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G. W. NISTLE & R. L. GIFFORD.  
ELECTROCHEMICAL CONCENTRATION OF LIQUIDS.

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Fig. 1.

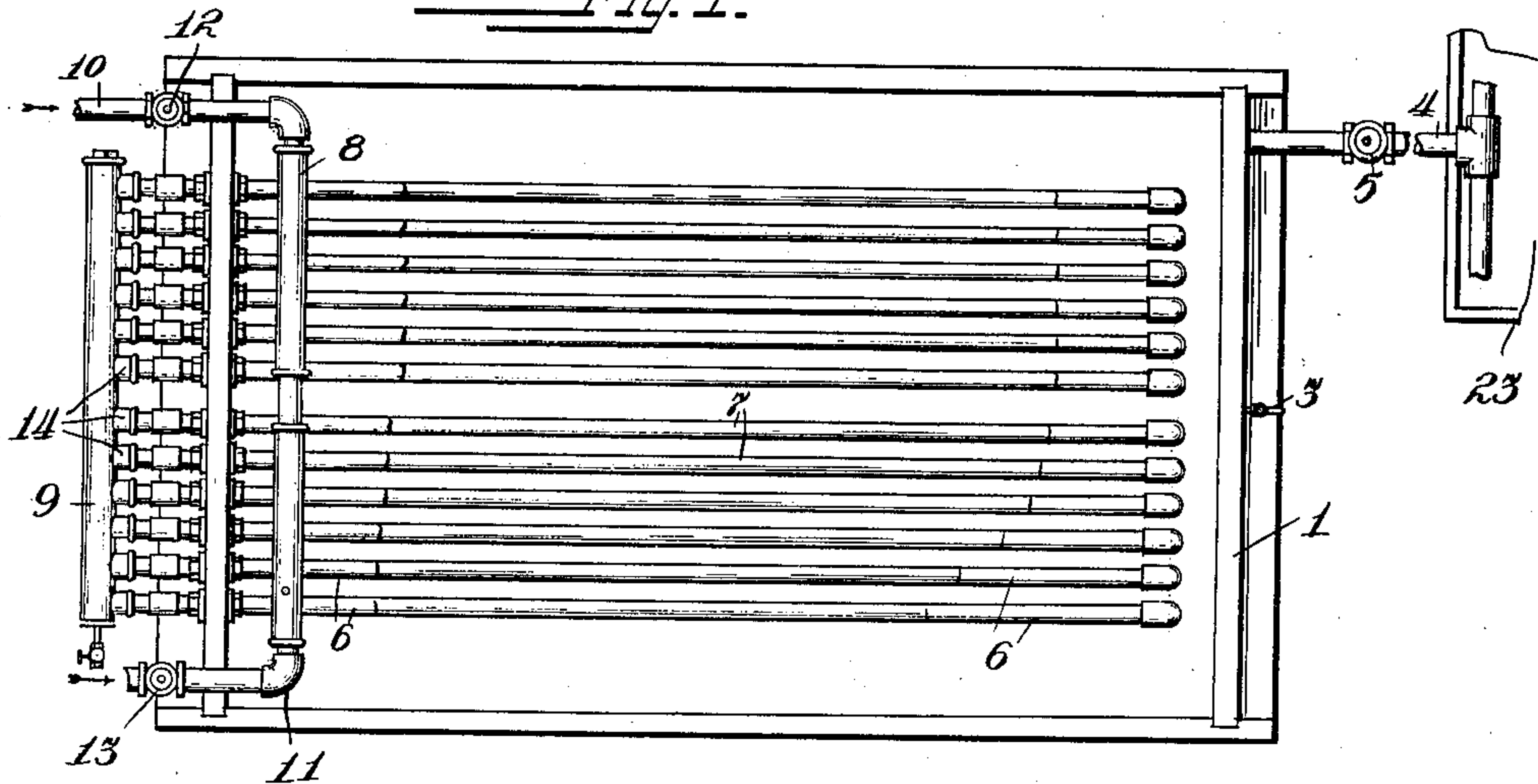
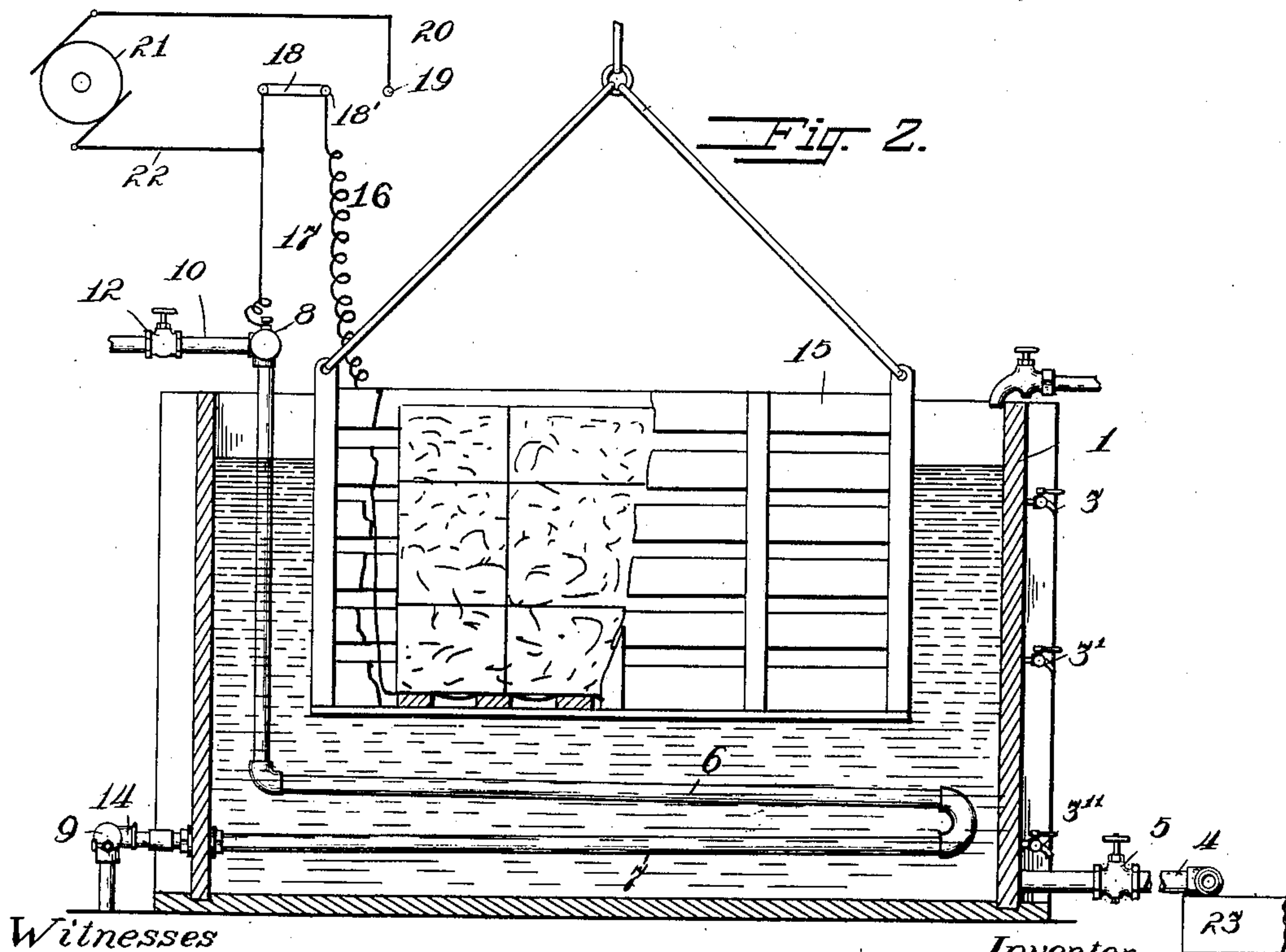


Fig. 2.



Witnesses

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# UNITED STATES PATENT OFFICE.

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## ELECTROCHEMICAL CONCENTRATION OF LIQUIDS.

No. 896,749.

Specification of Letters Patent.

Patented Aug. 25, 1908.

Application filed June 22, 1907. Serial No. 380,245.

*To all whom it may concern:*

Be it known that we, GEORGE W. NISTLE and ROBERT L. GIFFORD, citizens of the United States, residing, respectively, at  
5 North Muskegon, in the county of Muskegon and State of Michigan, and Chicago, in the county of Cook and State of Illinois, have invented a certain new and Improved Process in the Electrochemical Concentration of Liquids, of which the following is a specification.

This invention relates to an improved process for the electro chemical concentration of liquids, and relates more specifically to a process whereby the heat and chemical  
10 reaction incident to electrolysis is availed of to effect, or aid in effecting, the concentration of liquids of that character capable of acting as electrolytes.

Among the objects of the invention are to  
20 expedite the concentration of liquids; to facilitate the recovery of the maximum amount of a desired chemical in waste liquids of the character contemplated; to provide a process which expedites the conversion of the  
25 liquid into that condition which is favorable for crystallization of the contained chemical, following the concentrating part of the process; to provide a process which avoids repeated handling or transferring of the material, and in general to provide an improved  
30 process of the character referred to.

To the above ends the invention consists in the matters hereinafter described, and more particularly pointed out in the appended  
35 claims.

In the manufacturing art it is common to cleanse iron parts by placing them in an acid pickle for a desired length of time, and after such pickle has been used for a certain period  
40 its free acid is largely eliminated and the bath must be renewed. The partially exhausted pickle liquor is frequently thrown away, but it is sometimes concentrated and the free acid satisfied by supplying its affinity for iron in order that the chemical may be  
45 precipitated as a salt of iron.

As a specific example, it is customary to pickle sheet iron in a solution of sulfuric acid preparatory to using the iron for making  
50 enameled ware, and after the acid solution has become so weakened that the pickling process becomes uneconomical because of the length of time required to clean the iron, the liquid is sometimes concentrated by applying  
55 heat and evaporating it, and at the same time

scrap iron or filings are placed in the solution in order that the free acid may be fully satisfied. Thereafter, when the solution has been concentrated to the proper degree, the solution is cooled, whereupon the sulfate of iron  
60 crystallizes out; this being the by-product to be recovered in this instance.

We have discovered that galvanic action or electrolysis may be brought into use and used as an auxiliary in the concentration of such  
65 liquids with a marked shortening of the time required for concentration and a substantial increase in economy.

Describing the process in general terms, we place the liquid to be concentrated in any  
70 suitable receptacle within which is arranged a heating coil or the like which should, of course, be made of such metal as to be unaffected or substantially unaffected by the solution. Through this heating coil or the  
75 like is circulated a heat medium, such as steam or warm water, and within the solution and exposed to the action thereof is placed iron (usually scrap iron) to supply the affinity of the acid therefor. Now, inasmuch  
80 as we have the elements necessary to form a galvanic couple, in that the iron is attacked chemically by the acid, the acid is an electrolyte and the heating coil may be used as the negative, we electrically connect the  
85 mass of iron with the heating coil and avail of the galvanic action which ensues as a means of hastening the process.

Describing the method more specifically, and as carried out by the apparatus shown in  
90 the drawing, which is well suited for that purpose, 1 designates as a whole a suitable tank, which is desirably open at its top and is adapted to contain a desired quantity of the  
95 acid solution.

2 designates a supply pipe through which the acid solution may be discharged into the tank.

3, 3' and 3'' designate a series of test cocks arranged at various levels, and 4 designates  
100 a main eduction pipe leading from the bottom of the tank and controlled by a valve or turn-cock 5.

6 designates as a whole the heating coil which, as shown, consists of a series of loops  
105 7, each of which communicates at one end with a supply header 8, and at its opposite end with a return header 9. With each end of the supply header communicates a pipe, as 10 and 11; these pipes being respectively  
110



controlled by valves 12 and 13, and one pipe being arranged to communicate with a source of heating fluid and the other with a source of cooling fluid. The return header 9 is provided with an eduction pipe or outlet 14. In practice it is desirable that the series of heating and cooling loops 7 be distributed across the lower part of the tank in the manner shown, and inasmuch as said loops all connect with the common header 9, they are obviously electrically in metallic connection with the latter.

Within the tank, above and free from the loops 7, is supported a frame, which desirably takes the form of a crate or basket 15 of wood or other suitable insulating material made of open work construction so as to afford a free circulation of the acid electrolytic solution therethrough. Conveniently this crate is supported from overhead so that it may be raised out and lowered into the tank at will. Within the crate or basket is supported a mass of iron, preferably scrap iron, and in metallic connection with this mass of iron is an electric conductor 16. Preferably the conductor 16 is provided with a plurality of branch wires which are spread across the bottom of the crate before the mass of iron is placed therein so as to insure good metallic contact with the mass, and by arranging the wires in the bottom of the crate, the iron as it is consumed and settles down maintains good electrical contact with the conductors throughout the operation.

The conductor or conductors 16, and the heating and cooling pipes are made of brass, copper, or other metal not affected or substantially affected chemically or electrochemically. The conductor 16 is electrically connected with the heating and cooling system, at a point outside of the solution by means of a conductor 17, and in order that the external circuit thus formed may be opened and closed at will a switch 18 is interposed between the conductors 16 and 17.

When the electrolyte becomes extremely weak, *i. e.*, the free acid has nearly all been eliminated, the electrolytic action may be augmented or kept up by supplying electric current from an external generator, and to this end the switch 18 is adapted to close a circuit between the conductor 16 and a contact 19 which forms one terminal of a conductor 20 leading to any suitable generator 21. This opens the circuit between conductors 16 and 17. The other side of the generator is connected through a conductor 22 with the conductor 17, so that by simply changing the position of the switch 18 the generator circuit is included in the battery circuit.

The method of carrying out our improved process with the aid of this apparatus will be obvious, but may be briefly stated. A suitable quantity of the acid solution having

been placed in the tank, the basket or crate with its charge of scrap iron and with the conductor wires 16 properly connected with the iron is lowered into the tank and the connection made between the conductor 16 and the switch contact 18' in case it is not desired to connect the generator in circuit. The switch being in the position shown in the drawing, electrolytic action immediately ensues. At the same time a heating fluid, as for example steam, is introduced through one of the pipes, say pipe 10, and circulating through the series of loops the water of condensation passes out through the return header 9. Evaporation of the acid solution ensues, this evaporation being effected by the combining heat introduced through the heating system and that produced by electrochemical action, and furthermore the decomposition of the liquid by electrolysis gasifies substantial quantities thereof, and this gas in turn carries off with it vapor, so that the evaporation due to the conjoint connection of steam and electrolysis is comparatively rapid.

It is to be particularly noted that in treating some liquids, notably sulfuric acid solutions, the temperature must not be allowed to rise too high, because if the temperature exceeds a certain point (which is substantially below that at which steam is generated at ordinary atmospheric pressure) a chemical reaction is set up which results in producing a salt different from that wanted, which is sulfate of iron of the formula  $\text{FeSO}_4$ . The necessity of maintaining such comparatively low temperature obviously renders the evaporation and concentration of the liquid extremely low, unless expedited by the electrolytic action described, and it is this relatively slow process which has made the recovery of the by-product a matter of doubtful economy in the past.

After the liquid has been sufficiently concentrated and its affinity for iron substantially or approximately satisfied, we then shut off the circulation of heating fluid through the loop system and introduce instead a cooling fluid, and thereby rapidly lower the temperature of the solution in the tank to that stage at which crystallization will be best brought about. The liquid is then transferred to the crystallizing tank 23 and the salt allowed to crystallize out.

As an intermediate subsidiary step which may or may not be employed; after the electrolytic action has begun to subside as the affinity of the acid for iron approaches saturation, we change the position of the switch 18 so as to open the short circuit between the conductors 16 and 17 and include the generator circuit, whereupon the generator is operated and sends an auxiliary current to the battery. This reinforces the galvanic action; it being understood that the direction



of the current supplied by the generator would be the same as that generated by the galvanic battery itself. In this connection it is to be observed that inasmuch as the mass of iron constitutes the positive and the loops of the heating system the negative of the galvanic couple there will be no tendency on the part of the electrolyte to attack the metal of the heating and cooling system.

While we have given one specific example of a practical application of our process, we do not wish to be understood that the process is limited to the recovery of this by-product. On the contrary, the method may be employed for promoting the concentration of other acids where the conditions are such that a galvanic couple may be formed.

We claim as our invention:

1. The improvement in the art of concentrating electrolytic liquids of acid character which consists in combining with the acid a metal for which the acid has chemical affinity to act as an anode and another electrode which will form a negative electrode, electrically connecting said electrodes and thus effecting electro chemical action and supplying heat to said liquid to cooperate with the electro chemical action in concentrating the liquid.

2. The improvement in the art of concentrating acid solutions having a chemical affinity for iron which consists in placing in, or subjecting to the action of, the acid the mass of iron, arranging in or in contact with the acid a cathode electrode electrically connecting said cathode electrode with the mass of iron exteriorly of or out of contact with the acid and thus causing electro chemical action and concurrently supplying auxiliary heat to said liquid from an external source.

3. The improvement in the art of concentrating acid solutions which consists in placing in, or subjecting to the action of, the acid a mass of iron, submerging in the acid solu-

tion a heating coil, connecting the iron electrically with said heating coil to form with the acid solution, the mass of iron and the heating coil a galvanic battery and concurrently with the electro chemical action circulating heating fluid through said heating coil.

4. The improvement in the art of concentrating electrolytic liquids, which consists in combining with the liquid suitable anode and cathode elements to form with the liquid a galvanic couple, electrically connecting said elements and effecting electrolytic action, concurrently heating the liquid from an external source, continuing the combined electro chemical action and heating until the electrolytic action substantially subsides then passing electric current into and through the battery so formed and in the same current direction until the desired degree of concentration has been effected.

5. The improvement in the art of concentrating acid solutions, which consists in combining with the acid a mass of iron and a cathode electrode and connecting the iron and cathode to form a galvanic battery continuing the action of said battery and concurrently supplying heat to the liquid from an external source and augmenting the electrolytic action of said battery by passing electric current from an outside source through the battery in its normal flow direction.

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