To all whom it may concern:

Be it known that I, Anson Gardner Betts, a citizen of the United States, residing at Troy, in the county of Rensselaer and State of New York, have invented certain new and useful Improvements in Processes of Treating Arsenical Ores and Speiss, of which the following is a specification.

This invention relates to electrolytic processes of treating speiss as anode in solutions from which a metal derived from a source other than the speiss, is deposited at the cathode.

The principal object of my invention is to provide a clean, cheap and safe method of treating arsenical ores and speisses, particularly such as contain cobalt and silver.

A very important feature of my process, distinguishing it from some if not all of the other electrolytic processes of treating speiss, is that it can be readily carried out without the evolution of arseniuretted hydrogen fumes, which are extremely dangerous.

To accomplish these objects the ore is first smelted to speiss, if speiss has not already been produced, and the speiss is cast into anode form. The speiss anodes are dissolved by electrolysis preferably in a copper or lead depositing solution, copper sulfate being satisfactory, but a lead or copper fluosilicate solution offers some advantages. Using copper sulfate, enough of the salt is supplied in the process to insure at the cathode only the deposition of copper, and never the evolution of hydrogen, as if hydrogen appears it would probably contain the very dangerous \( \text{AsH}_3 \), reduced from the arsenic in the solution. As long as the solution contains at least one per cent. of copper, there is no danger, and the color of the solution is a guide.

The principal chemical reactions resulting from the electrolysis are:

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\begin{align*}
\text{Co} + \text{CuSO}_4 &= \text{Cu} + \text{CoSO}_4 \\
\text{Fe} + \text{CuSO}_4 &= \text{Cu} + \text{FeSO}_4 \\
\text{Ni} + \text{CuSO}_4 &= \text{Cu} + \text{NiSO}_4 \\
2\text{As} + 3\text{CuSO}_4 + 3\text{H}_2\text{O} &= \text{As}_2\text{O}_3 + 3\text{Cu} + 3\text{H}_2\text{SO}_4
\end{align*}
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Silver, gold and many impurities remain as an anode slime, which may be worked in any of the suitable known methods for the valuable contents.

It has been proposed in Andre's German patent, for instance, No. 6048, Nov. 1, 1877, to use mattes and speisses as anode in dilute sulfuric acid, wherein nickel, copper, etc., are to dissolve at the anode and copper to be deposited at the cathode. While copper will dissolve from an anode of matte and consequently be available for absorbing part of the cathode effect in depositing out there, it is very doubtful if it will dissolve and be found in the solution if an anode of nickel, cobalt or iron speiss is used. At any rate the reactions in Andre's process are such that hydrogen must be evolved in large quantities in the process, which is not the case in my process.

In my process I bring into the electrolytic dissolving tanks sufficient outside copper or equivalent salt, formed apart from the speiss-dissolving process, to make certain the deposition of metal only on the cathode, while the arsenic dissolved from the anode mostly remains in the solution, and none is liberated as gas. I prefer to conduct the electrolysis at a high temperature to keep the arsenic in solution during the electrolysis.

When the copper has been reduced in the solution to as low a proportion as is judged can be done with good results, the solution may be taken out of the electrolytic tanks and treated, as follows—On cooling a good deal of the arsenic acid may be crystallized out. The remaining arsenic acid and copper may be removed by electrolysis with insoluble lead or other anodes, provided the work is done out of doors, or by precipitation with \( \text{H}_2\text{S} \), or this purification may be omitted. The solution may then be evaporated and impure cobalt, nickel or iron sulfate, or a mixture of them, together with arsenic acid, recovered, to be worked up by well-known methods.

The impure acid mother liquor from the crystallization of the copper sulfate solution by treatment with roasted copper matte, or by running it through a shot-copper tower in presence of air, at the proper speed. The process thus works up on the side a certain amount of copper-bearing material into cathode copper.

If a lead salt is used in the process, it may be carried out as follows—The speiss anode is dissolved electrolytically in a first series of electrolytic tanks in a solution containing copper fluosilicate, while copper deposits on the cathodes and the solution grows richer in fluosilic acid, arsenious acid and cobalt, etc., salts. When the copper is
nearly all out, the solution is run over finely divided lead, which cements out copper, arsenic and many impurities. The solution now containing lead and cobalt, etc., fluosilicates principally is next used as electrolyte in a second series of electrolytic tanks with speiss anodes and lead or copper cathodes, wherein the cobalt and arsenic dissolve, and spongy lead deposits on the cathodes. The spongy lead is wiped off into cementing tanks through which the solution circulates, the lead being thereby dissolved, and the solution is then returned to the second series of electrolytic tanks, leaving the arsenic as a metallic precipitate in place of the dissolved lead. Finally the lead becomes reduced to a low percentage in the solution, and it mainly contains cobalt, etc., fluosilicates. The excess of spongy lead produced in the second electrolytic operation becomes available as cementing material for the first operation, with some left over for the preparation of lead anodes, to be used as seen below. The first operation, using a solution containing copper fluosilicate, may be omitted, as the operation will dissolve the speiss, form a metallic arsenic product by cementation, and yield a cobalt, etc., fluosilicate solution. The deposit of spongy, instead of solid lead, is obtained partly as a result of omitting glue from the solution as opposed to the now familiar lead refining electrolyte, and partly as a result of the solutions containing arsenic, which tends to cause a spongy lead precipitation. I may now remove small quantities of lead left in the solution by means of a little cobalt or other sulfate.

The treatment of the solution for iron, nickel and cobalt may be as follows—The solution is electrolyzed in a diaphragm cell, with lead anodes, for making lead fluosilicate solution at the anode, to be returned to the process, and a cathode deposit of iron-cobalt-nickel, cobalt-nickel, iron-nickel, or nickel or cobalt as the case may be.

What I claim as new and desire to secure by Letters Patent, is:

1. The process of treating speiss which consists in dissolving it as anode in a solution of a salt of a metal while depositing said metal without hydrogen on the cathode, and recovering metal of the speiss from the solution.

2. The process of treating speiss which consists in dissolving it as anode in a solution of a salt of a metal depositable more readily than hydrogen, while depositing said metal on the cathode and utilizing the full cathode effect of the current in metal deposition, and recovering metal of the speiss from the solution.

3. The process of treating speiss which consists in dissolving it as anode in a solution of a lead salt while depositing lead on the cathode, cementing arsenic from the solution by metallic lead, and recovering metal of the speiss from the solution.

4. The process of treating speiss which consists in dissolving it as anode in a solution of a lead salt, precipitating lead on the cathode, cementing arsenic from the solution by lead, and depositing metal of the speiss from the solution on a cathode by electrolysis with a lead anode, and using the solution resulting at the anode over again in the process.

In testimony whereof I have signed my name to this specification in the presence of two subscribing witnesses.

ANSON GARDNER BETTS.

Witnesses:

ETHEL B. BARNHISEL,
FREDERICK CLARK.