

(No Model.)

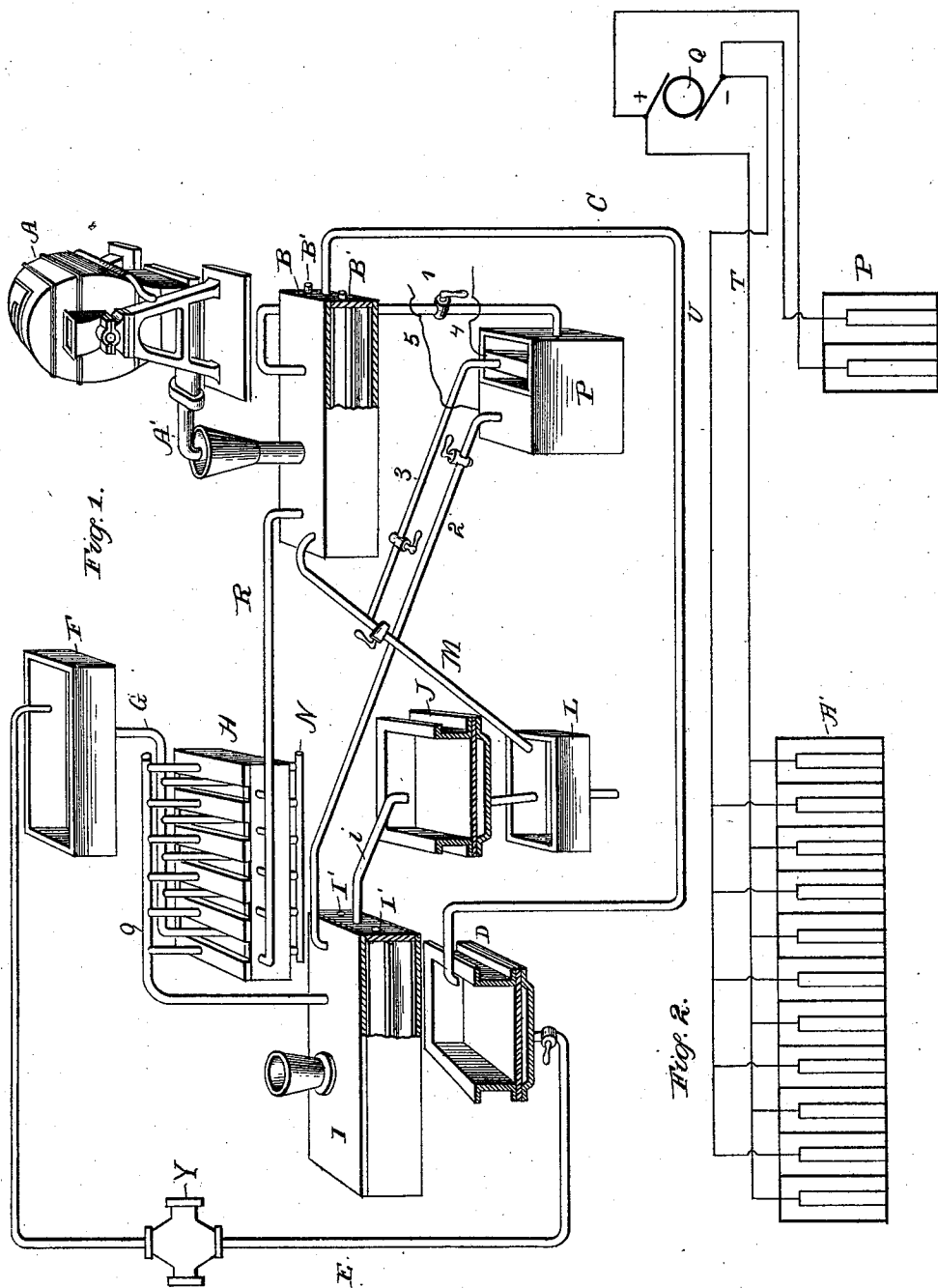
2 Sheets—Sheet 1.

V. ENGELHARDT.

PROCESS OF EXTRACTING METALS FROM SULFIDE ORES, &c.

No. 531,169.

Patented Dec. 18, 1894.



Witnesses.

Victor J. Evans.
L. M. Martin

Inventor.

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(No Model.)

2 Sheets—Sheet 2.

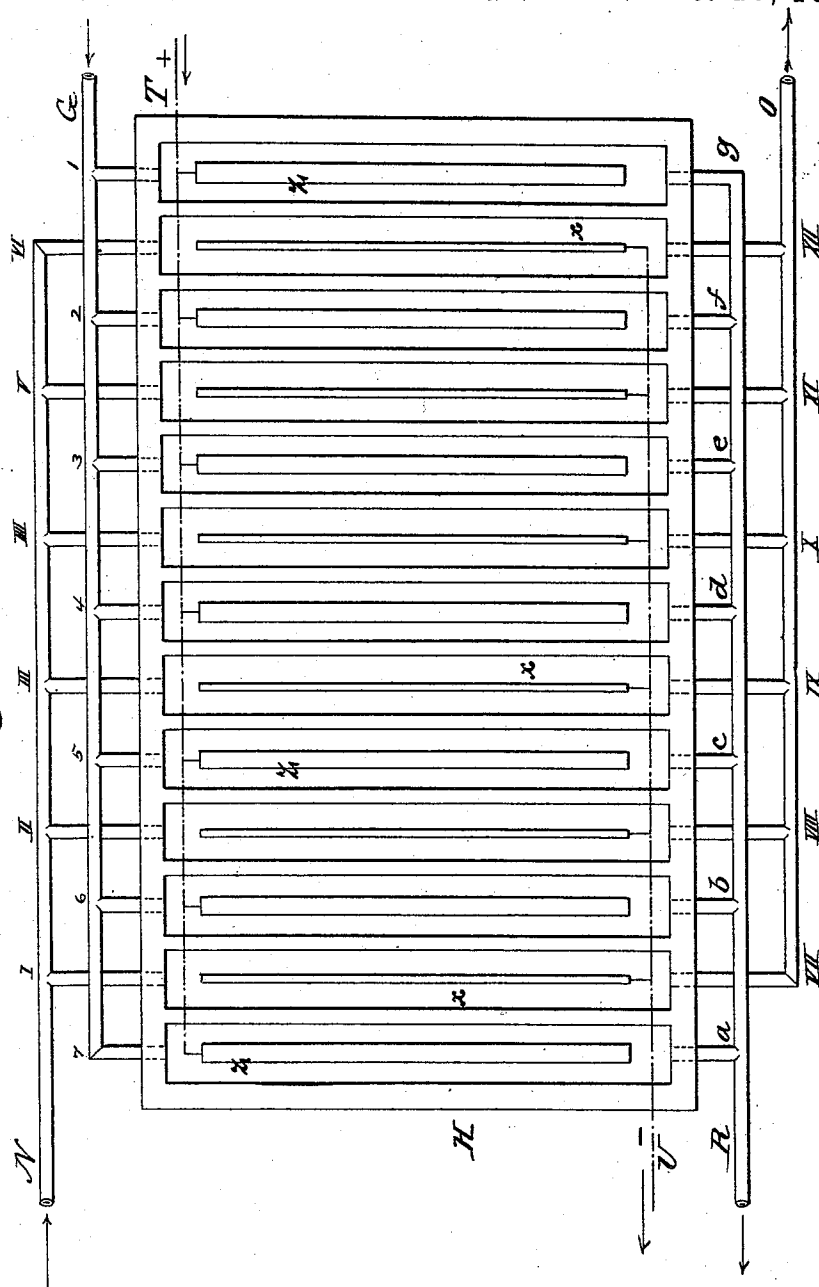
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Fig. 3.



WITNESSES:

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PROCESS OF EXTRACTING METALS FROM SULFIDE ORES, &c.

SPECIFICATION forming part of Letters Patent No. 531,169, dated December 18, 1894.

Application filed January 21, 1893. Serial No. 459,224. (No specimens.) Patented in Germany June 29, 1892, No. 67,973; in Austria July 5, 1892, No. 34,413; in Hungary July 5, 1892, No. 53,757; in France October 24, 1892, No. 225,145; in Italy October 26, 1892, No. 32,905; in Spain December 21, 1892, No. 13,898, and in England August 19, 1893, No. 18,966.

To all whom it may concern:

Be it known that I, VICTOR ENGELHARDT, a subject of the Emperor of Austria-Hungary, residing at Vienna, in the Empire of Austria-Hungary, have invented certain new and useful Improvements in an Electro-Chemical Process for Extracting Metals from Sulfide Ores, &c., (for which I have obtained Letters Patent in Germany, No. 67,973, dated June 29, 1892; in Great Britain, No. 18,966, dated August 19, 1893; in France, No. 225,145, dated October 24, 1892; in Italy, No. 32,905, dated October 26, 1892; in Spain, No. 13,898, dated December 21, 1892; in Austria, No. 34,413, dated July 5, 1892, and in Hungary, No. 53,757, dated July 5, 1892,) of which the following is a specification.

My improved process relates to an improved process for effecting the electrolytic decomposition of metallic sulphides, and other compounds of metal and sulphur, whether natural or artificially produced, and it consists in an improved process of accomplishing such electrolytic decomposition and recovery of the metal in a pure state, and of by the same process recovering certain foreign metals which are frequently found in the sulphide ores, which will be hereinafter fully described and particularly pointed out in the claims.

It is well known that the compounds of antimony, arsenic, &c., with sulphur are easily soluble in the alkaline sulph-hydrates, and that metallic arsenic, antimony, &c., are readily precipitated by electrolysis from their combinations with such alkaline sulph-hydrates. In none of the processes heretofore used, however, has the liquid of the anode been separated from that of the cathode. The result is that while the antimony, arsenic, &c., are precipitated and obtained in a pure state, the alkaline sulph-hydrate, which is reformed by the electrolytic action, and indeed acts only as a carrier for enabling the metal of the sulphide to be put in proper form for electrolytic action, is not separate and in a condition to be used over again, and can at best, be only partially reused, a large proportion of it being lost for the purposes of the

process. Moreover, these processes have provided no means for obtaining the metals, such as gold, silver, copper, mercury, bismuth, nickel, zinc, &c., which are frequently found in paying quantities in the sulphide ores.

The object of my invention is to provide an improved process for the electrolytic treatment of metallic sulphides by the use of which not only will the metal of the sulphides be recovered, but all of the alkaline sulph-hydrate will be obtained in a condition to be reused, and, further, provision will be made for recovering such foreign metals as may be found in the sulphide ores.

The process which I use to accomplish the above stated object of invention consists in treating such natural or artificially produced sulphides in a finely divided condition with an alkaline sulph-hydrate to form a solution of the sulphide, thereby generating sulphureted hydrogen; subjecting the solution thus obtained to electrolytic action in the cathode compartment of an electrolytic cell in which the anode and cathode divisions are separated by suitable septa, (which is however impervious to the anode and cathode liquids,) the anode compartment of the cell containing a liquid, such as sodium chloride, which will be decomposed by the electrolytic action with the generation of a gas which will act to dissolve out the foreign metals from the ore residues of the sulph-hydrate bath; thereby obtaining the metal to be recovered in a pure state, and reforming the alkaline sulph-hydrate, so that it is in a condition to be again used; extracting the foreign ores from the ore residues of the sulph-hydrate bath by means of the gas generated in the anode compartment of the electrolytic cell; and finally subjecting the solution thus formed to the action of the sulphureted hydrogen generated in the sulph-hydrate bath.

The metals which are principally applicable to this process are antimony and arsenic, whether naturally or artificially produced. Such sulphides are found in large quantities in nature, and usually in combination with some one or more of the foreign metals pre-

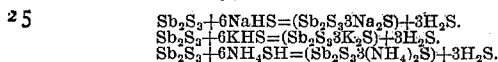
viously mentioned. They are also produced artificially, as for instance in the form of a by-product in copper smelting works.

In the drawings which accompany and form a part of this specification, I have represented one form of apparatus which may be used in carrying out my invention.

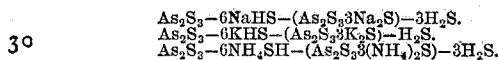
Figure 1 is a perspective view of such apparatus, with portions thereof removed in order to show the construction. Fig. 2 is a diagram of the circuits in connection with the generator and a battery. Fig. 3 is a longitudinal section of the battery itself.

In my process, the finely ground ore containing sulphide of arsenic or of antimony is passed from the grinding mill A, in which the material has been reduced to the proper degree of fineness, by the pipe A' to the extraction vessel B, which is charged with a solution of alkaline sulph-hydrate capable of dissolving the sulphur compounds of arsenic and antimony from their respective ores. The reaction which takes place is as follows:

For antimony,



For arsenic,



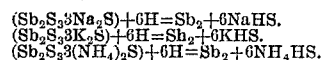
In the extractor the mass is subjected to a temperature of about 212° Fahrenheit, and is thoroughly agitated by means of the stirrers B', which are operated in any suitable manner. After the extracting action has been carried on long enough, the resulting solution of compound sulphide and ore particles suspended therein are conveyed by means of the pipe C to a filtering vessel D (one end of which is removed in the drawings to show the construction), whence the solution is conveyed by the pipe E to the filter F. The rotary pump Y affords the means for obtaining the desired circulation throughout the entire system. The suspended ore particles remain upon the bottom of the vessel D, and may be removed to be again treated. The finer particles constitute the precipitate which remains in the filter F, while the filtrate passes by means of the pipe G and the branch pipes 1-7 to the cathodes x of the electrolytic precipitating apparatus H, which is divided by diaphragms into anode and cathode compartments. The diaphragms used should be such as to offer a minimum resistance to the passage of the current, but to prevent as far as possible the diffusion of the two electrolytes contained respectively in the anode and cathode compartments. This is best effected by rapid circulation, and by the use of diaphragms of colloid materials, such as sheet asbestos boiled in gelatine and the like.

The anode compartments are closed gas tight, for a reason which will be hereinafter mentioned, and they contain insoluble anodes, such as carbon, platinum, &c, while the cath-

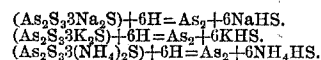
ode compartments are open, and generally contain metal plates, such as copper and antimony, as cathodes.

The precipitating action occurring at the cathode may be expressed by the following reactions:

For antimony,



For arsenic,



The extracted antimony and arsenic will thus be completely precipitated, and at the same time the sulph-hydrate is reformed, and in a condition to be reused to take up new quantities of arsenic, antimony, &c. The sulph-hydrate is returned through the branch pipes a-g and the main pipe R to the mixing vessel or extractor B to be used over again.

The nature of the liquid which circulates through the anode compartments of the electrolytic cell depends somewhat upon what metals are being treated, but in any case is a liquid which is decomposed by the electrolytic action, with the liberation of a gas which will act upon the ore residues resulting from the extraction bath in the vessel B, and dissolve out such valuable metals as may be there present.

Thus if the antimony ore treated contains gold, silver, copper, mercury, bismuth, zinc, cobalt, or nickel, the anode electrolyte may be an alkaline chloride, which during the electrolysis develops free chlorine. The alkaline chloride is introduced into the anode compartments by means of the pipe N, and the branch pipes I to VI, inclusive, and the free chlorine developed, together with the anode liquid, is conveyed by means of the branch pipes VII to XII and the main pipe O to the vessel I. In this vessel have previously been placed the ore residues collected in the filter D, and the chlorine, acting upon this residue, and being thoroughly agitated therewith by means of the agitators I' I', dissolves out any gold, silver, mercury, copper, bismuth, zinc, cobalt, or nickel that may be present. The solution thus formed is then separated from the gangue by means of the filter J, the contents of the vessel I being conveyed thereto by means of the pipe z. The solution is collected in the filter L, and is there treated with the sulphureted hydrogen generated in the extractor B, the sulphureted hydrogen being conveyed thereto by means of the pipe M. The further reduction of these metals is carried out by known processes, and forms no part of this process.

The quantities of alkaline sulphides and of chlorine required for the above described process, as also for making good the losses thereof that will result in practice, are prepared in an electrolytic vessel P by the decomposition of alkaline chlorides, and by the

introduction of sulphureted hydrogen into the cathode compartments. The alkaline sulphides thus formed are conveyed by pipe 1 to the extractor B, and the chlorine by the pipe 2 to the extractor I. The sulphureted hydrogen is introduced through the pipe 3.

The connection of the electrolytic cell H to the dynamo Q by means of the conductors T and U, and also the connection of the electrolytic cell P to said dynamo is shown in Fig. 3.

The extraction process thus described can be used with all metals which form soluble double sulphides when treated with the alkaline sulph-hydrates, and besides arsenic and antimony, I may mention gold, platinum, tellurium, molybdenum, and tin ores as suitable for treatment with this process.

The process may be carried on either at the ordinary temperatures, or with the application of heat.

Having thus fully described my invention, what I claim as new, and desire to secure by Letters Patent, is—

1. The herein described process of treating the sulphur compounds of metals, which consists in extracting the metals by treatment with an alkaline sulph-hydrate, subjecting the solution thus formed to the action of an electric current in the cathode compartment of an electrolytic cell, in the anode compartment of which is a solution of a suitable salt, which, under electrolytic action, is changed in its chemical properties, thereby obtaining the metals, reforming the alkaline sulph-hydrate, and changing the characteristics of the anode liquid, substantially as described.

2. The herein described process of treating the sulphur compounds of metals, which compounds have united therewith compounds of other metals not soluble in a solution of an alkaline sulph-hydrate, which consists in extracting the sulphur compounds by treatment with an alkaline sulph-hydrate, subjecting the solution thus formed to the action of an electric current in the cathode compartment of an electrolytic cell, in the anode compartment of which is a solution of a suitable salt, thereby obtaining the metals, reforming the alkaline sulph-hydrate, and changing the characteristics of the anode liquid, and treating the ore residues resulting from the sulph-hydrate bath with the anode liquid, substantially as described.

3. The herein described process of treating the sulphur compounds of metals, which compounds have combined therewith other ore compounds not soluble in a solution of an alkaline sulph-hydrate, which consists in extracting the sulphur compounds by treatment with an alkaline sulph-hydrate, thereby

liberating sulphureted hydrogen, subjecting the solution thus formed to the action of an electric current in the cathode compartment of an electrolytic cell, thereby obtaining the metals and reforming the alkaline sulph-hydrate, forming a solution of the ore residues resulting from the sulph-hydrate bath, and treating the solution thus formed with the sulphureted hydrogen resulting from the sulph-hydrate bath, substantially as described.

4. The herein described process of treating the sulphur compounds of metals, which compounds have combined therewith other ore compounds not soluble in a solution of an alkaline sulph-hydrate, which consists in extracting the sulphur compounds by treatment with an alkaline sulph-hydrate, thereby also generating sulphureted hydrogen, subjecting the solution thus obtained to the action of an electric current in the cathode compartment of an electrolytic cell, in the anode compartment of which is a solution of a suitable salt, thereby obtaining the metals, reforming the alkaline sulph-hydrate, and changing the characteristics of the anode liquid, treating the ore residues resulting from the sulph-hydrate bath with the anode liquid, thereby obtaining the metals in such residues in solution, and subjecting the solution thus obtained to the action of the sulphureted hydrogen first generated in the sulph-hydrate bath, substantially as described.

5. The herein described process of treating the sulphur compounds of metals, which compounds have combined therewith other ore compounds not soluble in a solution of an alkaline sulph-hydrate, which consists in extracting the sulphur compounds by treatment with an alkaline sulph-hydrate, thereby also generating sulphureted hydrogen, subjecting the solution thus formed to the action of an electric current in the cathode compartment of an electrolytic cell, in the anode compartment of which is an alkaline chloride, thereby obtaining the metals, reforming the sulph-hydrate, and liberating free chlorine, treating the ore residues resulting from the sulph-hydrate bath with such chlorine, and subjecting the solution thus obtained to the action of the sulphureted hydrogen first generated in the sulph-hydrate bath, substantially as described.

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

VICTOR ENGELHARDT.

Witnesses:

W. B. MURPHY.

A. SCHLESSING.