

No. 788,064.

PATENTED APR. 25, 1905.

A. S. RAMAGE.
UTILIZING SPENT PICKLE LIQUOR.
APPLICATION FILED JAN. 31, 1905.

Fig. 1.

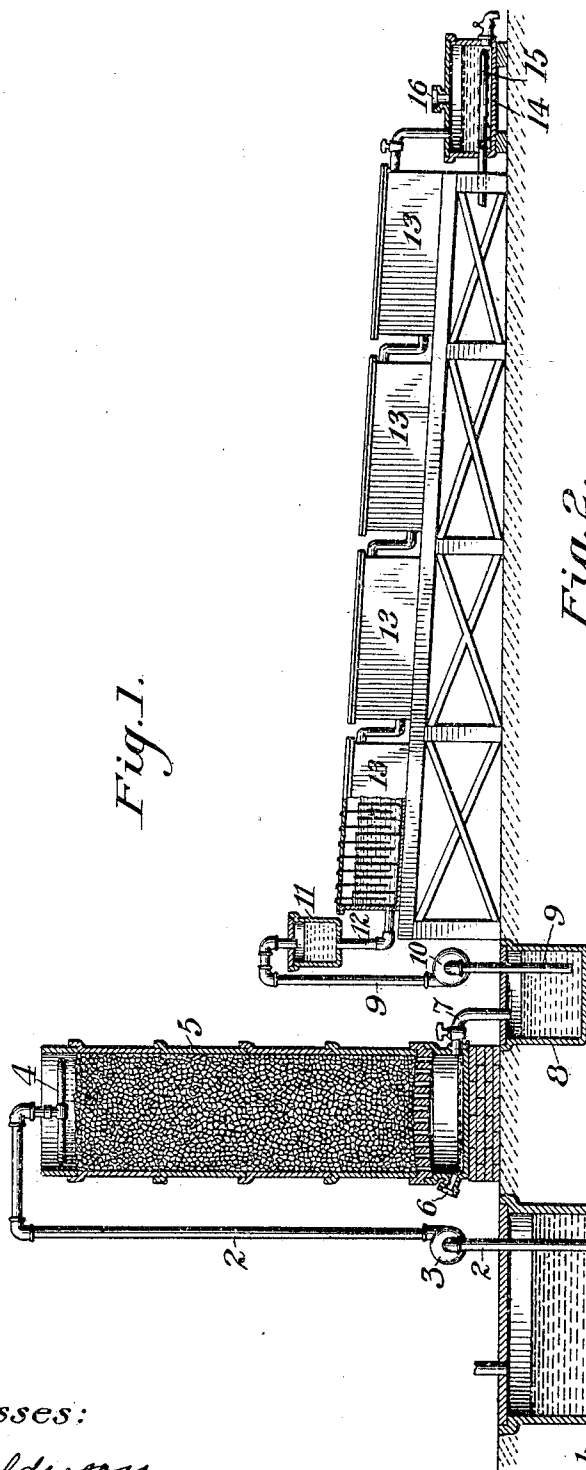
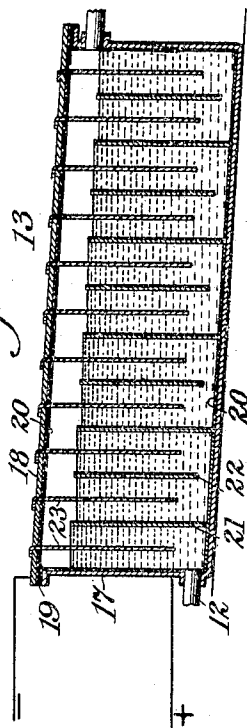


Fig. 2.



Witnesses:

R. A. Balderson.
J. B. Hill.

Inventor:

Alexander S. Ramage,
by *Quinn & Townsend*,
Attys.

UNITED STATES PATENT OFFICE.

ALEXANDER S. RAMAGE, OF DETROIT, MICHIGAN.

UTILIZING SPENT PICKLE LIQUOR.

SPECIFICATION forming part of Letters Patent No. 788,064, dated April 25, 1905.

Application filed January 31, 1905. Serial No. 243,558.

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 Utilizing Spent Pickle Liquor, of which the following is a specification.

This invention is a method of treating spent sulfuric-acid pickle liquor to recover metal and regenerate the liquor.

The invention will be described as applied to the utilization of ferrous sulfate liquors from the pickling of iron, but is also applicable to metal-bearing solutions obtained by pickling copper and other metals.

I prefer to proceed as follows: The pickle liquor containing ferrous sulfate and free sulfuric acid, the latter in quantity insufficient for economical pickling, is saturated with sulfur dioxide, preferably in a suitable absorption-tower, and then conducted through closed electrolytic vats each provided with anodes of lead and cathodes of iron. In these vats iron is deposited in a state of substantial purity on the cathodes, while free sulfuric acid accumulates in the electrolyte. The regenerated liquor is freed from any remaining sulfur dioxide by heat and again utilized in the pickling process. It is not economical to continue the pickling until all free acid is combined by reason of the slow action of weak liquors, nor, on the other hand, is it desirable to continue the electrolysis until all of the combined acid is liberated, by reason of the low efficiency of deposition from dilute metal-bearing solutions. I prefer, therefore, to so regulate the process that both pickling and electrodeposition are rapidly and economically effected. I do not limit myself to any specific proportions of acid or of metal in the liquor at any stage of the process; but I have found it practicable to continue the pickling until the free-acid content is reduced to one-half to one and one-half per cent., and thereafter to continue the electrolysis until the free acid is increased to five to fifteen per cent. The function of the sulfur dioxide is threefold. First, by its oxidation it yields sulfuric acid, thereby increasing the free-acid content of

the liquor at a greater rate than corresponds to the deposition of the metal; second, it provides the excess of sulfuric acid required to prevent the precipitation of basic sulfate of iron, which would quickly interrupt the electrolysis were it attempted to directly electrolyze the pickle liquor, and, third, it serves to reduce the electromotive force required for the electrolysis, as is well understood in connection with the deposition of metals.

An arrangement of apparatus suitable for carrying out my process is shown in the accompanying drawings, wherein—

Figure 1 is an elevation, partly in section, of the apparatus for treating pickle liquors; and Fig. 2 is a vertical longitudinal section of one form of electrolytic vat.

1 represents a storage-tank for spent pickle liquor, and 2 3 a pipe and pump for transferring the liquor to an absorption-tower 5. This tower may be of any suitable type and is preferably filled with coke, over which the liquor is distributed by a reaction-mill or other suitable device 4.

6 represents the inlet for sulfur dioxide or for a mixture of sulfur dioxide and air in case it is desired to take advantage of the formation of sulfuric acid by the oxidation of sulfur dioxide in the absorption-tower.

The acid liquor containing sulfuric and sulfurous acids and ferrous sulfate is permitted to flow through pipe 7 into a reservoir 8 and is thence carried through pipe 9 and pump 10 to a supply-tank 11, which is connected through pipe 12 with a series of covered electrolytic vats 13. In these vats metal is deposited and free acid formed, as above described, and the resulting regenerated liquor is permitted to overflow into a tank 14, from which it is withdrawn for further utilization in the pickling of metal. Tank 14 is preferably provided with a heating-coil 15, whereby any dissolved sulfur dioxide may be expelled through outlet 16 to be returned to the tower 5.

The electrolytic vats are preferably so constructed as to provide a tortuous flow of the electrolyte successively past anodes 21 22 and cathodes 23. As illustrated, each electrolytic vat 13 comprises a body 17 and a lining

20, which is preferably of lead and in electrical connection with the anodes 21 22, the latter consisting of partitions extending transversely across the vat. The vats are mounted at a slight inclination, and the transverse anode-plates 21 22 are so disposed that the liquor may pass alternately above and below successive anode-plates. The cathodes 23, which may be of iron, depend between the anodes and are preferably supported by and in electrical connection with the metallic cover 18, insulation 19 being interposed between the cover and the body of the vat.

I claim—

1. The process of utilizing spent sulfuric-acid pickle liquor, which consists in dissolving sulfur dioxid in the liquor, electrolyzing the resulting solution with insoluble anodes, thereby depositing metal at the cathode, and freeing the combined acid and oxidizing the dissolved sulfur dioxid at the anode, and employing the regenerated liquor to pickle metal, substantially as described.

2. The process of utilizing spent sulfuric-acid liquor from pickling iron, which consists in dissolving sulfur dioxid in the liquor, electrolyzing the solution with insoluble anodes, thereby depositing iron at the cathode and freeing the combined acid and oxidizing the dissolved sulfur dioxid at the anode, and employing the regenerated liquor to pickle iron, substantially as described.

3. The process of regenerating spent pickle liquors containing ferrous sulfate, which consists in dissolving sulfur dioxid in the liquor, and electrolyzing the solution with insoluble anodes, thereby depositing iron at the cathode and freeing the combined acid and oxidizing the dissolved sulfur dioxid at the anode, substantially as described.

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

ALEXANDER S. RAMAGE.

Witnesses:

IRVING W. DURFEE,
F. A. PLATT.