

Dec. 5, 1933.

G. BAUM

1,937,621

ELECTROLYTIC APPARATUS

Original Filed Jan. 3, 1927 3 Sheets-Sheet 1

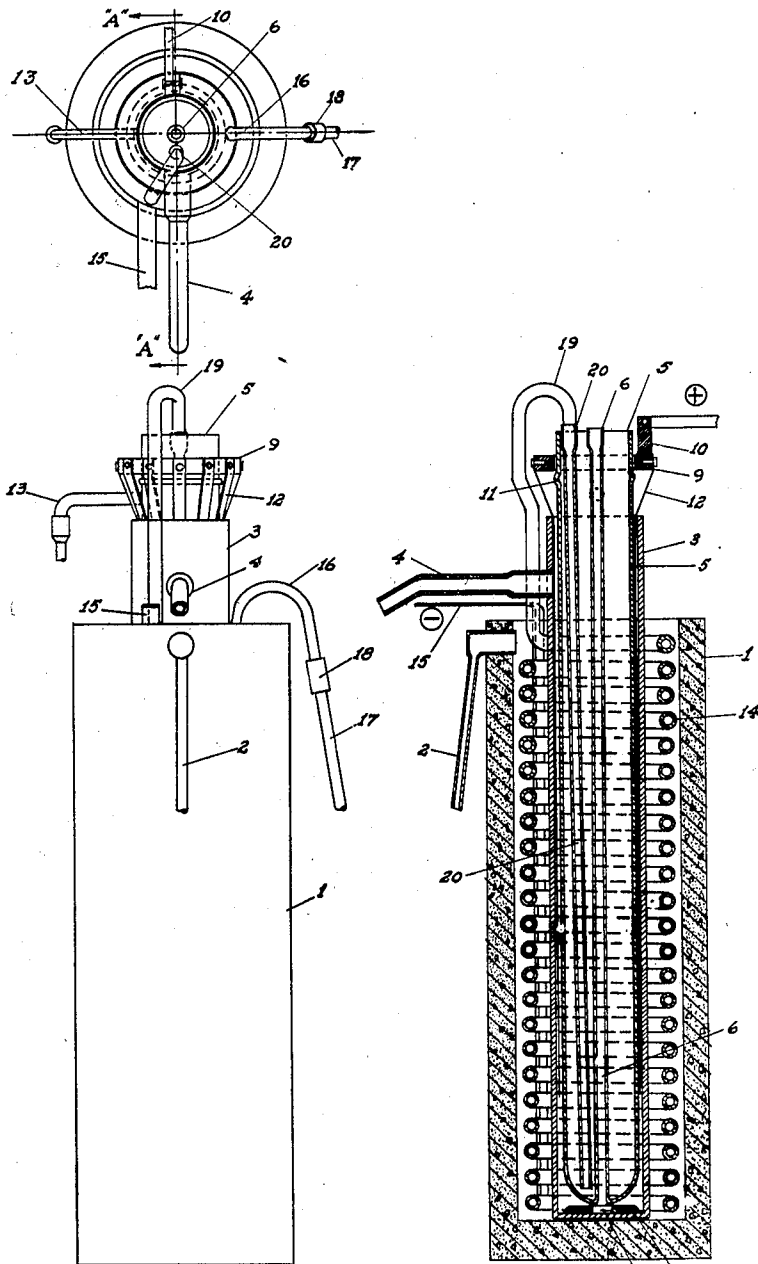


FIG. I.

SECTION AT A-A

FIG. II.

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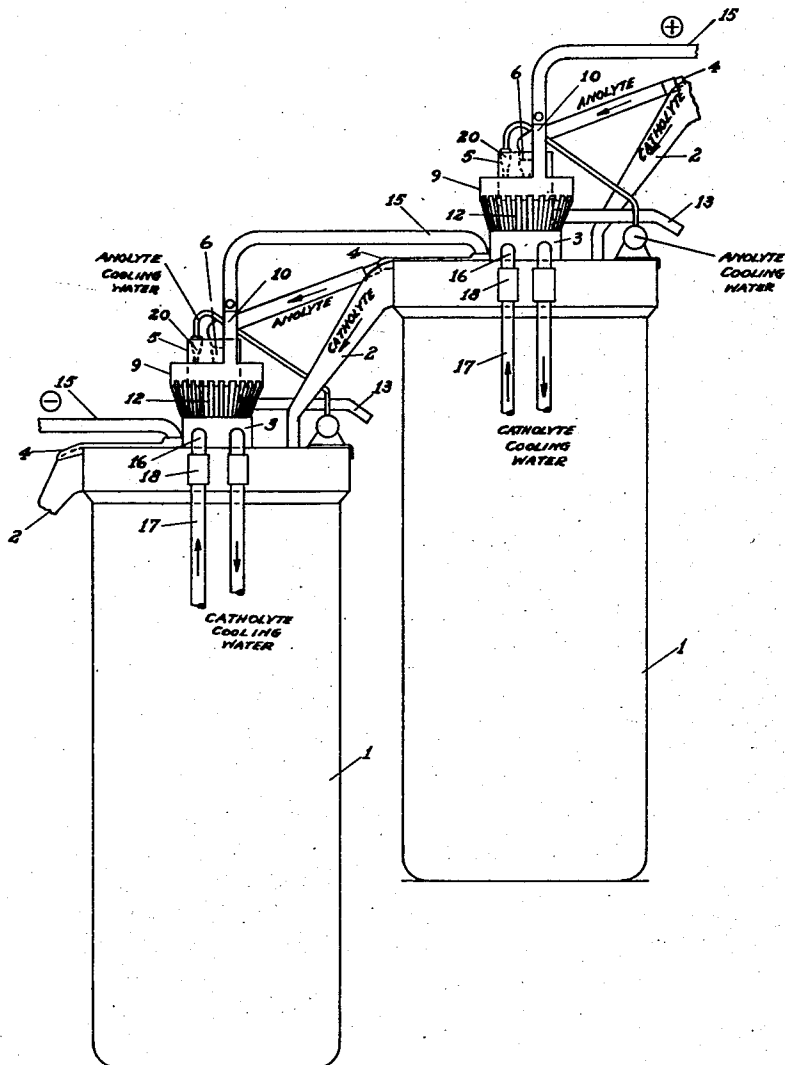


FIG III

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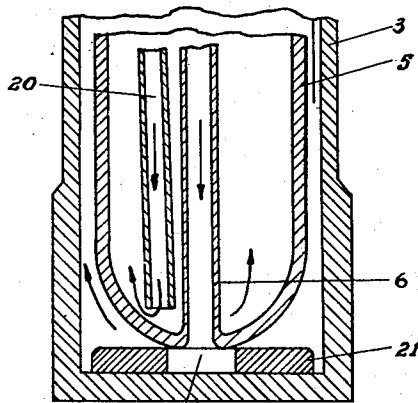
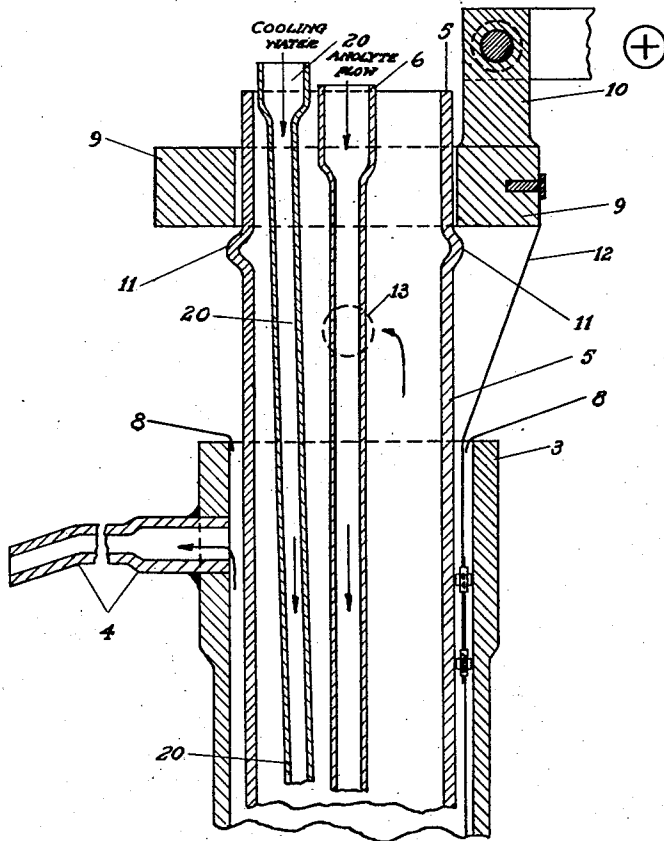


FIG IV

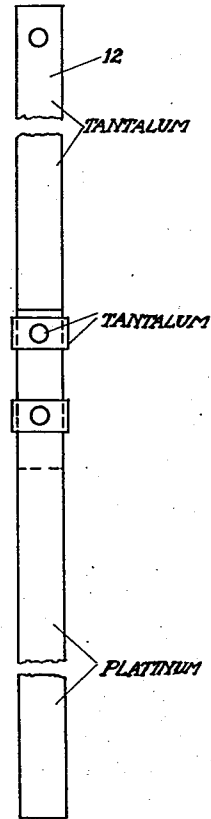


FIG. VI

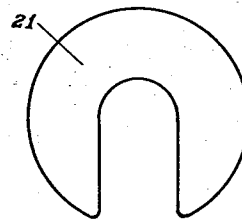


FIG. V

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1,937,621

ELECTROLYTIC APPARATUS

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Original application January 3, 1927, Serial No. 158,457, now Patent No. 1,837,177, and in Austria January 28, 1926. Divided and this application May 8, 1931. Serial No. 535,819

12 Claims. (Cl. 204—9)

This invention relates to the production of persulphuric acid and materials derived therefrom, such as persulphates and hydrogen peroxide, by electrolysis, and has for its object to provide an improved process and electrolytic cell whereby these results can be accomplished more efficiently and cheaply than heretofore and with a minimum of expense of investment in the platinum required for anodes. This application is a division of my copending application S. N. 158,457 which issued as U. S. Patent 1,837,177 on December 15, 1931. Persulphuric acid or the persulphates can be decomposed or hydrolyzed to give sulphuric acid, or sulphates, as the case may be, and hydrogen peroxide.

It has heretofore been proposed to electrolyze an aqueous solution of sulphuric acid in a cell having a platinum anode in the anolyte, and a lead cathode in the catholyte, the anolyte and the catholyte being separated by a porous diaphragm. Such arrangements have not heretofore to my knowledge been commercially successful for a number of reasons. Among these are excessive heat generated in the cell by internal resistance, decomposition of product and side reactions due to the heat generated, low current density, contamination of anolyte due to prolongation of the time of electrolysis in the effort to increase the yield, polarization of the anode, etc. It has been attempted to overcome the objection of heating by cooling the anode and the electrolyte, but these expedients have only been of slight benefit to the yield or to the efficiency and have not reduced the expense of installation and of maintenance to such extent as to be of practical benefit.

I have discovered that a minimum internal resistance of a diaphragm cell of this type is not only necessary to reduce heating but is also of decided advantage in permitting higher current concentrations to be used, and that the higher the current concentration used, the greater the unit conversion to persulphuric acid. I have further found that in order to avoid side reactions or decomposition in a cell having high current concentration and minimum internal resistance, the amount of anolyte between the anode and the diaphragm must be as thin as possible in the form of a thin sheet or film, and that such a film must be continually circulated both for the purpose of carrying away from the immediate anode surface the high concentration of persulphuric acid as rapidly as formed, and also the heat, and further to reduce any tendency to polarization. In such a cell I find it advantageous to cool both the anolyte and catholyte, but do not find it nec-

essary to use refrigeration for this purpose in order to maintain the desired working temperature at the desired high current concentration employed. Previous attempts at this electrolysis required electrolyte temperatures of below 10° C. to 15° C.

The above advantages are all realized in an electrolytic cell wherein the anolyte, diaphragm, catholyte and cathode are concentric, with the anode at the center because thereby its entire surface is effectively utilized and its volume is at a minimum. The anolyte is preferably circulated lengthwise of the anode as a thin sheet in a narrow annular space between the anode and diaphragm. Inasmuch as platinum is today the preferable anode material, the total cost of platinum in a large plant becomes very material, but by having a platinum anode at the center within the anolyte, or in a centrally located concentric anode chamber, the total investment for platinum is materially reduced. The lead cathode can conveniently be in the form of a coiled tube encircling the diaphragm, through which cooling water can be passed to maintain the desired catholyte temperature. The internal resistance of a cell constructed as above described is substantially less than that of any prior cell with which I am familiar, and a current concentration can be employed from two to upwards of five times that heretofore employed in any cell with which I am familiar. I have been able by using current concentrations of between 300 and 550 amperes per liter, and preferably about 400 to 450 amperes per liter to obtain exceptionally valuable results.

Previous attempts to produce per-sulphuric acid or persulphates in high concentrations furthermore have not been successful since in all cases the electrolysis was carried on in a large volume of liquid in a single vessel. This arrangement did not allow of rapid diffusion of the persulphuric acid from the anodes and decomposition and overheating resulted. I have overcome this by utilizing a small volume of liquid per unit of anode surface and by electrolyzing in this space with a high current concentration. In order now to increase the total overall concentration of persulphuric acid, a further feature of my invention comprises the operation in cascade of a number of such cells. Operating in this way I have obtained solutions containing up to 30% or more of per-sulphuric acid with high yields at a temperature of about 20° C. These remarkable results have hitherto never been attained. Inasmuch as a number of anodes and dia-

phragms as above described can be connected in parallel in one catholyte, it is within the broad scope of this invention to connect single cells in cascade or a plurality of units having a single catholyte and multiple anode units in cascade. Besides the advantage realized in increase of overall concentration of per-sulphuric acid by cascading of cells, I have found that while the anolyte may be circulated from cell to cell, and the catholyte similarly circulated from cell to cell, a decided gain in yield is obtained if the anolyte from the last unit, after being treated to separate hydrogen peroxide, is then passed through the catholyte circulating system before being returned to the anolyte circulating system. Apparently the cathodic action on this regenerated sulphuric acid removes substances which are otherwise deleterious in the anolyte. Make-up solutions of sulphuric acid may also be subjected to this cathodic treatment.

In order to carry out my improved process I have constructed an electrolytic cell of novel features. This will be described with reference to the attached drawings. Fig. I is an external front view of the cell; Fig. II is a vertical cross-section of a cell along line A—A of Fig. I, showing the arrangement of parts; Fig. III shows a cascade arrangement of cells for series operation in a continuous process; Fig. IV shows in detail the method of anode insertion in the anode chamber; Fig. V shows a slotted porous disk and Fig. VI shows one form of anode strip. The same numbers are used throughout to designate the same or similar portions of each cell.

Referring to the drawings, 1 is the cell container, constructed of material resistant to the action of the electrolyte or lined with such material, such as lead or a resinous compound. The container is provided with an overflow 2, at or near the top. The container is shown as having a round cross section but may be square or oval. In the center of the container is a cylindrical diaphragm 3 of thin porous material and closed at the bottom; this may be of unglazed porcelain. The space between the diaphragm and the container wall forms the cathode chamber. The cathode chamber is made large enough to carry a lead coil 14 which serves as the cathode and also for carrying cooling water. An overflow 4 is provided near the top of the diaphragm cylinder above the container wall. Inside the diaphragm cylinder is a glass tube 5 open at the top but sealed at the bottom having a glass tube 6 leading through the seal into the anode chamber at 7. An overflow 13 leads from near the top of the tube 5 over the top of the diaphragm. The tube 5 is of such diameter that a narrow annular space 8 of less than about 3 millimeters is formed between the tube and the diaphragm. This narrow space is the anode chamber. The glass tube 5 rests on a slotted porous disk 21 (Fig. V).

The anode may be any suitable arrangement of non-attackable metal having the proper electrolytic characteristics, such as platinum, inserted in the anode chamber 8. I prefer to construct my anode as follows:

A lead ring 9 having a connector 10 is fitted over the tube 5 and rests on a shoulder 11 formed on the tube. On the circumference of the ring 9 I fasten several strips 12 of platinum of such length that they reach well into the anode chamber. The length of the strips and the number of the strips may be varied to adjust the anode surface to any amount desired. The anode sur-

face is adjusted so as to give an anode current density of less than 2 amperes and preferably about 0.6 to 0.8 amperes per square centimeter. I have found that very thin platinum strips may be used; these are preferably reenforced by being rivetted or clamped to a strip of other metal not attacked during the electrolysis. Thus I have found that an anode strip of tantalum and platinum such as described in my U.S.P. 1,477,099 one form of which is shown in Fig. VI, gives satisfactory results even though the tantalum is in contact with the electrolyte. The strips are fastened to the lead anode ring by rivets, screws, or by brazing or soldering.

The cathode is formed by the coil of lead tubing 14 arranged in the cathode chamber. A lead connector 15 is fastened to the coils to act as the cathode lead. The lower end of the cathode coil is carried up and over the edge of the container as at 16 and connects with the cooling water supply 17 by a rubber or other non-conducting tube 18. The upper end 19 of the cathode coil is carried up and bent over so as to feed into a tube 20 inserted into the glass tube 5. Cooling of the anolyte can thus be effected. The cooling water enters from 17 passes into the coil 14 and out at 19 into the tube 20 to the bottom of 5 thence rising and overflowing through 13 to the sewer. The anolyte is cooled by contact with the outside of the glass tube 5. In some cases because of structural features it is preferable to cool the anolyte by a separate cooling water supply. In this case the cathode cooling water is run directly to the sewer and a separate cold water supply led to the tube 20 as shown in Fig. III.

In operation the anolyte is fed into the central tube 6 and flows to the bottom of the diaphragm cylinder and then rises in the anode chamber in contact with the anode and overflows through 4. The catholyte is fed into the cathode chamber and overflows through 2. The passage of the current between the electrodes oxidizes the sulphuric acid or the sulphates to per-sulphuric acid or to the corresponding persulphate as the case may be.

As noted above, the current concentration is a most important factor in this electrolysis. It is now seen that I can easily apply high current densities per unit of volume. For example, if the anode chamber has an average diameter of about 5.0 centimeters, a depth about 50 cm. and a thickness of 0.2–0.3 centimeter its volume will be about 0.18 to .23 liters. If 80 to 100 amperes are passed through there will be an anolyte current concentration of between 300–550 amperes per liter.

This type of cell construction enables me to obtain very low internal diaphragm resistances. The diaphragm can be made very thin as it does not support weight nor is it exposed to unbalanced pressures. I can thus obtain voltage drops of less than 0.5 volts across a porous ceramic diaphragm; the value of this is seen when it is realized that in previous work on this problem diaphragm resistances have been such that voltage drops of 0.8 to 1 volt have occurred.

The rate of flow of the anolyte can of course vary within wide limits. I have found that a suitable rate in a cell of the above dimensions is about 3.25 cc/ampere/minute. Thus if the cell is carrying a current of 100 amperes the flow will be about 0.325 liters per minute. At the rates and current densities noted above and at about 20° C. I have obtained a solution containing over 1% persulphuric acid from one passage through the cell. This solution can be recirculated in the

anode chamber of this cell to increase the per-sulphuric acid content; successive passages through such a cell will add to the per-sulphuric acid concentration until a concentration of well over 25% is reached.

In order to rapidly secure high concentrations of per-sulphuric acid in substantial amounts the anolyte is preferably passed through the anode chambers of several cells at a rapid rate. Any suitable number of these cells, for example 20, may be arranged in a cascade system and interconnected as shown in Fig. III. The anolyte is fed into the tube 6 of the topmost cell, passes through the anode chamber and overflows through 4 into the anode feed tube 6 of the next cell; the catholyte is likewise fed into the topmost cell and overflows through 2 into the cathode chamber of the next cell. The voltage drop across each cell is from 4 to 8 volts. This allows a series electrical connection of the cascade, giving for 20 cells a total voltage drop of about 80 to 160 volts.

In order to best utilize the current supply several of these series cascades may be arranged in parallel electrically. In this last case it is convenient to have a number of anode units including the diaphragm in one large cathode chamber containing one large lead cathode coil. These several anode units are connected together and then connected to the cathode of the preceding cell thus giving a series-parallel electrical connection. The anolytes from each anode unit in such an arrangement flow from one anode unit into a corresponding anode unit in the next set while the catholyte flows from the one common cathode chamber to the next.

When the anolyte leaves the lowest cell of such a cascade it contains a high concentration of persulphuric acid; the persulphuric acid is now decomposed to give hydrogen peroxide and sulphuric acid. The recovered acid is then raised to the upper cell and preferably made the catholyte supply. After passing the last cathode chamber the acid is returned to the upper cell and then added to the anolyte supply. This anolyte supply is adjusted by fresh acid and pure water so that its specific gravity will be preferably about 1.285 although other concentrations may be used.

The anode chambers of the cells of the dimensions given above in a bank of 20 would have a total volume of 3.6 to 4.6 liters. The electrolyte would then be subjected to anode action for a total period of about 10 to 15 minutes.

I have thus electrolyzed in a 17-cell bank of cells, as described above, a solution of sulphuric acid containing about 500 grams sulphuric acid per liter at a temperature of 20° C. to 21° C. and an anolyte current concentration of 400 amperes per liter. The anode current density was about 0.8 amperes/cm². A 30.8% solution of persulphuric acid was obtained with a current efficiency of 71.5%.

Solutions of sulphates can also be employed. Thus, I have electrolyzed a solution containing 20% ammonium sulphate, 2% sulphuric acid and 7½% K₂SO₄ at a temperature of 35° C. in the above apparatus. The per salts were obtained by cooling outside of the apparatus and showed a current efficiency of 74%. I have also obtained satisfactory results but lower current efficiencies at as low as 300 amperes per liter.

The cell described above is most suitable for my process but I do not wish to be limited to its structure since the high current concentration, thin flowing sheets of electrolyte and other features may be attained in other structures equivalent

to that described. Nor do I wish to be limited to the exact rates, temperature and compositions given. My invention, as will be seen from the above, is applicable to a great variety of solutions, therefore, in the appended claims wherein I refer to sulphuric acid solutions I mean not only an aqueous solution of sulphuric acid alone, but I also intend to include such solutions containing various addition agents, stabilizers, etc., from which per-sulphuric acid or per-salts can be obtained by anodic action.

I claim:

1. An anode for an electrolytic cell comprising an annular conducting ring having suspended from its circumference an anode member comprising platinum.

2. An anode for an electrolytic cell comprising an annular lead ring having suspended from its circumference anode members consisting of an upper tantalum portion and a lower platinum portion mechanically united.

3. An anode for an electrolytic cell comprising an annular lead ring having suspended from its circumference anode members consisting of a tantalum portion and a platinum portion mechanically united.

4. An anode member for an electrolytic cell comprising a supporting tantalum member having a platinum member mechanically fastened to and suspended from it.

5. An anode chamber unit for electrolytic cells comprising a cylindrical porous diaphragm having glass cylinder inserted therein so as to form a narrow annular anode chamber between said glass wall and said diaphragm.

6. An anode chamber unit for electrolytic cells comprising a cylindrical porous diaphragm having glass cylinder inserted therein so as to form a narrow annular anode chamber between said glass wall and said diaphragm of less than 0.3 mm. thickness.

7. An anode chamber unit for electrolytic cells comprising a cylindrical porous diaphragm provided with an overflow and closed at the bottom, a glass cylinder sealed at the bottom and provided with an overflow inserted in said porous cylinder so as to form a narrow annular anode chamber between said glass cylinder and said diaphragm and a glass tube inside said glass cylinder and leading through said sealed bottom and communicating with said anode chamber.

8. In an apparatus for the electrolytic production of persulphuric acid a centrally located annular anode chamber having a depth between anode and diaphragm of less than 0.3 centimeters.

9. A cell for the electrolytic production of persulphuric acid comprising a centrally located anode assembly consisting of an anode member in a narrow anode chamber, said chamber being formed by an impervious cylinder and a porous diaphragm concentric therewith, and a concentric cathode chamber about said diaphragm.

10. An electrolytic cell comprising a container, a coiled lead tube cathode, a cylindrical closed-bottom porous diaphragm provided with an overflow inside the coils of said cathode, a glass cylinder sealed at the bottom, and provided with an overflow, inserted in said porous cylinder so as to form a narrow annular anode chamber between said glass cylinder and said diaphragm, a glass tube inside said glass cylinder leading through said sealed bottom so as to communicate with said anode chamber and an anode suspended in said anode chamber.

11. An electrolysis system comprising a plurality of cells according to claim 9 in cascade flow arrangement and in series electrical connection, means connecting the anolyte overflow of each cell but the lowest with the anolyte supply tube of the next lower cell, means connecting the catholyte overflow of each cell but the lowest with the cathode chamber of the next lower cell, means for separately supplying anolyte and catholyte to the upmost cell and means for separately collecting said anolyte and catholyte flowing from the lowest cell.
12. An electrolysis system for the production of per salts comprising a plurality of cells, having anode and cathode chambers, in cascade flow arrangement and in series electrical connection, means connecting the anolyte overflow of each cell but the lowest with the anolyte supply tube of the next lower cell, means connecting the catholyte overflow of each cell but the lowest with the cathode chamber of the next lower cell, means for separately supplying anolyte and catholyte to the upmost cell and means for separately collecting said anolyte and catholyte flowing from the lowest cell.

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15	90
20	95
25	100
30	105
35	110
40	115
45	120
50	125
55	130
60	135
65	140
70	145
	150