A. S. RAMAGE.

PROCESS OF MAKING SULFURIC ACID AND ELECTROLYTIC IRON.

APPLICATION FILED JAN. 9, 1909. RENEWED JULY 14, 1910.

984,703. Patented Feb. 21, 1911.

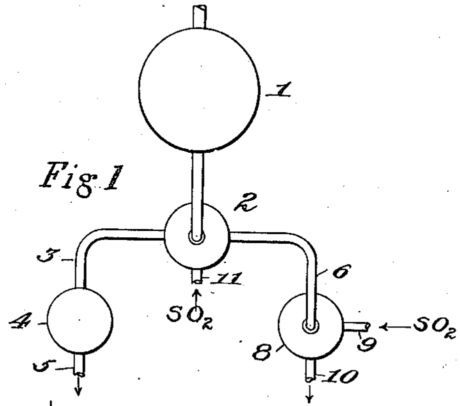

Fig 1

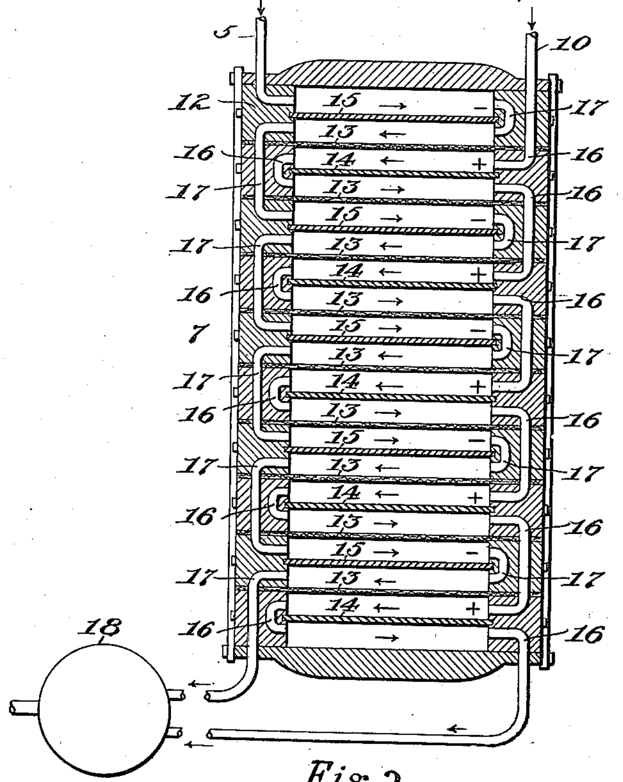

Fig 2

Witnesses:
Geo. E. Gauett
Chas. H. Potter.

Inventor:
Alexander S. Ramage
by Byrnes, Townsend & Brickenstein,
Att'ys.

UNITED STATES PATENT OFFICE.

ALEXANDER S. RAMAGE, OF DETROIT, MICHIGAN, ASSIGNOR, BY MESNE ASSIGNMENTS, TO NATIONAL TUBE COMPANY, OF PITTSBURG, PENNSYLVANIA, A CORPORATION OF NEW JERSEY.

PROCESS OF MAKING SULFURIC ACID AND ELECTROLYTIC IRON.

984,703. Specification of Letters Patent. **Patented Feb. 21, 1911.**

Application filed January 9, 1909, Serial No. 471,526. Renewed July 14, 1910. Serial No. 572,020.

To all whom it may concern:

Be it known that I, Alexander S. Ramage, a citizen of the United States, residing at Detroit, in the county of Wayne and State of Michigan, have invented certain new and useful Improvements in Processes of Making Sulfuric Acid and Electrolytic Iron, of which the following is a specification.

This invention relates to the production of electrolytic iron from ferric ores, with the coincident production of sulfuric acid.

According to the invention a ferric solution obtained by treating a suitable ore of iron with sulfuric acid is first reduced to the ferrous state, and is then subjected to electrolysis with insoluble anodes, the anode being depolarized during the electrolysis by means of dissolved sulfur dioxid.

In practicing the process it is necessary that means should be provided for preventing admixture of the positive electrolyte containing dissolved sulfur dioxid with the electrolyte surrounding the cathodes; for if such admixture should occur a reduction of sulfur dioxid would take place in the region of the cathode resulting in the contamination of the metallic iron. This reduction of sulfur dioxid is primarily due to the fact that when the acid liquor from the anode compartment is permitted to flow to the region of the cathode there occurs a considerable evolution of hydrogen by which the sulfur dioxid is quickly reduced. Moreover, the acid liberated at the anodes or there produced by the oxidation of the sulfur dioxid, is distributed throughout the electrolyte, and redissolves the deposited iron at a progressively increasing rate, thereby greatly reducing the efficiency of the operation. By the use of a diaphragm or equivalent means for preventing admixture of the positive and negative electrolytes, the cathode compartment is readily maintained free or substantially free from sulfur dioxid and sulfuric acid.

I prefer to proceed substantially as follows: A ferric ore, as for example hematite, is dissolved in sulfuric acid, the solution being preferably aided by heat and by the fine division of the ore, with agitation if necessary. The resulting ferric solution is then reduced to the ferrous state, preferably by means of sulfur dioxid, conveniently supplied in the form of gases from pyrites or sulfur burners. This ferrous solution is then supplied in separate streams to the anode and cathode compartments of a suitable electrolytic cell, that portion of the solution flowing to the positive compartment of the cell containing an excess of sulfur dioxid and being preferably saturated with the gas. The portion of the electrolyte flowing to the negative compartment is on the other hand substantially free from the dissolved gas.

For a full understanding of the invention reference is made to the accompanying drawing, in which—

Figure 1 is a diagrammatic plan view of a suitable arrangement of saturating apparatus, and Fig. 2 is a horizontal section of the electrolytic cell on a relatively large scale.

In said drawing 1 represents a solution tank, tower or apparatus of any desired type, wherein the ore is subjected to the action of a suitable solvent liquid. The solvent liquid may consist initially of sulfuric acid, an acid pickle liquor, or other liquid containing sulfuric acid, but in the after stages of the process will preferably consist of the acid liquor flowing from the electrolytic cells, or a portion thereof, as hereinafter described. From the solution apparatus 1 the liquid containing ferric sulfate flows to a suitable tower or scrubber 2, wherein it is substantially reduced to the ferrous state by sulfur dioxid introduced through the pipe 11 from pyrites or sulfur burners. From the tower 2, a portion of the liquor flows through conduit 3 to a tank 4 wherein any excess of sulfur dioxid may be removed, as for example by the careful addition of ferric sulfate solution. The ferrous sulfate solution then flows through conduit 5 to the negative compartments of the electrolytic cell 7. A like volume of liquor flows from the tower 2 through conduit 6 to a second tower or scrubber 8, wherein it is treated with sulfur dioxid supplied through pipe 9, being preferably fully impregnated or saturated with the gas. This impregnated liquor then flows through conduit 10 to the positive compartments of the electrolytic cell.

The electrolytic cell may be of any desired type, that illustrated comprising a series of abutting wooden frames 12 between which are clamped asbestos diaphragms 13. Each frame contains an electrode, the anodes 14 being preferably of lead, and the cathodes 15 consisting usually of iron. The anodes and cathodes are disposed in alternate frames, and passages are so arranged in the frame walls that the impregnated liquor may be caused to flow, through passages 16, through the several anode compartments in succession, while the unimpregnated liquor flows through similar passages 17 to the several cathode compartments.

It will be observed that the arrangement of the several compartments of the cell, and of the intermediate passages, is such that the anode and cathode liquors on opposite sides of the several diaphragms flow always in the same direction with respect to each other; that is to say, the flow is relatively uni-directional. This arrangement has been found in practice to be highly effective in avoiding undue diffusion between the several compartments in cases where porous diaphragms of low resistance and high permeability are employed. Preferably the effluent liquors from both anode and cathode compartments are united in a common receiving tank 18, from which they are removed for utilization.

It will be understood that any number of electrolytic cells may be used in series or in multiple, the best results being obtained by removing a portion only of the iron and maintaining the liquor in continuous circulation through the solution apparatus and the electrolytic cells. By proceeding in this manner the operations of solution and electro-deposition are rendered regular in character, and the operation proceeds with the minimum of attention. The fall of potential in individual cells is usually from 1½ to 2 volts, the current density varying according to the character of deposit required from 30 to 100 amperes per square foot. A temperature between 100 and 120° Fahrenheit is preferred.

The reduction of the ferric solution by sulfur dioxid yields a large amount of sulfuric acid, as per the following equation:

$$Fe_2(SO_4)_3+SO_2+2H_2O=2FeSO_4+2H_2SO_4.$$

A further quantity of acid is produced during the electrolytic operation by oxidation in the region of the anode of the dissolved sulfur dioxid. The liquor flowing from the cells contains therefore a large excess of sulfuric acid and I prefer to concentrate this liquor, or a portion of the same, and to distil sulfuric acid therefrom, whereby the acid is directly recovered in marketable form. The residual liquor, after such dilution as may be required, is returned to the solution apparatus, for re-use in the process, which is therefore cyclical in character.

It will be understood that instead of depositing the iron in the form of sheets or plates suited for re-melting, it may be directly deposited in the form of tubes or such articles as may be desired.

I claim:

1. The process of producing sulfuric acid and electrolytic iron, which consists in dissolving a ferric ore in sulfuric acid, reducing the ferric sulfate to ferrous sulfate by sulfur dioxid, electrolyzing the resulting ferrous sulfate solution in an electrolytic cell provided with an insoluble anode and with means for preventing admixture of the positive and negative electrolytes, and depolarizing the anode by sulfur dioxid while maintaining the electrolyte in the region of the cathode substantially free from sulfur dioxid.

2. The process of making sulfuric acid and electrolytic iron, which consists in dissolving a ferric ore in sulfuric acid, reducing the ferric sulfate to ferrous sulfate by sulfur dioxid, electrolyzing the resulting ferrous solution in an electrolytic cell provided with a diaphragm and an insoluble anode, and depolarizing the anode by sulfur dioxid while maintaining the electrolyte in the region of the cathode substantially free from sulfur dioxid.

3. The process of producing sulfuric acid and electrolytic iron, which consists in dissolving a ferric ore in sulfuric acid, reducing the ferric sulfate to ferrous sulfate by sulful dioxid, electrolyzing the resulting ferrous sulfate solution in an electrolytic cell provided with an insoluble anode and with means for preventing admixture of the positive and negative electrolytes, depolarizing the anode by sulfur dioxid, separating sulfuric acid from the electrolyte, and employing the residual acid liquor for the solution of a ferric ore.

4. The process of making sulfuric acid and electrolytic iron, which consists in dissolving a ferric ore in sulfuric acid, reducing the ferric sulfate to ferrous sulfate by sulfur dioxid, electrolyzing the resulting ferrous solution in an electrolytic cell provided with a diaphragm and an insoluble anode, maintaining a uni-directional flow of the positive and negative electrolytes, and depolarizing the anode by sulfur dioxid while maintaining the electrolyte in the region of the cathode substantially free from sulfur dioxid.

5. The process of making sulfuric acid and electrolytic iron, which consists in dissolving a ferric ore in sulfuric acid, reducing

the ferric sulfate to ferrous sulfate by sulfur dioxid, electrolyzing the resulting ferrous solution by passing the same successively in proximity to a plurality of cathodes in an electrolytic cell provided with diaphragms and insoluble anodes, maintaining a relatively uni-directional flow of the positive and negative electrolytes on opposite sides of said diaphragms, and depolarizing the anodes by sulfur dioxid.

In testimony whereof, I affix my signature in presence of two witnesses.

ALEXANDER S. RAMAGE.

Witnesses:

VIDA M. SMITH,
C. P. TOWNSEND.