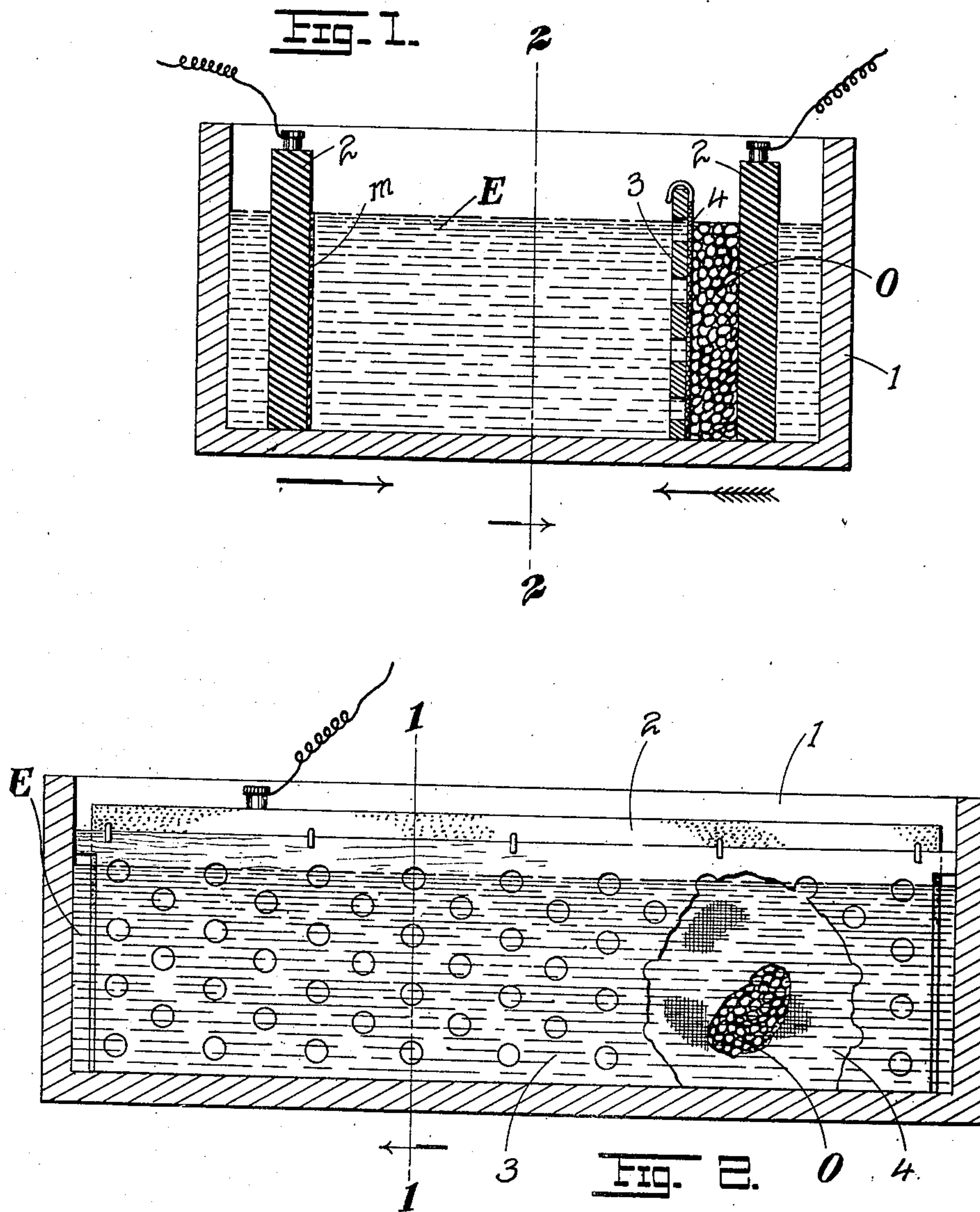


No. 862,871.

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E. L. ANDERSON.  
PROCESS OF REDUCING METALLIC SULFIDS.  
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WITNESSES:

*Phil. J. Dawn*  
*Jos. Michel*

INVENTOR.  
Edward L. Anderson

BY

*Emil Storer*  
ATTORNEY.



# UNITED STATES PATENT OFFICE.

EDWARD L. ANDERSON, OF ST. LOUIS, MISSOURI, ASSIGNOR OF ONE-FOURTH TO THOMAS B. HARVEY, OF ST. LOUIS, MISSOURI.

## PROCESS OF REDUCING METALLIC SULFIDS.

No. 862,871.

Specification of Letters Patent.

Patented Aug. 13, 1907.

Application filed February 23, 1907. Serial No. 358,946.

*To all whom it may concern:*

Be it known that I, EDWARD L. ANDERSON, a citizen of the United States, residing at St. Louis, State of Missouri, have invented certain new and useful Improvements in Processes of Reducing Metallic Sulfids, of which the following is a full, clear, and exact description, reference being had to the accompanying drawings, forming a part hereof.

My invention has relation to improvements in processes of reducing metallic sulfid ores and other metallic compounds and ores electrolytically; and it consists in the novel series of steps more fully set forth in the specification and pointed out in the claims.

In the drawings, Figure 1 is a vertical transverse section on line 1—1 of Fig. 2 of the reduction tank; and Fig. 2 is a longitudinal vertical section on the line 2—2 of Fig. 1 with part of the diaphragm broken away.

The object of my invention is to effect the electrolytic reduction of metallic sulfids, carbonates, oxids, and other compounds notably of copper and lead (though the process is not restricted to these metals). In cases where the ore or compound is initially a sulfid, use is made of the nascent hydrogen disengaged from the electrolyte at the cathode which, acting upon the sulfur constituent of the ore, converts the same into sulfureted hydrogen, the elimination of the sulfur in the manner indicated leaving the metal behind in the metallic state. By then reversing the current, the metal goes into solution in the electrolyte and is subsequently deposited from said solution on what now becomes the cathode end of the circuit. Where the ore or compound is a carbonate or oxid or any other compound capable of entering into initial solution in the electrolyte, the passage of the current from the anode to the cathode at once causes the metal of the solution to be deposited on the cathode.

Various solutions and acids have been employed as the electrolyte, notably sulfuric acid which has the capacity of dissolving the majority of metallic compounds, and in the case of zinc and iron even the sulfids are dissolved by sulfuric acid; and where iron is present, as is usually the case of copper ores, the iron entering the solution in time saturates the electrolyte so that the copper can no longer be taken up and the process comes to an end. Again, insoluble anodes such as graphite, in sulfate solutions disintegrate so completely, the carbon diffusing itself throughout the solution as to materially interfere with the deposition of the metal at the cathode; and the metal which does deposit is generally impregnated with the objectionable carbon. For the foregoing reasons, sulfuric acid is not only not desirable but is objectionable, and I accordingly avoid it.

An important feature of my process is the selection and use of an electrolyte which, though fully capable of dissolving the metals to be recovered, shall have little affinity for ferric oxid and sulfid which so readily combine with sulfuric acid, and whose solution gives rise to the objections above referred to. Sulfids of iron and zinc do not reduce at the cathode under the action of nascent hydrogen (as above explained) and if present in copper and lead ores which do reduce and subsequently pass into solution, they (the iron and zinc sulfids) can be readily separated since they simply precipitate themselves in an insoluble form to the bottom of the tank; and to the extent that the iron may dissolve in the electrolyte entering into my process, it will be converted at the anode into a higher oxid of iron practically insoluble in the electrolyte and likewise precipitate itself to the bottom of the tank. My electrolyte therefore offers the advantage in that it does not disintegrate the anode to any material extent (an unavoidable consequence with sulfate solutions), but it also has so slight an affinity for iron and zinc sulfids, and similar foreign metals not intended to be recovered, that it in no wise interferes with the electrodeposition of the metals sought (copper or lead). Where two or more recoverable metals are present in the solution, they may be deposited independently and separately on the cathode by properly regulating the current density and working voltage by which their dissociation from the solution is effected. The electrolyte employed in my process is silico-hydrofluoric (hydro-fluo-silicic) acid,  $H_2SiF_6$ , and as an illustration of my process I will take copper sulfid as the ore to be treated.

Referring to the drawings, 1 represents a wooden reduction tank of suitable shape and dimensions in which is contained an aqueous solution of the electrolyte E. Into this are inserted the electrodes 2, 2 of carbon or graphite one of said electrodes at the first stage of the process serving as an anode and the other as a primary cathode. Disposed in proximity to what for the time being is the primary cathode is a perforated wooden plate or diaphragm 3, from which is suspended a linen or canvas sheet or filter 4 which allows for the circulation of the liquid, but intercepts the fine particles of the ore O packed between the primary cathode and the diaphragm 3. The ore by its proximity to the primary cathode serves as an additional or secondary cathode, the secondary cathode being decomposable under the action of the current. Assuming that the ore is initially a sulfid of copper, and assuming that the current passes through the electrolyte from left to right, that is toward the ore and cathode along which the same is disposed, there will at once be a disengagement of nascent hydro-



gen (from the water) at the cathode. The hydrogen immediately attacks the sulfur of the ore, forming sulfureted hydrogen gas which passes off, and if desirable may be conducted to any point of consumption. After  
5 a certain quantity of the sulfid is thus reduced, (the reduction resulting in metallic copper at the cathode) the current is reversed, so as to pass from the ore to the opposite electrode, the cathode becoming the anode, and the anode becoming the cathode. The plain arrow  
10 indicates the direction of the reducing or original current, and the feathered arrow that of the electro-depositing current. Upon reversal of the current the metal previously reduced goes into solution (as a salt of copper,  $\text{CuSiF}_6$ ) and the copper becomes deposited  
15 as a sheet *m* on the electrode which now has become the cathode. These sheets of copper may be peeled off from time to time as is obvious.

Where the ore or compound is a sulfid, it is of course insoluble in the electrolyte and its solution can be ef-  
20 fected only after reduction in the manner indicated; and the current may be first passed in one direction and then the other until the total quantity of metal is reduced and recovered, the sheets *m* being of course  
25 always peeled off previous to the conversion of the electrode to which the sheet adheres, into an anode.

Where the compound or ore is initially soluble in the electrolyte which is the case with carbonates or  
30 oxids, there will be no occasion in placing the ore in contact with the electrode serving initially as the cathode, as there is no sulfur to be got rid of and the ore can be dumped into the electrolyte and the current started  
35 in either direction, the sheet metal depositing on the cathode as already described. In some cases I may use hydro-fluoric acid to produce the soluble fluorid of the metal to be recovered.

Having described my invention what I claim is:

1. In the reduction of metallic sulfids, the process of  
subjecting the sulfid to the action of an electric current  
flowing from an insoluble anode to a correspondingly insol- 40  
uble cathode and to the sulfid, in an electrolyte capable of  
dissolving the metal constituent of the sulfid and forming a  
salt therewith, then reversing the current whereby the  
salt is decomposed and the metal of said salt is deposited  
on the electrode which now becomes the cathode, substan- 45  
tially as set forth.

2. In the reduction of sulfid ores, the process of subject-  
ing the ore to the action of an electric current flowing  
from an insoluble anode to the ore serving as a cathode,  
in an electrolyte capable of dissolving the metal constit- 50  
uent of the ore when freed of its sulfur, then reversing the  
current whereby the salt solution thus formed is decom-  
posed and the metal becomes deposited on the resulting  
cathode, substantially as set forth.

3. In the reduction of sulfid ores, the process of subject- 55  
ing the ore to the action of an electric current flowing  
from an insoluble anode to a primary insoluble cathode in  
the presence of a quantity of the ore serving as a  
secondary decomposable cathode, in an electrolyte capable  
of dissolving the metal constituent of said secondary 60  
cathode, then reversing the current whereby the solution  
of the salt of the metal of the ore is decomposed and the  
metal is deposited on the electrode which becomes the  
cathode, substantially as set forth.

4. In the reduction of metallic compounds the process of 65  
first forming an aqueous solution of the salt resulting  
from the union of the metal constituent of the compound  
and silico-hydro-fluoric (hydro-fluo-silicic) acid then sub-  
jecting said salt solution to the action of an electric cur-  
rent flowing from an insoluble anode to a cathode im- 70  
mersed in said solution, whereby the metal is deposited on  
the cathode, substantially as set forth.

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

EDWARD L. ANDERSON.

Witnesses:

EMIL STAREK,  
JOS. A. MICHEL.