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[54] **PREPARATION OF CHLORINE BY ELECTROLYSIS OF HYDROCHLORIC ACID AND POLYVALENT METAL CHLORIDES**

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[51] **Int. Cl.** **C01b 7/06**, C01b 11/26

[58] **Field of Search** 204/128

[56] **References Cited**

UNITED STATES PATENTS

3,486,994	12/1969	Dönges et al.	204/128
2,468,766	5/1949	Low	204/128

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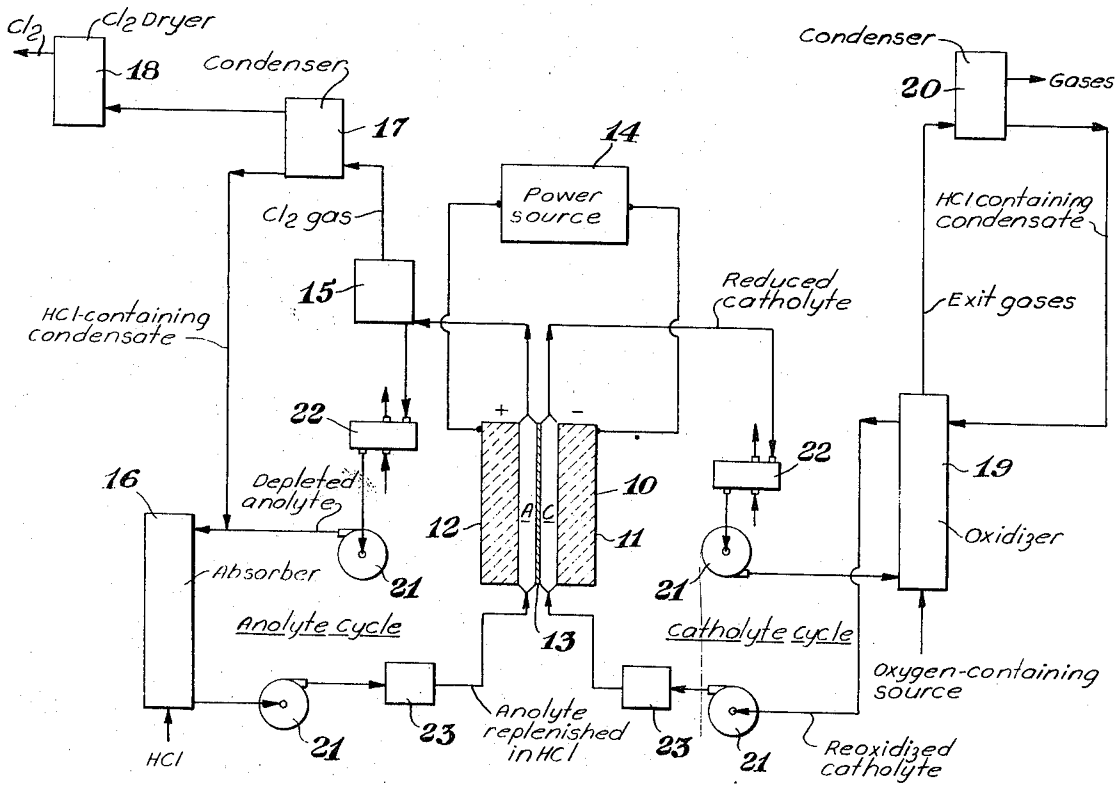
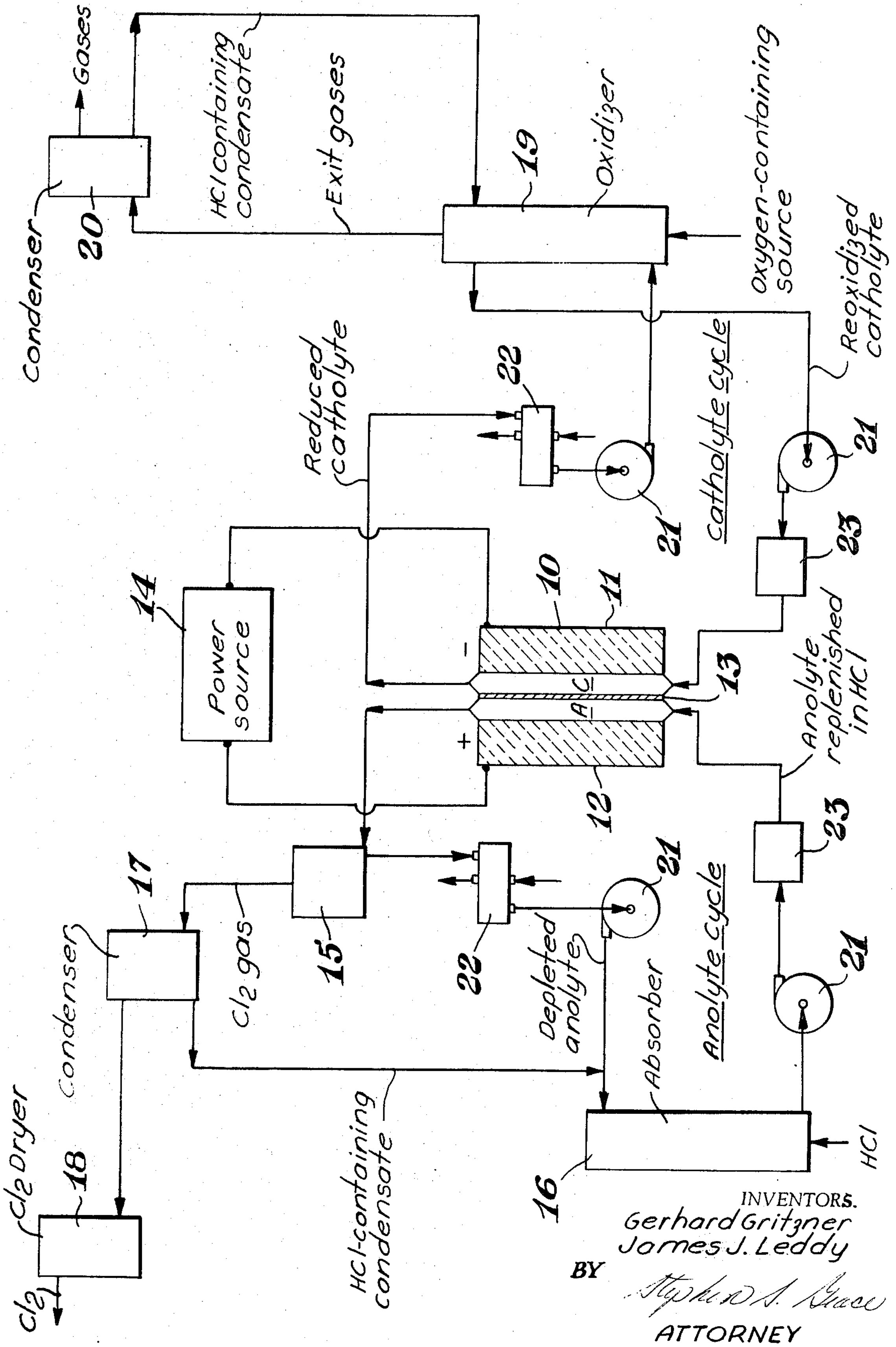
[57] **ABSTRACT**

The present invention relates to a dual electrolyte system utilizing a diaphragm electrolytic cell. The anolyte and catholyte, containing aqueous HCl and a polyvalent reducible metal chloride, are processed and recycled separately. The system of the present invention produces high-purity Cl_2 at higher than conventional current efficiencies.

5 Claims, 1 Drawing Figure





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PREPARATION OF CHLORINE BY ELECTROLYSIS OF HYDROCHLORIC ACID AND POLYVALENT METAL CHLORIDES

BACKGROUND of the INVENTION

One method of producing Cl_2 by electrolysis of HCl utilizes a polyvalent metal chloride in the electrolyte solution. For example, U.S. Pat. No. 2,468,766 describes an electrolysis method which comprises: introducing an electrolyte containing HCl and a polyvalent metal chloride, e.g., $CuCl_2$, into the space between anode and cathode of a nondiaphragm cell, liberating Cl_2 at the anode, reducing the polyvalent metal chloride at the cathode, withdrawing the electrolyte through the porous cathode and reoxidizing the polyvalent metal chloride with air and HCl for recycle. Such a method does reduce the cell voltage normally necessary for direct electrolysis of HCl. However, current efficiency suffers due to the inherent flow characteristics of the system which permit back reaction of dissolved chlorine and the lower valence state metal chloride.

German Pat. No. 1,277,216 discloses an electrolysis system which attempts to change the electrolyte flow pattern by use of a diaphragm between the anode and cathode. By maintaining a pressure differential of zero, the diaphragm reduces reaction of the dissolved Cl_2 (anode side) with the lower valence metal chloride (cathode side). Although this does increase the current efficiency, there is still room for improvement. The German system carries out the reoxidation of the polyvalent metal chloride inside the cathode compartment of the cell. Since reoxidation is the slowest reaction taking place in the cell, this limits cell efficiency and cell size. Furthermore, improved results are only obtained using oxygen as the oxidizing gas.

It is a principal object of the present invention to provide a method and system of preparing Cl_2 by electrolysis of HCl and a polyvalent metal chloride.

A further object of the present invention is to provide such a method and system which has high current efficiency.

THE INVENTION

The above and other objects and advantages are found in the present invention which utilizes separate, dual-stream flow of electrolyte containing hydrochloric acid and a reducible polyvalent metal chloride. The invention employs an electrolytic cell with a diaphragm which divides the cell into into anode and cathode compartments. Anolyte and catholyte are fed into the anode and cathode compartments. Preferably the cell is operated to achieve essentially zero fluid flow through the diaphragm.

The anolyte passes through the anode compartment where the hydrochloric acid is electrolyzed to form gaseous Cl_2. The Cl_2-containing anolyte is withdrawn from the cell and the gaseous chlorine separated from the remainder of the anolyte. The anolyte can be replenished in hydrochloric acid by absorption of HCl and recycled through the anode compartment.

The catholyte passes through the cathode compartment where polyvalent metal chloride is reduced to the lower valence state metal chloride, e.g., $CuCl_2$ reduced to Cu_2Cl_2. This reduced catholyte is removed from the cathode compartment. The metal chloride can be reoxidized to the higher valence state and the reoxidized catholyte recycled through the cathode compartment.

The dual-stream method of the present invention produces high-purity chlorine at extremely high current efficiency, on the order of 95 percent, indicating a minimum of back reaction in the cell between the chlorine produced and the lower valence state metal chloride. Further the reoxidation of the catholyte takes place outside of the cell which permits use of more versatile equipment and apparatus. This permits more efficient operation of the system since the reoxidation rate does not limit the cell reaction.

The anolyte and catholyte can contain hydrochloric acid and any polyvalent metal chloride which exists in at least two oxidation states, e.g., copper chloride, iron chloride and chromium chloride. Copper chloride is preferred. Although concentration ranges can vary quite widely and the concentrations can differ between catholyte and anolyte, a particular preferred concentration range is from about 0.5 to about 2 molar $CuCl_2$ and from about 3 to about 8 molar HCl. In fact, if diaphragm and process conditions are appropriate, the catholyte can be essentially polyvalent metal chloride and/or the anolyte can be essentially HCl.

The reactions taking place in the system of the present invention using an HCl-$CuCl_2$ electrolyte are as follows:

Cathode reaction: $2CuCl_2 \rightarrow Cu_2Cl_2+2Cl^-$

Anode reaction: $2HCl \rightarrow 2H^+ + Cl_2$

Oxidation reaction: $Cu_2Cl_2+\frac{1}{2}O_2+2H^+ +2Cl \rightarrow 2CuCl_2+H_2O$

These reactions add up to an overall reaction of

$$2HCl+\frac{1}{2}O_2 \rightarrow Cl_2+H_2O$$

PREFERRED EMBODIMENTS

The FIGURE is a schematic flow diagram illustrating one embodiment of the dual flow electrolysis system of the present invention.

Referring to the FIGURE, electrolytic cell **10**, composed of cathode **11**, anode **12** and diaphragm **13**, is connected to power source **14**. The materials of construction of the electrodes are those normally employed in electrolytic cells, such as carbon or graphite. Diaphragm materials can include synthetic materials which retain substantial strength and dimensional stability such as polypropylene and copolymers of vinyl chloride and acrylonitrile, and polyvinyl chloride.

The anolyte cycle comprises feeding anolyte containing hydrochloric acid and a polyvalent metal chloride is fed into the anode compartment A of the cell. The HCl in the anolyte is electrolyzed to produce Cl_2 gas. The anolyte is removed from the cell and the chlorine gas separated in a degassing unit **15**. The depleted anolyte passes through heat exchanger **22** into an absorption tower **16** where it is contacted with HCl in gaseous or liquid form, preferably gaseous. HCl is absorbed in sufficient amount to replenish the HCl consumed during electrolysis. The replenished anolyte is then recycled through a filter **23** into the cell.

The Cl_2 gas produced by the present method can be further processed by passing the gas through a condenser **17**, which removes a substantial portion of the HCl in the Cl_2 gas, and drying in chlorine dryer **18**, e.g., utilizing H_2SO_4. The HCl-containing condensate can be added back to the anolyte.

In the catholyte cycle, the catholyte is fed through the cathode compartment C where polyvalent metal chloride is reduced to the lower oxidation state. The reduced catholyte is withdrawn from the cell and carried through heat exchanger **22** to an oxidation tower where it is oxidized, for example by admixing it with an oxidizing atmosphere, e.g., oxygen-containing gas or dilute chlorine-containing gas, to reoxidize the metal chloride. While the oxidizer **19** is shown in the FIGURE as one utilizing concurrent flow, it is understood that any tower or tank unit or the like which permits contact of the oxidizing atmosphere with the reduced anolyte is within the scope of the present system. The reoxidized anolyte is then recycled through a filter **23** into the cathode compartment.

The exit gases blown out of the oxidizing tower contain some HCl which can be recovered by passing the gases through a condenser **20**. The HCl-containing condensate can be recycled to the oxidizer. A more elaborate recovery system, which can be used but is not necessary to the present invention, is described in U.S. Pat. No 2,666,024.

The anolyte and catholyte can be cycled for example by means of pumps **21** or other conventional means. It is preferable to control temperature which can be done by use of heat exchangers **22**. It is also desirable in many instances to filter the incoming electrolyte streams to remove any solids. Any type of filter means **23** can be employed.

While the FIGURE shows a single cell system, it is understood that a series of cells connected in series could be employed in the present invention. For example, the cells could be arranged so that one side acts as the cathode for one cell and the other side acts as an anode for a second cell.

The following examples serve to further illustrate the present invention. The following general procedure and apparatus were used for the experiments. Unless otherwise indicated the term electrolyte refers to anolyte and catholyte.

A dual-flow system similar to the FIGURE was set up. Catholyte and anolyte were circulated separately by means of pumps. The flow rate could be regulated from 0 to 650 ml./min. The flow of anolyte and catholyte was measured by means of two rotameters. Copper (I) chloride formed on the cathode was reoxidized with oxygen or air in the oxidizer. The latter was made out of Pyrex Glass, having an active volume of about 66 in.^{3} (21 inches high). The exit gas stream passed through a condenser. Oxygen or air was fed into the oxidizer through a sintered glass disc (medium size). The absorption of hydrochloric acid took place in a glass tube. The tubing for the connection was either polyethylene or pure gum rubber.

The electrode used for the cell was machined from a graphite block. The active electrode area was 15 in.^{2}, and the electrodes were spaced one-sixteenth from the diaphragm. All other parts except the electrode area itself were painted with Saran-type cement in order to prevent electrolysis on those surfaces. Teflon- or Saran-type nipples were used for the inlets and outlets of the electrolyte. Two of these electrodes were clamped together with a cloth diaphragm between them to form the electrolytic cell. Leaks were minimized by a Silastic film along the 1-inch frame of the cell by painting the same area on the diaphragm with Saran cement and by melting the edges of the diaphragm. A copper plate to which the copper leads were soldered was bolted to the external side of each graphite plate by means of two short brass bolts. The complete setup was placed in a temperature-controlled hotbox.

Hydrochloric acid concentration was determined by titration with 1 N NaOH sol. using methyl red as the indicator.

Copper (II) concentration was measured in the catholyte by the standard idometric way.

Copper (I) concentration was determined by the following procedure. A sample was quickly added to a ferric ammonium sulfate solution in sulfuric acid. The amount of iron (II) formed was oxidized to iron (III) with 0.1 N ceric sulfate solution using Ferroin as indicator.

Chlorine was absorbed in 600 ml. of a KI solution (400 g./l.) in sulfuric acid, diluted to 1,000 ml., and aliquots were titrated with 0.1 N sodium thiosulfate.

Gas analyses were made with the Orsat Method.

Current efficiency is determined by comparing the actual amount of Cl_2 produced with that theoretically producable.

TABLE I

Conditions:
Composition of electrolyte: 1.505 M $CuCl_2$, 5.8 M HCl.
Electrolyte flow: 610 ml./min.
Diaphragm: Copolymer of vinyl chloride and acrylonitrile.
Resistance between anode and cathode connectors: 33 milliohms (70° C.).

	Current density, amps/in.^{2}	Volts	Temp., ° C.	Current efficiency, percent
Example No.:				
1	0.33	0.960	71	94.36
2	0.50	1.110	71	95.95
3	0.67	1.270	71	96.93
4	0.83	1.440	71	97.77
5	1.00	1.680	71	97.64
6	0.33	0.92	80	95.33
7	0.50	1.055	80	95.97
8	0.67	1.20	80	96.13
9	0.83	1.35	80	97.52
10	1.00	1.51	80	97.90

Table I shows the current efficiencies of the present system at various current densities and corresponding voltage at two temperatures. As indicated, extremely high current efficiencies, 95 percent or above in almost all cases, are achieved even at very low current densities, i.e., 0.33 a./in.^{2}, and correspondingly low cell voltages, i.e., less than 1 volt.

TABLE II

Conditions:
Composition of electrolyte: 1.46 M $CuCl_2$, 5.03 M HCl.
Electrolyte flow: See table below.
Diaphragm: Polypropylene.
Resistance: 17 milliohms.
Temperature: 70–70.5° C.

	Current density, amps/in.^{2}	Volts	Electrolyte flow rate, ml./min.	Current efficiency, percent
Example No.:				
11	0.5	0.890	610	95.97
12	0.5	0.895	510	95.97
13	0.5	0.895	400	95.97
14	0.5	0.900	300	95.32
15	0.5	0.910	213	95.75
16	1.00	1.055	610	97.69
17	1.00	1.07	510	97.69
18	1.00	1.10	400	97.69
19	1.00	1.17	300	97.47
20	0.33	0.825	510	92.75
21	0.50	0.890	510	95.32
22	0.67	0.945	510	96.13
23	0.83	0.995	510	97.13
24	1.00	1.060	510	97.68

Table II shows two aspects of the present system. First, high current efficiencies can be achieved over a wide range of electrolyte flow rates (examples 11–15 and 16–19). These examples showed little if any decrease in current efficiency when the flow rate is decreased. Second, current efficiency can be increased by increasing the current density (examples 20–24).

TABLE III

Conditions:
Composition of electrolyte: 1.40 M $CuCl_2$ 6.0 M HCl.
Electrolyte flow: 510 ml./min.
Diaphragm: Polypropylene.
Resistance: 17 milliohms.
Temperature: 70–70.5° C.

	Current density, amps/in.^{2}	Volts	O_2 flow in oxidizer, ml./min.	Amt. Cu^+ in reox. catholyte, g./l.	Current effic., percent
Example No.:					
25	0.50	0.90	660	0	90.39
26	0.67	0.96	660	0	94.20
27	0.83	1.04	660	0	94.43
28	1.00	1.12	660	0	95.65
29	0.50	0.92	35	1.3	88.26
30	0.67	0.995	45	1.3	91.62
31	0.83	1.055	80	1.4	93.26
32	1.00	1.14	95	1.4	92.64
33	0.50	0.92	25	2.9	79.2
34	0.67	0.99	21	3.8	82.6
35	0.83	1.055	65	2.7	89.53
36	1.00	1.14	90	2.5	92.6

Table III reflects yet another feature of the present system—the ability to produce Cl_2 at relatively high efficiencies even with incomplete reoxidation of the polyvalent metal chloride. Examples 25–28 are similar to those shown before with a substantial excess of oxidizing gas over that sufficient to convert essentially all of the Cu_2Cl_2 to $CuCl_2$. However, even where the flow of the oxidizing gas in the oxidizer is reduced, thereby resulting in a significant amount of Cu^+ remaining in the recycled catholyte, the present system and method continue to show high current efficiencies especially at high current densities (examples 33–36).

A representative chlorine gas analysis for any of the above examples is

Cl_2—99.69%
CO_2—0.24
O_2 —0.01
N_2 —0.06

Thus the system and method of the present invention can be employed to produce high-purity Cl_2 from electrolysis of HCl and a polyvalent metal chloride at very high current efficiencies over wide ranges of electrolyte concentrations, current densities and flow rates.

EXAMPLES 37–41

A larger diaphragm cell, having an active electrode area of 64 square inches, was incorporated into the system of the present invention. The cell design was similar to that used in the previous examples. Air at a flow rate of about 42.5 liters/min. was used in the oxidation tower as the oxidizing gas.

TABLE IV

Composition of electrolyte: 1.50 M $CuCl_2$, 5.5 M HCl.
Electrolyte flow: See table below.
Diaphragm: Polypropylene.
Resistance: Not measured.
Temperature: 70° C.

	Current density, amps/in.^{2}	Volts	Electrolyte flow, ml./min.	Current eff., percent
Example No.:				
37	0.5	0.94	85	91.4
38	0.5	0.92	185	92.0
39	0.5	0.89	400	92.0
40 [1]	0.5	1.0	760	95.5
41 [1]	0.5	1.0	190	93.2

[1] Active electrode area of 56 sq. in; diaphragm to electrode distance of ⅛ inch.

Table IV demonstrates the high current efficiencies achieved by the present system and method using air as the oxidizing gas over a wide range of electrolyte flow rates. Examples 40 and 41 were taken from a continuously operated miniplant setup.

EXAMPLES 42–43

If desired, the present system can be operated with different HCl concentrations in the anolyte and catholyte, with the same excellent current efficiencies, as shown by the following examples using the cell of examples 40–41.

TABLE V

Composition of electrolyte: 1.50 M $CuCl_2$, 5.5 M HCl.
Electrolyte flow: 180 ml./min.
Diaphragm: Polypropylene.
Resistance: Not measured.
Temperature: 72–73° C.

	Current density, amps/in.^{2}	Volts	HCl conc., moles/liter		Current eff., percent
			Anolyte	Catholyte	
Example No.:					
42	0.5	1.02	6.0	3.8	92.1
43	0.5	1.00	7.5	4.2	91.5

What is claimed is:

1. A continuous process for preparing chlorine which comprises:
   a. passing separate anolyte and catholyte streams through anode and cathode compartments respectively of an electrolysis cell divided into said compartments by a diaphragm; said anolyte and catholyte containing aqueous HCl and a polyvalent metal chloride; whereby Cl_2 gas is produced at the anode and polyvalent metal chloride is reduced from a higher valence state to a lower valence state at the cathode; said cell being operated at a current density of up to about 1 ampere per square inch;
   b. removing the Cl_1 gas-containing anolyte stream from the anode compartment and the reduced catholyte stream from the cathode compartment;
   c. separating the Cl_2 gas from the anolyte stream;
   d. feeding HCl into the anolyte stream to replenish the HCl consumed in the electrolysis and recycling the replenished anolyte stream into the cell anode compartment;
   e. feeding an oxidizing atmosphere into the reduced catholyte stream to reoxidize polyvalent metal chloride and recycling the reoxidized catholyte stream into the cell cathode compartment, thereby to achieve a current efficiency of at least about 90 percent when the polyvalent metal chloride is completely reoxidized.

2. The process of claim 1 including the additional step of operating the cell so that essentially no fluid flow occurs across the diaphragm.

3. The process of claim 1 wherein the polyvalent metal chloride is copper chloride.

4. The process of claim 1 wherein the compositions of catholyte and anolyte comprise from about 0.5 to about 2 M $CuCl_2$ and from about 3 to about 8 M HCl.

5. The process of claim 1 wherein the oxidizing atmosphere is air.

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