G. A. GABRIEL.

PROCESS OF TREATING ELECTROLYTIC AND SIMILAR SOLUTIONS.

APPLICATION FILED MAY 31, 1907.

959,730.

Patented May 31, 1910.

2 SHEETS—SHEET 1.

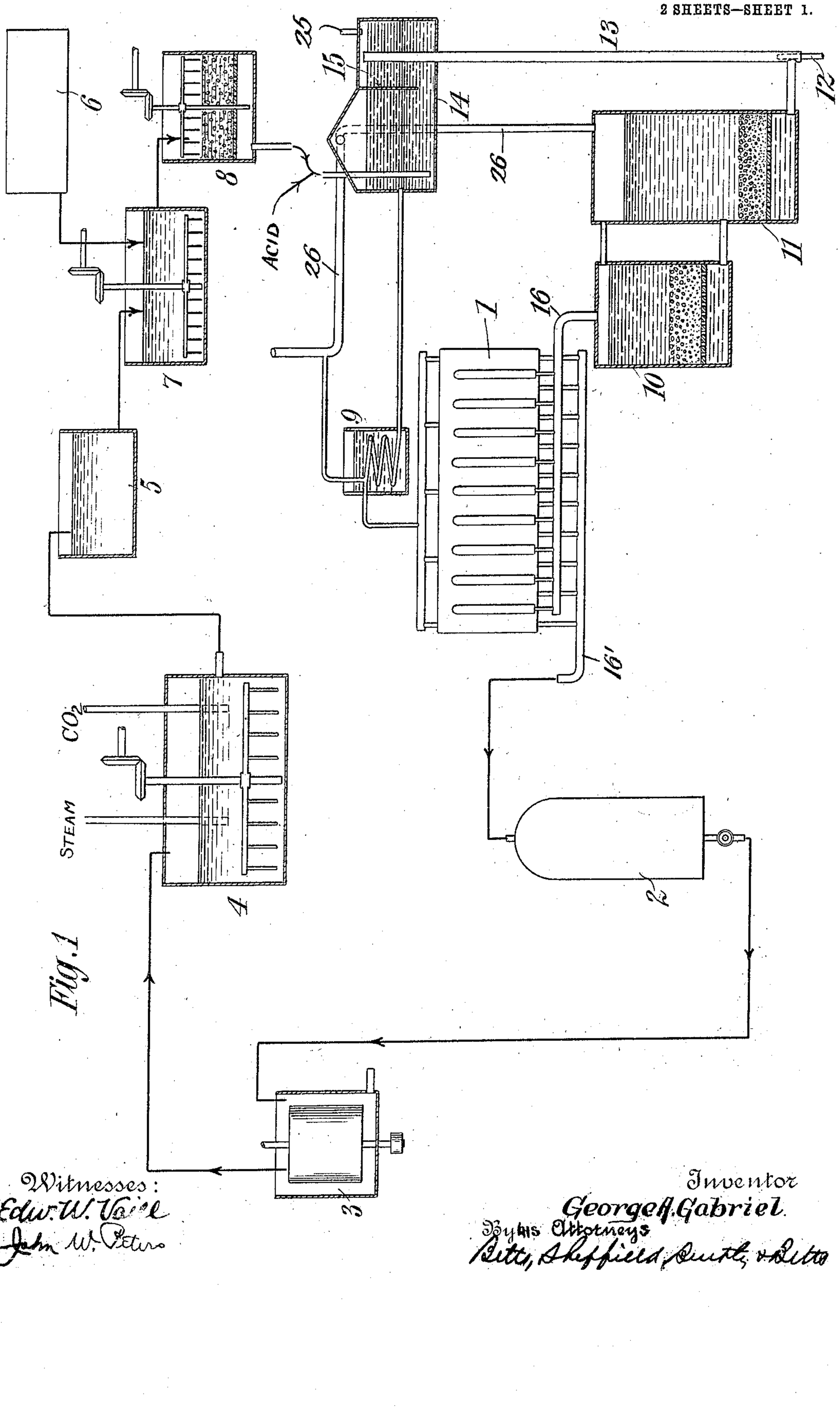

Fig. 1

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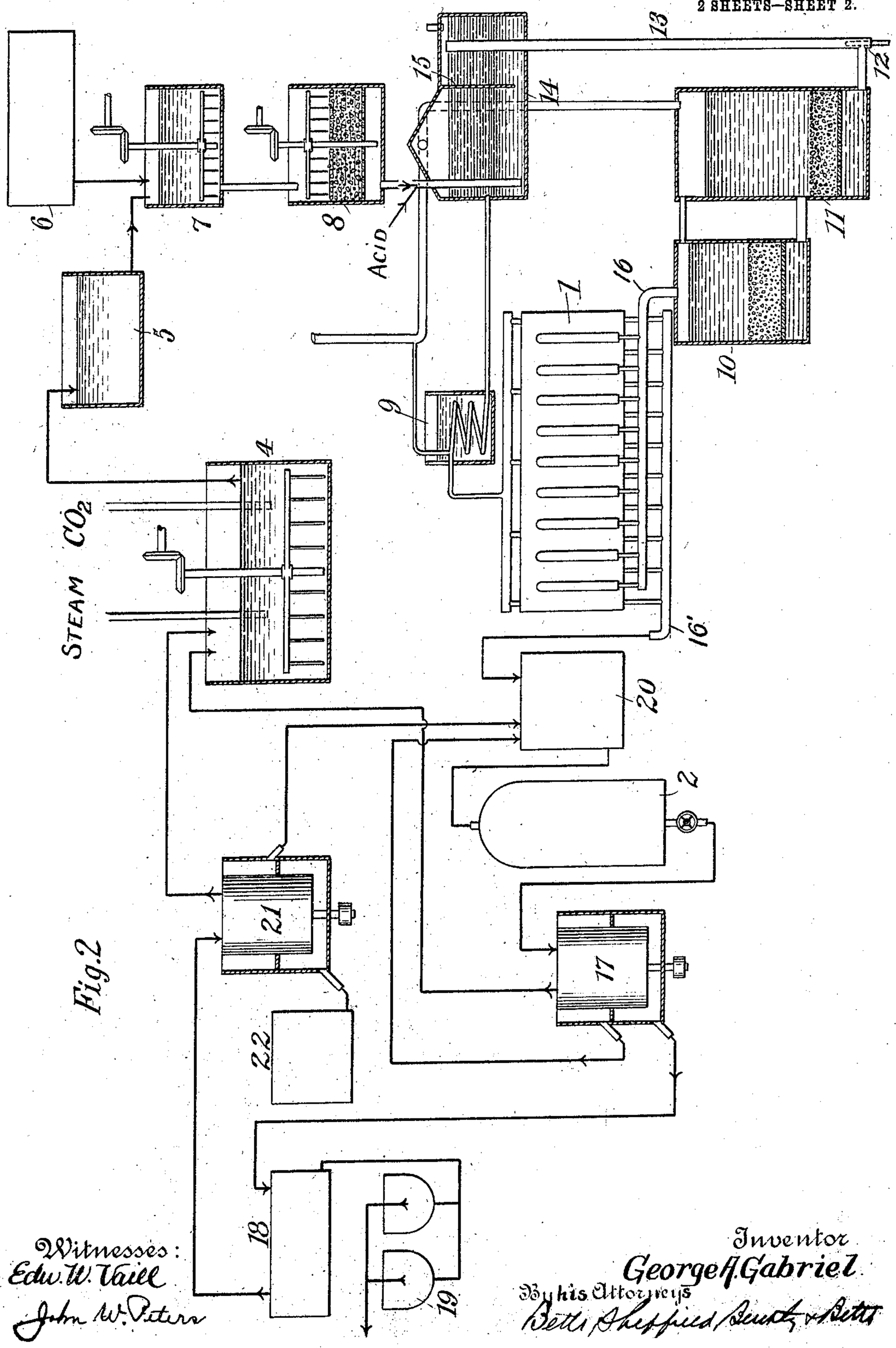

Fig. 2

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UNITED STATES PATENT OFFICE.

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PROCESS OF TREATING ELECTROLYTIC AND SIMILAR SOLUTIONS.

959,730. Specification of Letters Patent. Patented May 31, 1910.

Application filed May 31, 1907. Serial No. 376,647.

To all whom it may concern:

Be it known that I, GEORGE A. GABRIEL, a citizen of the United States, and a resident of the borough of Brooklyn, in the city and State of New York, have invented certain new and useful Improvements in Processes of Treating Electrolytic and Similar Solutions, of which the following is a full, clear, and complete disclosure.

This invention relates to processes or methods of forming or purifying solutions of different salts used in large quantities in the chemical arts, and is particularly applicable to the purification and production of solutions used in electrolytic cells, such as of the Hargreaves or vertical type, having the anode and cathode chambers separated by a diaphragm for producing chlorin and caustic soda by the electrolysis of brine. In electrolytic cells of this type, the electrolyte passes through the diaphragm owing to the action of the electric current and the hydrostatic pressure of the anolyte and is acted upon at the cathode. However, more anolyte passes through the diaphragm than is decomposed at the cathode and the liquid discharged from the cathode chamber, therefore, contains some of the active or undecomposed electrolyte, which, if not collected and separated from the products of decomposition, would be wasted. One of the objects of my invention, therefore, is to separate the active electrolyte discharged from the cathode chamber from the products of decomposition, so that the same may be returned to the anode chamber of the cell in the form of pure electrolyte.

One feature of my invention has for its object the establishing of complete cycles or circuits through which the solutions used may be continuously passed so that the impure or partly spent solution may be successively treated in series of steps to purify or strengthen the same and then immediately be returned to the apparatus in which it is used, while at the same time the by-products are reduced to commercial substances in the form of solids or solutions.

A further object of my invention is to provide processes of the nature above mentioned that are of high efficiency, both as to materials employed and the energy consumed, and also that lessen the time and labor which has heretofore been necessary in producing similar results.

These and other objects and features of my invention will be hereinafter more fully set forth and claimed in the accompanying claims.

Briefly, one embodiment of my invention comprises concentrating the active electrolyte of the partly decomposed or impure solution from an electrolytic cell or similar apparatus in which it has been used, to a salt, or to a substantially solid state, dissolving the same in the presence of heat and at the same time converting the remaining products of decomposition into compounds, such as carbonates which may precipitate the impurities of the raw or new electrolyte, after which the impurities may be filtered out and the electrolyte returned to the electrolytic cell or other apparatus or process for further decomposition or treatment. The concentration is preferably accomplished by the use of suitable evaporators and by centrifugal separators or driers, the liquid thrown off by the latter either being subsequently changed to a solid form or allowed to remain as a liquid, thereby constituting two different forms of finished by-product. After the electrolyte has been filtered to remove the precipitate, and before returning to the electrolytic cell or other apparatus, it is preferably treated with an acid which reacts upon the remaining small amounts of the products of decomposition which have been converted into carbonates, such as sodium carbonate, and neutralizes the latter, forming solutions of salts which are not injurious to the further use of the brine.

In the use of electrolytic cells it is desirable that the electrolyte may be continuously supplied to the cell and also that the electrolyte may be continuously purified during the operation of the cell, thereby obviating the necessity of interrupting the electrolytic process for the purpose of replenishing or cleansing the fluid.

When the process above outlined is used for the purpose of utilizing the discharge from the cathode chamber for purifying and producing the liquid supplied to the anode chamber of an electrolytic cell, I may combine the same with a process which is carried out in the circulating system connected with the anode chamber of the electrolytic cell. The action of the anolyte of the electrolytic cell upon the anode and other parts

with which it comes in contact causes the anolyte to take up certain impurities in the form of solids and gases which, if allowed to remain in the anolyte, impair its action. Briefly, this process of renewing and purifying the anolyte comprises withdrawing the anolyte from the cell, passing the same through suitable bodies of the salt used in solution in the anode chamber, filtering, freeing from entrained gases or air, mixing with additional quantities of the fresh anolyte equal, at least, to the amount of the anolyte that has passed through the diaphragm or been decomposed, heating the mixture to substantially the temperature maintained in the electrolytic cell and then returning to the anode chamber. This process is preferably in continuous operation, the fresh anolyte being continuously supplied in the requisite quantities to the circulating system or process. The first process or series of steps above mentioned constitutes a cycle in the treatment of the partly decomposed electrolyte from the cathode chamber and is in the nature of a continuous circulation of the active undecomposed electrolyte from the cathode chamber to the anode chamber of the cell. The second process or series of steps constitutes a cycle for the purification and strengthening of the anolyte and is a continuous circulation of the liquid. From the point at which the active purified electrolyte resulting from the first or main cycle or circulation is added to the second or auxiliary cycle or circulation, until the electrolyte enters the anode chamber of the cell, the two cycles are preferably coincident. The main cycle of the process supplies the cell with an amount of the electrolyte equal to that discharged into the cathode chamber and that decomposed, while the auxiliary cycle or circulation is of a larger volume and continuously and rapidly purifies and strengthens the electrolyte in the anode chamber.

For descriptions of different embodiments of my invention which I deem preferable, reference may be had to the following specification and to the accompanying drawings forming a part thereof, in which—

Figure 1 is a diagram of essential steps of one form of my invention and also indicating the apparatus employed therewith, and Fig. 2 is a similar diagram showing additional features of the process.

Referring to Fig. 1 the numeral 1 indicates an electrolytic cell of the Hargreaves or vertical type from which the effluent or partly decomposed electrolyte from the cathode chamber is discharged. In the case of the electrolysis of brine this effluent contains caustic soda and unused sodium chlorid. The effluent emerges from the cell 1 by the pipe 16′ and is first passed through suitable concentrating apparatus, such as the evaporator 2 and the centrifugal separator or drier 3, which reduce the solution to the form of the salt of sodium chlorid, moistened with a slight amount of water, and traces of caustic soda. The salt is then dissolved in water with the addition of steam, for heating, and a suitable re-agent, such as carbon dioxid, is also added. The carbon dioxid acts upon the remaining caustic soda or similar alkali and produces sodium carbonate or other carbonates. This step is preferably carried out in an agitator as indicated at 4, which thoroughly mixes the ingredients referred to with the solution of sodium chlorid. When the liquid containing the sodium carbonate in solution, together with the solution of sodium chlorid leaves the agitator, it has a specific gravity of about 25.5° B. It is stored in a suitable reservoir 5, where it is allowed to cool, and there becomes supersaturated. The sodium carbonate is then decomposed and produces an insoluble salts which are precipitated. This precipitation is preferably accomplished by adding to the solution suitable quantities of fresh brine from a source of supply such as the reservoir 6, and which usually contain impurities in the form of salts of calcium, magnesium, etc. These salts act upon the sodium carbonate or similar substances produced by the conversion of the alkali, and form insoluble salts, such as calcium carbonate, which are precipitated.

The mixing of the brine with the solution being treated and the precipitation of the impurities are preferably carried on in a mixer indicated at 7. The mixture is then passed through a filter, as indicated at 8, to free the same from the precipitated matter. After passing through the filter a small quantity of acid may be added to the mixture, and this is for the purpose of neutralizing any excess alkali carbonate, thereby converting the same into salts that are not injurious to use in the electrolytic cell or other apparatus. The purified mixture or solution is then added to the circulating cycle or system connected with the anode chambers of the electrolytic cell or cells.

This preferably comprises, first, heating the electrolyte to a temperature approximating that of the anolyte, and is accomplished by passing the electrolyte through a coil placed in a tank of hot water or otherwise externally heated, as indicated at 9. After passing into the anode chamber and being acted upon by the electric current, the electrolyte is then withdrawn through the pipe 16 and passed through a plurality of filters such as indicated at 10 and 11, which filters contain a quantity or layer of salt crystals whereby any weakening of the electrolyte may be compensated for. The filter 11 is preferably provided with an outlet pipe 26 for the escape and collection of gas en-

trained in the electrolyte. These filters remove any particles of foreign or solid matter and dirt which may be the result of the action of the electrolyte upon the anode, or other parts of the electrolytic cell. The electrolyte is then conducted to, and mixed with, the incoming brine or electrolyte, the circulation being aided by suitable means, such as an air lift, as indicated at 12. Air is introduced into the vertical pipe 13, thereby lowering the effective specific gravity of the mixture causing its flow upward. The mixing of the filtered electrolyte from the anode chamber with the purified brine being introduced, is preferably accomplished in a receptacle 14 which has a central partition 15 extending toward the bottom of the receptacle, and beneath which the liquid must pass. The first compartment formed by the partition 15 is provided with an air outlet 25 through which the air introduced by the air lift may be discharged. In passing into the second compartment of the receptacle 14, any gas contained in the electrolyte is allowed to pass off through a connection with the pipe 26, and as the new or purified electrolyte mixed with the brine is also conducted to this compartment, they both become mixed and then continue on through the circulating systems.

The above is one of the simplest embodiments of my invention, but certain changes or additions may be made therein, as indicated in Fig. 2. In this embodiment of the invention, the automatic centrifugal separator 17 is preferably provided with two liquid discharge sections, from the lower one of which strong caustic soda with some unused sodium chlorid is discharged. This is then carried to a "boat pan" 18, from which it is fed into suitable evaporating kettles 19. The product of these kettles then forms one of the finished by-products, such as caustic soda in solid form.

Water is added to the upper section of the centrifugal separator 17, for washing the concentrated salts therein, and this water, containing some salt in solution and a slight amount of alkaline matter, such as the caustic soda, is carried to a storage tank 20, into which the effluent of the cell preferably discharges before passing to the evaporator 2. This washing solution is thereby returned to the main circuit of the process and then passes through the evaporator and the concentrator and is subjected to the steps of the process just described. I also prefer to employ a second automatic centrifugal separator 21. This also has upper and lower liquid discharge sections, the upper one of which is supplied with water for washing the crystals or solid matter being treated thereby. This washing water as discharged contains a slight amount of caustic soda, together with a slight amount of sodium chlorid that has been dissolved from the crystals in the separator, and is then also added to the storage tank 20 and subjected to the concentrating steps of the process. The discharge from the lower section of the separator 21 is conducted to a storage tank 22 and since said discharge consists of practically pure caustic soda, the contents of the storage tank constitute one form of commercial liquid by-product.

The crystals or solid matter discharged by the centrifugals 17 and 21, are carried to the agitator 4 and heated in a suitable manner such as by the introduction of steam, said steam also of course providing water which dissolves the solid matter supplied to the agitator. The crystals added to this agitator also contain a small amount of caustic soda, and in order to convert this into a substance which may be precipitated, I add a suitable reagent, such as carbon dioxid, which acts upon the caustic soda producing sodic carbonate. The mixture thereby obtained, in this instance the solution of salt which is heated to a high temperature and therefore becomes supersaturated, together with the sodic carbonate in solution, is conducted to a storage tank 5, in which the solution is allowed to cool. The remainder of the process is the same as before described in connection with Fig. 1; that is to say, the sodic carbonate precipitates the impurities of the new brine, in the mixer 7. The mixture is then filtered and a slight amount of acid added to neutralize whatever slight excess of sodic carbonate may remain in the mixture. The mixture or solution is then supplied to the circulating system connected with the anode chambers of the electrolytic cells as before described.

In using the term "brine" I wish to be understood as referring to a solution of any salt that is used as the principal substance to be treated in the process in conjunction with an electrolytic cell or other apparatus or process.

I wish it to be understood that I do not consider the invention to be limited to the exact details of arrangement, materials and procedure shown and described, for the invention is applicable to the purification of solutions used in other apparatus and processes and to solutions used in other types of electrolytic cells.

Various modifications are also possible and will occur to persons skilled in the art, without departing from the spirit and scope of my invention.

Having thus described these forms of my invention, what I claim and desire to protect by Letters Patent is:

1. In an electrolytic process, in combination with the step of electrolysis, a continuous cycle of steps constituting a circulation of the electrolyte, for supplying pure

electrolyte equal to that decomposed or discharged and a cycle of steps constituting an auxiliary circulation for purifying and strengthening the electrolyte, treating in said cycle a greater volume than in the main cycle.

2. In an electrolytic process, in combination with the step of electrolysis, a continuous cycle of steps constituting a circulation of the electrolyte and comprising, concentrating the same to solid form, dissolving, and introducing amounts of raw electrolyte, and a cycle of steps constituting an auxiliary circulation of such electrolyte in the form of an aqueous solution, and including the steps of purifying and strengthening the same.

3. In an electrolytic process, in combination with the step of electrolysis, a continuous cycle of steps constituting a circulation of the electrolyte and comprising concentrating the same to solid form, dissolving and introducing amounts of new electrolyte, and a cycle of steps constituting an auxiliary circulation of the electrolyte in the form of an aqueous solution and comprising the step of adding quantities of the pure electrolyte.

4. In an electrolytic process, in combination with the step of electrolysis, a continuous cycle of steps constituting a circulation of the electrolyte and comprising, concentrating and separating said electrolyte from the products of decomposition so that the same may be again submitted to electrolysis, and a cycle of steps constituting an auxiliary circulation of the anolyte for purifying and strengthening the same.

5. In an electrolytic process, in combination with the step of electrolysis, a continuous cycle of steps constituting a circulation and treatment of the electrolyte for eliminating the products of decomposition and supplying pure electrolyte, and a cycle of steps constituting an auxiliary circulation for purifying and strengthening the electrolyte, said cycles including the step of heating to the temperature of the electrolyte maintained during electrolysis.

6. In an electrolytic process, in combination with the step of electrolysis, a continuous cycle of steps constituting a circulation and treatment of the electrolyte for eliminating the products of decomposition and supplying pure electrolyte, and a cycle of steps constituting an auxiliary circulation for purifying and strengthening the electrolyte, the last step of said cycles being the heating of the electrolyte to its temperature during electrolysis.

7. In an electrolytic process, in combination with the step of electrolysis, a continuous cycle of steps constituting a circulation and treatment of the electrolyte for supplying pure electrolyte, and a cycle of steps constituting an auxiliary circulation, comprising, the step of removing solid impurities, the step of removing entrained gases, and the step of supplying additional quantities of pure electrolyte.

8. In an electrolytic process, in combination with the step of electrolysis, the process of treating the discharged electrolyte remaining in the catholyte, which comprises removing the undecomposed electrolyte by concentrating the main body of the products of decomposition, converting the remaining products of decomposition contained therein into substances which purify the raw electrolyte, and then submitting the purified electrolyte to said step of electrolysis.

9. In an electrolytic process, in combination with the step of electrolysis, the process of treating the discharged electrolyte remaining in the catholyte, which comprises removing the undecomposed electrolyte associated with a predetermined amount of the product of decomposition, converting the said product of decomposition into substances which purify the raw electrolyte, adding definite amounts of the raw electrolyte, and then submitting the purified electrolyte to said step of electrolysis.

10. In an electrolytic process, in combination with the step of electrolysis, the process of treating the discharged catholyte containing the undecomposed electrolyte, which comprises, separating out said electrolyte associated with a predetermined amount of the product of decomposition, converting said product into a purifier for the raw electrolyte, adding quantities of said raw electrolyte, and then submitting the liquid obtained to said step of electrolysis.

11. In an electrolytic process, in combination with the step of electrolysis, the process of treating the discharged product containing the original undecomposed electrolyte, which comprises separating out said electrolyte associated with a predetermined amount of the product of decomposition, converting said product into a substance which will precipitate the impurities of the raw electrolyte, adding quantities of said raw electrolyte, removing the precipitate, and then submitting the liquid obtained to said step of electrolysis.

12. In an electrolytic process, in combination with the step of electrolysis, the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, concentrating to solid form and separating out the said electrolyte associated with a small amount of the product of decomposition, washing the same with water, reconcentrating said wash water, treating said concentrated electrolyte and associated product to form a purifier for the raw electrolyte, adding quantities of the raw electrolyte, and then submitting to said step of electrolysis.

13. In an electrolytic process, in combina-

tion with the step of electrolysis, the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, concentrating the said electrolyte to solid form, mechanically separating said concentrated electrolyte associated with a small amount of the product of decomposition, washing the same, dissolving, and then submitting to said step of electrolysis.

14. In an electrolytic process in combination with the step of electrolysis, the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, concentrating said electrolyte, separating out said electrolyte associated with a small amount of the product of decomposition, said concentration and separation being effected in a plurality of similar successive steps and producing the electrolyte as a solid after each step, dissolving the same, and then submitting to said step of electrolysis.

15. In an electrolytic process in combination with the step of electrolysis, the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, separating out said electrolyte associated with a small amount of the product of decomposition, converting the latter into a substance which may be used for precipitating, and then adding a solution containing matter to be precipitated.

16. In an electrolytic process in combination with the step of electrolysis, the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, separating out said electrolyte associated with a small amount of the product of decomposition, precipitating thereby the impurities in the raw electrolyte, neutralizing any excess of the converted product of decomposition, and then submitting to said step of electrolysis.

17. In an electrolytic process, in combination with the step of electrolysis the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, separating out said electrolyte associated with a small amount of the product of decomposition, precipitating, by a suitable mixture thereof with reagents, the impurities in the raw electrolyte, adding a suitable acid to neutralize any excess of said reagents, and then submitting to said step of electrolysis.

18. In an electrolytic process, in combination with the step of electrolysis the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, separating out said electrolyte associated with a predetermined amount of the product of decomposition, treating the same with a gaseous reagent, adding a supply of the raw electrolyte, removing the separated impurities thereby obtained, and then submitting the purified electrolyte to said step of electrolysis.

19. In an electrolytic process in combination with the step of electrolysis, the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, separating out said electrolyte associated with a predetermined amount of the product of decomposition, heating to a predetermined temperature, treating with a gaseous reagent, adding a supply of the raw electrolyte, removing the separated impurities thereby obtained, and then submitting the purified electrolyte to said step of electrolysis.

20. In an electrolytic process in combination with the step of electrolysis, the process of treating the discharged product containing the original undecomposed electrolyte, which comprises, separating out said electrolyte associated with a predetermined amount of the product of decomposition, treating with carbon dioxid, adding a supply of the raw electrolyte, removing the separated impurities thereby obtained, and then submitting the purified electrolyte to said step of electrolysis.

21. The process of purifying an electrolyte discharged from a cathode chamber, which comprises, separating out the undecomposed electrolyte associated with a predetermined amount of the product of decomposition, converting said associated product of decomposition into a purifier for the raw electrolyte, and adding a supply of said raw electrolyte.

22. The process of purifying an electrolyte, which comprises, separating the undecomposed electrolyte associated with a predetermined amount of the product of decomposition, converting said associated product of decomposition into substances which will precipitate the impurities of the raw electrolyte, adding raw electrolyte, and removing the precipitate by filtration.

23. The process of purifying an electrolyte which comprises, separating undecomposed electrolyte associated with a predetermined amount of the product of decomposition, converting said associated product of decomposition into substances which will precipitate the impurities of the raw electrolyte, adding raw electrolyte, removing the precipitate, and then neutralizing any excess of the converted product of decomposition.

24. In an electrolytic process, in combination with a continuous main circulation of the electrolyte discharged from a cathode chamber, for purifying and supplying the electrolyte, a local or auxiliary circulation of the anolyte, including the steps of electrolysis and filtering.

25. In an electrolytic process, in combina-

tion with a continuous main circulation of the electrolyte discharged from a cathode chamber, for purifying and supplying the electrolyte, a local or auxiliary circulation of anolyte, including the steps of electrolysis, filtering, and extracting the entrained gases.

26. In an electrolytic process, in combination with a continuous main circulation of the electrolyte discharged from a cathode chamber, for purifying and supplying the electrolyte, a local or auxiliary circulation of the anolyte, including the steps of electrolysis, passing through crystals of the anolyte, and filtering.

27. In an electrolytic process, in combination with a continuous main circulation of the electrolyte discharged from a cathode chamber, for purifying and supplying the electrolyte, a local or auxiliary circulation of the anolyte, including the steps of electrolysis, passing through crystals of the anolyte, filtering, extracting the entrained gases, and heating.

28. The process of treating solutions discharged from the cathode chambers of electrolytic cells, which comprises removing the undecomposed electrolyte associated with a small amount of the product of decomposition, converting the latter into a purifier for the raw electrolyte, adding such raw electrolyte, removing the separated impurities, subjecting the resulting electrolyte to the action of the electrodes, replenishing with a suitable salt, filtering, adding fresh electrolyte, and then submitting to the action of the electrodes.

29. The process of treating electrolytes which comprises, subjecting the same to the action of electrolysis in the anode chamber, withdrawing the anolyte, replenishing the same with a suitable salt, filtering, adding fresh quantities of the anolyte equal to the electrolyte discharged or decomposed, and again submitting the anolyte to electrolysis.

30. The process of treating electrolytes which comprises, subjecting the same to the action of electrolysis in the anode chamber, withdrawing the anolyte, replenishing and purifying the same, adding fresh quantities of the anolyte equal to the electrolyte discharged or decomposed, and again submitting the anolyte to electrolysis.

31. The process of treating electrolytes which comprises, heating the same, subjecting the same to the action of electrolysis in the anode chamber, withdrawing the anolyte, replenishing and purifying the same, adding fresh quantities of the anolyte equal to the electrolyte discharged or decomposed, and again submitting the anolyte to electrolysis.

32. The process of treating electrolytes which comprises, heating the same, subjecting the same to the action of electrolysis in the anode chamber, withdrawing the anolyte, replenishing the same with a suitable salt, filtering, adding fresh quantities of the anolyte equal to the electrolyte discharged or decomposed, heating, and again submitting the anolyte to electrolysis.

33. The process of treating electrolytes which comprises, heating the same, subjecting the same to the action of electrolysis in the anode chamber, withdrawing the anolyte, replenishing and filtering the same, cooling, changing the effective specific gravity, removing the entrained gases, mixing with fresh quantities of the anolyte equal to the electrolyte discharged or decomposed, heating, and again submitting the anolyte to electrolysis.

34. The process of treating electrolytes which comprises, heating the same, subjecting the same to the action of electrolysis in the anode chamber, withdrawing the anolyte, replenishing the same with a suitable salt, filtering, introducing air for changing the effective specific gravity, removing said air, removing the entrained gases, adding fresh quantities of the anolyte equal to the electrolyte discharged or decomposed by a cell, heating, and again submitting the anolyte to electrolysis.

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