at least one of the pipes comprises an insert positioned within the pipe said insert having an outer surface which is in register with the inner wall of the pipe, and in which at least one of the inner wall of the pipe and/or the outer surface of the insert comprises a circumferential groove which provides a channel through which electrolyte may be

charged to or liquid product of electrolysis may be removed from the electrode compartment.

The circumferential groove is continuous in order that in operation of the cell comprising the insert the groove forms a continuous channel through which in operation electrolyte may be charged to or liquid product of electrolysis may be removed from the electrode compartment.

For simplicity the electrolyte and the liquid product of electrolysis will hereafter, and where appropriate, both be referred to as liquor, and it is to be understood that the electrolytic cell of the invention may be used in the electrolysis of a wide variety of electrolytes in addition to the aqueous alkali metal chloride solution hereinbefore referred to.

The means for controlling leakage currents is provided by the pipe through which liquor is charged to or discharged from the electrode compartment of the electrolytic cell in combination with the insert in the pipe.

Both the pipe and insert will generally be of circular cross-section as with a circular cross-section the insert is readily installed in the pipe. However, the pipe and the insert are not necessarily of circular cross-section. The circumferential groove may be a spiral circumferential groove.

The current leakage control means provided by the pipe and the insert may take a variety of different forms. For example, the inner wall of the pipe may have a smooth ungrooved surface and the outer surface of the insert may have a circumferential groove such that when the insert and the pipe are in register a channel for charging or discharging liquor is formed by the groove and the inner wall of the pipe. In an alternative embodiment the inner wall of the pipe may have a circumferential groove and the outer surface of the insert may have a smooth ungrooved surface such that when the insert and the pipe are in register a channel for charging or discharging liquor is formed by the groove and the outer surface of the insert. Alternatively, both the outer surface of the insert and the inner wall of the pipe may have a circumferential groove although such an embodiment is not preferred as difficulty may be experienced in bringing the grooves into register so as to form the channel for charging and discharging liquor.

The current leakage control means preferably comprises an insert having a circumferential groove on the outer surface thereof as such an insert is readily manufactured and installed in a pipe.

In this specification we have referred to the ratio of length to diameter, ie to the L/D ratio, of the channel through which liquor is charged to or removed from the electrode compartment of the electrolytic cell. The circumferential groove in the insert and/or in the wall of the pipe which forms the channel may not of course be circular in cross-section and thus it may not have a diameter as such. For example, it may be of rectan-

gular cross-section, eg of square cross-section. However, for simplicity we will continue to refer to the L/D ratio of the channel formed by the circumferential groove, and also for simplicity the invention will be described with reference to the preferred embodiment in which the circumferential groove is in the outer surface of the insert and is in the form of a spiral in this outer surface.

The L/D ratio of the channel is governed inter alia by the pitch of the groove, i.e. of the spiral groove, by the length of the surface of the insert over which the groove is positioned, and by the cross-sectional area of the groove. Thus, the L/D ratio is greater the smaller is the pitch of the groove, that is the smaller is the distance between adjacent parts of the spiral groove, and the greater is the length of the surface of the insert over which the groove is positioned. The L/D ratio is greater the smaller is the cross-sectional area of the groove. The pitch of the groove and the length of the surface of the insert over which the groove is positioned also govern the total length of the channel. Thus, the length of the channel is greater the smaller the pitch of the groove and the greater the length of the insert over which the groove is positioned.

The dimensions of the channel, that is its length and cross-sectional area, will be chosen to suit the particular electrolysis which is to be effected in the electrolytic cell. In particular, they will be chosen such that the desired flow of liquor through the channel may be achieved, such that the pressure drop through the channel is not too great, and, most importantly, such that the desired suppression of current leakage is achieved. The dimensions may be determined by calculation and/or by simple experimentation. Where a high flow rate of liquor through the channel is desired a relatively high cross-sectional area for the channel is desirable and/or a relatively short channel. On the other hand substantial suppression of the current leakage requires a relatively long channel and/or a low cross-sectional area for the channel.

The insert may be in the form of a cylindrical plug, that is a plug having the same circular cross-section throughout its length, which is designed to fit in the pipe and to be in register with the inner wall of the pipe. The insert may be a tight fit in the pipe or the insert may be held in position in the pipe by any suitable means for example, by means of a screw threaded sleeve. Alternatively, the insert may be tapered, that is the circular cross-section of the insert may vary, and usually decrease, along its length, in order to ensure a good fit in a correspondingly tapered section of pipe.

The materials of construction of the pipe and of the insert which form the leakage current control means may be of any suitable material, and the material will be chosen to suit the liquors which are to be passed through the pipe. In particular, the materials of construction which are chosen for the insert and for at

least that part of the pipe which is in register with the insert will be materials which are resistant to chemical attack by the liquors and which have a high electrical resistivity, i.e. which are effectively electrically non-conducting. In some cases the materials may be plastics materials. Suitable plastics materials, depending of course on the nature of the liquors may be thermoplastic materials, e.g. polyolefins, polymers of halogen-containing olefins, e.g. polyvinyl chloride, acrylic polymers, and acrylonitrile-butadiene-styrene polymers, the latter being generally resistant to chemical attack by the liquors present when aqueous alkali metal chloride solution is electrolysed. The plastics material may be a thermoset material, and such materials which may be mentioned include polyesters, e.g. fibre-reinforced polyesters, for example glass fibre-reinforced polyesters, and epoxy resins.

The electrolytic cell may comprise a plurality of anodes and cathodes and thus a plurality of electrode compartments, and in the electrolytic cell a separator may be positioned between each adjacent anode and cathode thus providing the electrolytic cell with a plurality of anode and cathode compartments. The separator may be a hydraulically-permeable diaphragm or a substantially hydraulically impermeable ionically perm-selective membrane, e.g. a cation perm-selective membrane.

The electrolytic cell may be a monopolar or a bipolar electrolytic cell.

Where the electrolytic cell comprises a plurality of anode and cathode compartments it may also comprise a manifold or header provided with a plurality of branches which lead to, or from, the anode and cathode compartments of the cell.

The pipe in which the insert is positioned, may lead to or from the manifold or header, or it may form part of the manifold or header.

Where aqueous alkali metal chloride solution is to be electrolysed the anode of the electrolytic cell is suitably made of a film-forming metal or an alloy thereof, for example of zirconium, niobium, tungsten or tantalum, but preferably of titanium, and the operative surfaces of the anode suitably carry a coating of an electro-conducting electrocatalytically-active material. The coating may comprise one or more platinum group metals, that is platinum, rhodium, iridium, ruthenium, osmium or palladium, and/or an oxide of one or more of these metals. The coating of platinum group metal and/or oxide may be present in admixture with or in the form of a solid solution with one or more non-noble metal oxides, particularly one or more film-forming metal oxides, e.g. titanium dioxide. Electro-conducting electro-catalytically active materials for use as anode coatings in an electrolytic cell for the electrolysis of aqueous alkali metal chloride solution, and methods of application of such coatings, are well known in the art. The coating is suitably applied at least to those faces of the anodes which in the elec-

trolytic cell face the cathode. The anode may be made of any material suitable for use with the electrolyte which is to be electrolysed in the cell, and the foregoing description of anodes suitable for use in an electrolytic cell in which aqueous alkali metal chloride solution is to be electrolysed is given by way of example only.

Where aqueous alkali metal chloride solution is to be electrolysed the cathode is suitably made of iron or steel, or of other suitable metal, for example nickel or nickel alloy, particularly where the cathode is to be installed in a membrane cell. The operative surfaces of the cathode may be treated, e.g. by roughening the surfaces and/or by coating the surfaces with a suitable material, e.g. a platinum group metal and/or oxide thereof, in order to reduce the hydrogen over-voltage at the cathode.

Where the separator, if any, to be used in the electrolytic cell is a hydraulically permeable diaphragm the nature of the diaphragm will depend on the nature of the electrolyte which is to be electrolysed in the cell. The diaphragm should be resistant to degradation by the electrolyte and by the products of electrolysis and, where an aqueous solution of alkali metal chloride is to be electrolysed, the diaphragm is suitably made of asbestos or of an organic polymeric material which is resistant to degradation for example, a fluorine-containing polymeric material, as such materials are generally resistant to degradation by the chlorine and alkali metal hydroxide produced in the electrolysis.

Preferably, the diaphragm is made of polytetrafluoroethylene, although other materials which may be used include, for example, tetrafluoroethylene-hexafluoropropylene copolymers, vinylidene fluoride polymers and copolymers, and fluorinated ethylene propylene copolymers.

Suitable microporous diaphragms are those described, for example, in UK Patent No. 1503915 in which there is described a microporous diaphragm of polytetrafluoroethylene having a microstructure of nodes interconnected by fibrils, and in UK Patent No. 1081046 in which there is described a microporous diaphragm produced by extracting a particulate filler from a sheet of polytetrafluoroethylene. Other suitable microporous diaphragms are described in the art.

Where the separator, if any, to be used in the cell is an ion-exchange membrane the nature of the membrane will also depend on the nature of the electrolyte which is to be electrolysed in the cell. The membrane should be resistant to degradation by the electrolyte and by the products of electrolysis and, where an aqueous solution of alkali metal chloride is to be electrolysed, the membrane is suitably made of a fluorine-containing polymeric material containing cation-exchange groups, for example, sulphonic acid, carboxylic acid or phosphonic acid groups, or derivatives thereof, or a mixture of two or more such groups.

Suitable cation-exchange membranes are those described, for example, in UK Patents Nos. 1184321, 1402920, 1406673, 1455070, 1497748, 1497749, 1518387 and 1531068.

In the electrolytic cell the individual anode compartments of the cell will be provided with means for feeding electrolyte to the compartments, suitably from a common header, and with means for removing products of electrolysis from the compartments. Similarly, the individual cathode compartments of the cell will be provided with means for removing products of electrolysis from the compartments, and optionally with means for feeding water or other fluid to the compartments, suitably from common headers.

The common headers may be formed by openings in the gaskets, and optionally in the anodes and cathodes of the electrolytic cell, which openings together form lengthwise channels which serves as headers. The means for feeding electrolyte to, and removing the products of electrolysis from, the anode and cathode compartments of the cell may be channels in the walls of the gaskets or of the anodes and cathodes which lead from the lengthwise channels to the anode and cathode compartments.

A specific embodiment of the invention is now described with reference to the accompanying figure which shows a cross-section through a part of an electrolytic cell, the part shown being that which is required to describe the invention.

The monopolar electrolytic cell 1, a part only of which is shown, comprises a plurality of anodes 2 and cathodes 3 which are positioned in an alternating manner with each anode 2 being separated from an adjacent cathode 3 by an ion-exchange membrane 4. The anodes and cathodes are also electrically insulated from each other by suitable gaskets which for the sake of simplicity are not shown. Each of the anodes, cathodes and gaskets have an opening therein which in the cell form a lengthwise header 5 to which liquor may be discharged from the anode compartments of the cell or from the cathode compartments of the cell formed, respectively, by the space between an anode 1 and an adjacent membrane 4 or the space between a cathode 3 and an adjacent membrane 4. Each anode 2 is connected by means of a copper connector 6 to a bus-bar 7. The header 5 is connected by means of a metallic section of pipe 8 to a section of pipe 9 made of a plastics material of high electrical resistivity and the latter section of pipe 9 is connected to a metallic pipe 10 through which liquor may be discharged from the electrolytic cell 1. The sections of pipe 8 and 9 are of circular cross-section as is the pipe 10.

The section of pipe 9 contains an insert 11 made of a plastics material which is also of circular cross-section and which is a tight fit in the section of pipe 9 such that the outer surface of the insert 11 is in register with the inner wall of the section of pipe 9. The

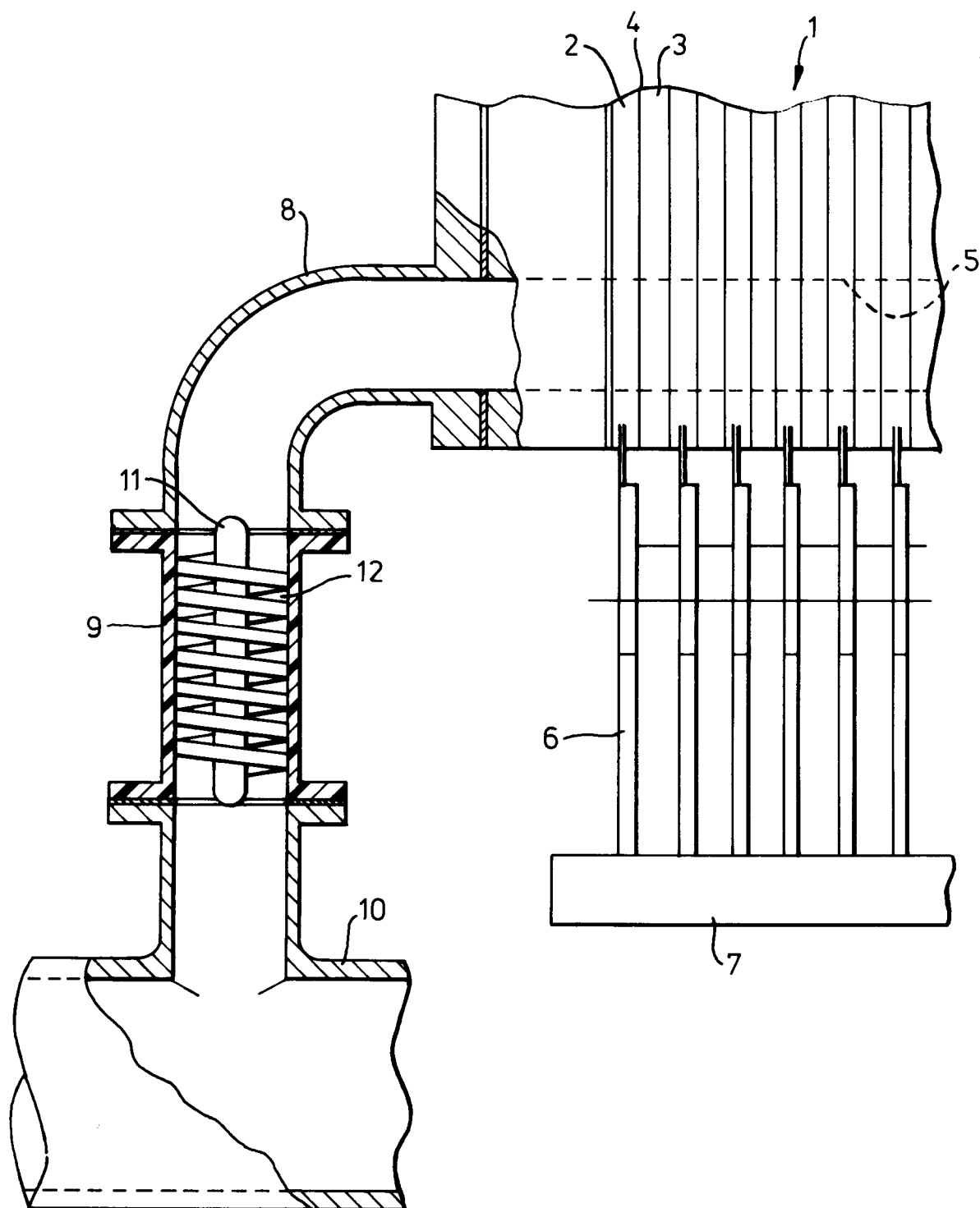
insert 11 comprises a circumferential spiral groove 12 which, together with the inner wall of the section of pipe 9 forms a channel of high L/D ratio through which in operation liquor is discharged from the electrolytic cell.

Claims

1. An electrolytic cell which comprises at least one electrode compartment and a pipe through which electrolyte may be charged to the electrode compartment and a pipe through which liquid products of electrolysis may be discharged from the electrode compartment, in which at least one of the pipes comprises an insert positioned within the pipe said insert having an outer surface which is in register with the inner wall of the pipe, and in which at least one of the inner wall of the pipe and/or the outer surface of the insert comprises a circumferential groove which provides a channel through which electrolyte may be charged to or liquid product of electrolysis may be removed from the electrode compartment. 10 15 20 25
2. An electrolytic cell as claimed in claim 1 in which the pipe and the insert are of circular cross-section.
3. An electrolytic cell as claimed in claim 1 or claim 2 in which at least one of the inner wall of the pipe and/or the outer surface of the insert comprises a spiral circumferential groove. 30
4. An electrolytic cell as claimed in any one of claims 1 to 3 in which the outer surface of the insert comprises a circumferential groove. 35
5. An electrolytic cell as claimed in claim 1 in which the pipe and the insert are of rectangular cross-section. 40
6. An electrolytic cell as claimed in any one of claims 1 to 4 in which the insert is in the form of a cylindrical plug. 45
7. An electrolytic cell as claimed in any one of claims 1 to 6 in which the material of construction of the insert and that part of the pipe in register with the insert is a material which is resistant to chemical attack by the liquors and which has a high electrical resistivity. 50
8. An electrolytic cell as claimed in any one of claims 1 to 7 in which the electrolytic cell is a bipolar electrolytic cell. 55
9. An electrolytic cell as claimed in any one of claims

1 to 8 which comprises a plurality of anodes and cathodes and a separator positioned between each adjacent anode and cathode thus providing a plurality of anode and cathode compartments, the electrolytic cell further comprising a manifold or header provided with a plurality of pipes which lead to or from the anode and cathode compartments of the cell, at least one of the pipes having an insert provided therein.

10. An electrolytic cell as claimed in claim 9 in which the pipe in which the insert is positioned forms part of the manifold or header.





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 7119

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 056 759 (CREUSOT-LOIRE) * page 3, line 30 - line 36 * * page 5, line 4 - line 26 * * claims 1-8; figures 1,3,4,5 * ---	1-4, 6-10	C25B15/08
A	DE-A-2 821 980 (HOOKER CHEMICALS) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C25B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 NOVEMBER 1991	Examiner GROSEILLER P. A.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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