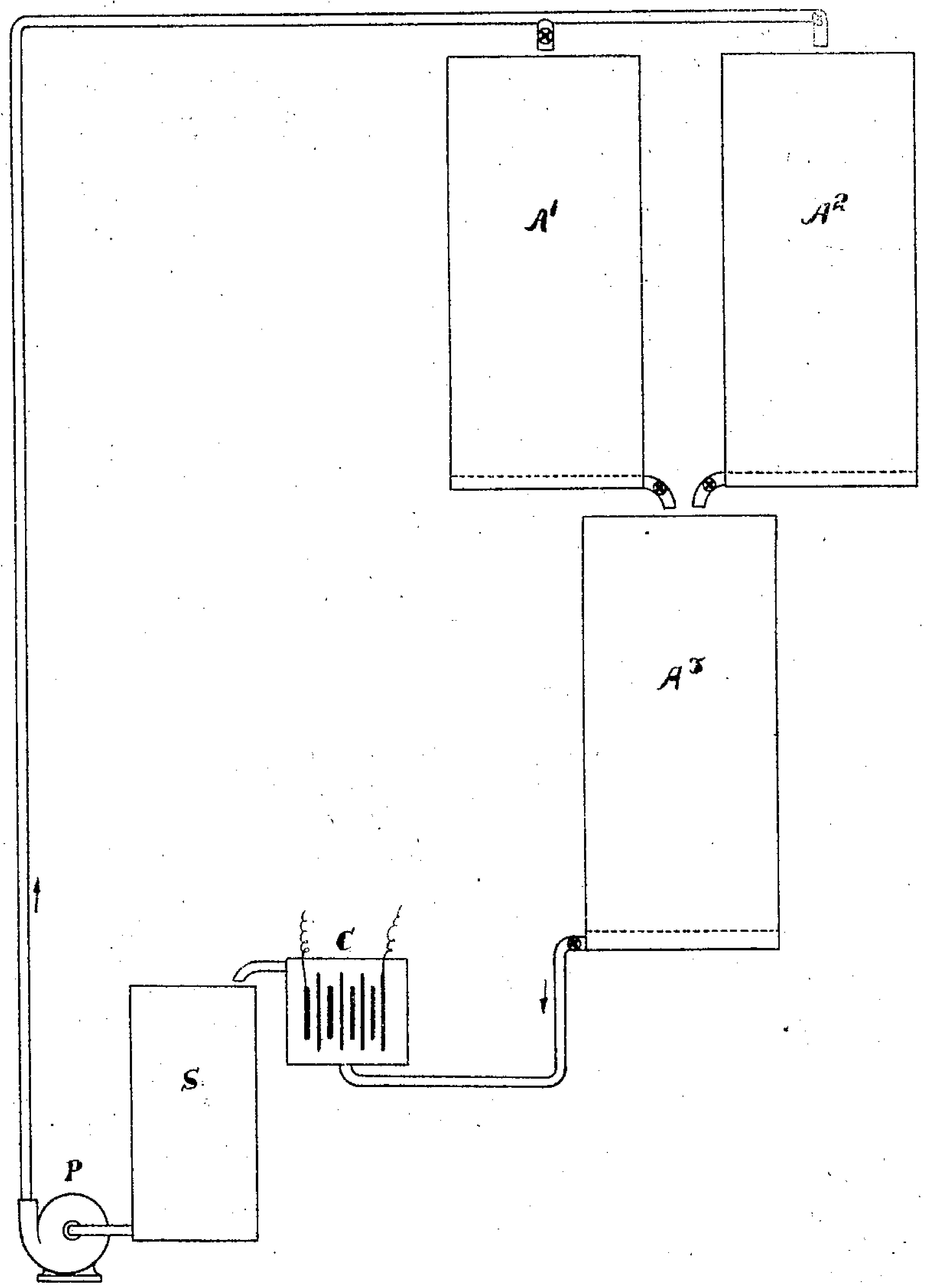
O. BEST.

EXTRACTION, PURIFICATION, AND ELECTROLYTIC PRECIPITATION OF METALLIC ZINC FROM SMELTER FUMES, ZINC ORES, AND THE LIKE.

APPLICATION FILED SEPT. 16, 1911.

1,154,601. Patented Sept. 28, 1915.



WITNESSES

N. B. Keating.
F. C. Fliedner

INVENTOR
Otto Best,

BY
F. M. Wright
ATTORNEY

UNITED STATES PATENT OFFICE.

OTTO BEST, OF SAN FRANCISCO, CALIFORNIA.

EXTRACTION, PURIFICATION, AND ELECTROLYTIC PRECIPITATION OF METALLIC ZINC FROM SMELTER-FUMES, ZINC ORES, AND THE LIKE.

1,154,601. Specification of Letters Patent. Patented Sept. 28, 1915.

Application filed September 16, 1911. Serial No. 649,719.

To all whom it may concern:

Be it known that I, OTTO BEST, a citizen of the United States, residing at San Francisco, in the county of San Francisco and State of California, have invented new and useful Improvements in the Extraction, Purification, and Electrolytic Precipitation of Metallic Zinc from Smelter-Fumes, Zinc Ores, and the like, of which the following is a specification.

The object of this invention is the extraction of zinc, as zinc sulfate from zinc fumes, and the electrolytic separation of metallic zinc. This I accomplish by roasting and leaching the same, purifying the salt obtained, precipitating, partly or entirely, the purified zinc salt in the form of hydroxid, carbonate, and the like, (either unmixed or mixed with an indifferent body like gypsum) by means of caustic alkali, alkali carbonate, alkaline earth, such as caustic soda, sodium carbonate, lime or magnesium oxid, and electrolyzing the salt, to obtain the zinc in a metallic shape, while neutralizing the acid, which is then, at the same time, freed by running it over the purified zinc hydroxid, carbonate or other zinc compound, insoluble in water, but soluble in weak acid and returning the liquor in a neutral or almost neutral condition, with practically the same saturation of zinc salts, and absolutely pure, to the electrolytic cell.

The successful electrolytic preparation of metallic zinc has been hampered in practice by the facts, that impure zinc salts, when electrolyzed, deposit the zinc in a spongy form, that cannot be remelted. Again, the proper amount of free acid in solution and the proper control of the same has been found rather difficult to obtain. Since these conditions are constantly changing, the current conditions have to be changed accordingly, which is another obstacle to the successful carrying out of this process.

In order to be a practical success, the chemical extraction must be simple and fairly complete, purification of the zinc salt practically complete, and chemical and electrical conditions in the cell must be as uniform as possible, so that if the best conditions for depositing electrically a pure remeltable zinc are once established, they can be kept the same for weeks and months, when the same results must be obtained for a corresponding period.

In the drawing, the figure is a diagrammatic view of an apparatus for carrying out a part of my improved process.

In the following described process, I have obtained these ideal conditions, and have thus obtained a pure zinc, not spongy, but capable of remelting. The zinc obtained in the laboratory from "fumes" has tested 99.2% and can easily be remelted.

The experiments were mainly carried out with so called smelter "fumes," which is a dust, collected in a bag house provided for that purpose in some smelters. It is a very refractory material, containing up to 30 and 35% metallic zinc, mainly in the form of zinc oxid and sulfate. It contains furthermore many kinds of products, partly valuable, partly valueless, such as silica, iron, alumina, lime, magnesia, arsenic, antimony, cadmium, lead, sulfur, sulfuric acid, organic matter, and others; furthermore silver and gold. The value of the latter two is largely depreciated through the presence of zinc, the terror of the smelter; the zinc on the other hand is difficult to extract and to purify, on account of the many impurities present. Instead of smelter fumes, ore or other sources of zinc, with slight modifications, may be used.

I proceed in my process first chemically and then electrolytically, which are both part of one and the same process. The chemical part of the process is as follows: The "fumes" are first roasted at a low temperature, that is, made filterable and partially purified by the application of heat at a temperature below that of sulfatic roasting. The temperature is kept only high enough to char the organic matter and sublime the arsenic. In the presence of sulfates of a heavy metal, like iron or zinc sulfate, the arsenic sublimes readily, and practically completely. By this step, the most important of the chemical process, the following advantages are reached: (1) The material, that was, before roasting, difficult to filter, is made filterable; (2) the organic matter is destroyed and therefore no oxidation agents are necessary to destroy it (for instance coloring matter); (3) the material is free of arsenic, while the arsenic can be recovered at the same time; (4) the iron is oxidized and practically insoluble in weak acids and makes purification of the mother liquor easier and whatever traces of iron go into solution are present in ferric form, and are easily removed by an addition of zinc oxid, or better, hydroxid; (5) small amounts of sulfids are oxidized to oxids and sulfates and can be extracted by weak acid (copper, for instance). The roasted material is now extracted with weak acid, for instance, sulfuric, hydrochloric, or other suitable acid, in slight excess, and, if necessary, heated somewhat. Practically all the zinc is easily dissolved with some other salts. In the laboratory experiments 92% of the zinc and over were extracted with sulfuric acid. All impurities can easily be removed by zinc oxid and a little sodium sulfid, used either successively or in one process, according to the products present and the object to be attained. The present process only relates, however, to the solution, as this contains the zinc desired. The solution, as before stated, obtained from the roasted ore, is much purer than from the unroasted ore under otherwise the same conditions. This highly purified mother liquor of zinc salts is now precipitated in the form of hydroxid, carbonate, sulfid or other insoluble compound, that is insoluble in water, but soluble in weak acids by means of a caustic alkali, alkali sulfid, alkali carbonate, alkaline earth like caustic soda, sodium sulfid, sodium carbonate, lime, magnesium, oxid and the like. For instance:

(1) $ZnSO_4+2NaOH=Zn(OH)_2+Na_2SO_4+2H_2O$

(2) (*a*) $ZnSO_4+Ca(OH)_2=Zn(OH)_2+CaSO_4$

or—

(*b*) $ZnSO_4+Mg(OH)_2=Zn(OH)_2+MgSO_4$

(3) $ZnSO_4+Na_2CO_3=ZnCO_3Na_2SO_4$.

I now wash these precipitates until all soluble impurities are removed and am ready for the next part of the process, that of electrolysis.

The pure zinc salt solution is placed in the electrolytic cell. Any suitable salt may be used with any suitable density, at any suitable temperature, with any suitable electrode, with or without a diaphragm. A small amount of pure sulfuric acid, best suited for the electrolysis, is added to this solution. As the zinc salts used are pure, there is quite a leeway, from a few hundredths of one per cent, of 10 per cent. and over, without danger of getting spongy zinc. Of course it is not advantageous, to go too high in free acid, as the loss on electricity is otherwise too high. In so far as I am aware, it is broadly new to use any salt, organic or inorganic, and particularly any zinc salt in this connection. One way of accomplishing this result is as follows: Referring to the drawing, C indicates an electrolytic cell, which is filled with a zinc salt, preferably zinc sulfate. The same runs over into a storage tank S and contains zinc sulfate and some sulfuric acid. A pump P lifts it to two filters A_1 and A_2 with false bottoms, filled with zinc hydroxid-gypsum mixture at such rate, as to get the desired acidity in the electrolytic cell. Of course any other suitable filter may be used. In running the acid zinc sulfate solution through this layer of zinc hydroxid gypsum mixture, the free sulfuric acid is neutralized and at the same time zinc hydroxid is dissolved, leaving the gypsum behind, insoluble. The neutral solution may pass another filter, A_3, holding zinc hydroxid gypsum mixture to get rid of the last trace of free sulfuric acid and any possible mechanical and chemical impurities and be returned to the cell C at the bottom in a pure, neutral state. The aim, however, is to get the most suitable concentration of acid and zinc salt and otherwise the most suitable conditions, and to keep this concentration of acid and zinc salt and other conditions as much as possible the same.

By regulating the speed of the circulating liquor the desired amount of free acid in the cell is obtained. I can of course place the precipitated zinc compound also into the cell, separating it from the cathode by a porous wall, filter or the like; I may press it into anode plates, alone or with insoluble or indifferent materials.

The part of the "electrolytic cycle" of the process can of course be carried out with other metallic hydroxids like copper hydroxids made by the "ammonia", or "ammonia-cyanid" or any other process, or any metallic hydroxids or water-insoluble compound in a pure state, however obtained, preferably freshly precipitated to be easily soluble in dilute acids, as described by the zinc hydroxid.

I claim:—

1. In the extraction of metallic zinc from zinc fumes, or the like, the preliminary step of obtaining a zinc salt suitable for forming the electrolyte, which comprises subjecting the fumes to a purifying roast, in the presence of sulfates, at a low temperature, thereby rendering the fumes filterable, and leaching with a small excess of sulfuric acid; substantially as described.

2. In the extraction of metallic zinc from zinc fumes, or the like, the preliminary step of obtaining a zinc salt suitable for forming the electrolyte which comprises roasting the fumes in the presence of sulfates at a low temperature leaching with a small excess of sulfuric acid and purifying the solution thus obtained with zinc oxid and sodium sulfid; substantially as described.

3. In the extraction of metallic zinc from zinc fumes, or the like, the preliminary step of obtaining a zinc salt suitable for forming the electrolyte which comprises roasting the fumes in the presence of sulfates at a low temperature and leaching with a small excess of sulfuric acid, purifying the solution obtained with zinc oxid and sodium sulfid, and precipitating the pure zinc sulfate solution with lime to form zinc hydrate gypsum mixture; substantially as described.

4. In the extraction of metallic zinc from zinc fumes, or the like, the preliminary step of obtaining a zinc salt suitable for forming the electrolyte which comprises roasting the fumes in the presence of sulfates at a low temperature and leaching with a small excess of sulfuric acid, purifying the solution obtained with zinc oxid and sodium sulfid, precipitating the pure zinc sulfate solution with lime to form zinc hydrate gypsum mixture and washing said mixture with water to get rid of the soluble impurities; substantially as described.

5. In the extraction of metallic zinc from zinc fumes, or the like, the process which comprises roasting the fumes in the presence of sulfates at a low temperature and leaching with a small excess of sulfuric acid, purifying the solution obtained, precipitating the pure zinc sulfate solution with lime to form zinc hydrate gypsum mixture, washing said mixture with water to get rid of the soluble impurities, electrolyzing the pure zinc sulfate obtained and thereby depositing zinc on the cathode and forming sulfuric acid at the anode, pumping the acid zinc sulfate solution over the mixture of zinc hydrate and gypsum to neutralize the sulfuric acid, and returning the neutralized solution to the cell; substantially as described.

6. In the extraction of zinc from zinc fumes or the like, the preliminary step of obtaining a solution appropriate for introduction into an electrolytic cycle, which comprises precipitating a metallic compound in a water-insoluble form, easily soluble in dilute acids, and introducing the same into the electrolytic cycle; substantially as described.

In testimony whereof I have hereunto set my hand in the presence of two subscribing witnesses.

OTTO BEST.

Witnesses:
FRANCES M. WRIGHT,
D. B. RICHARDS.