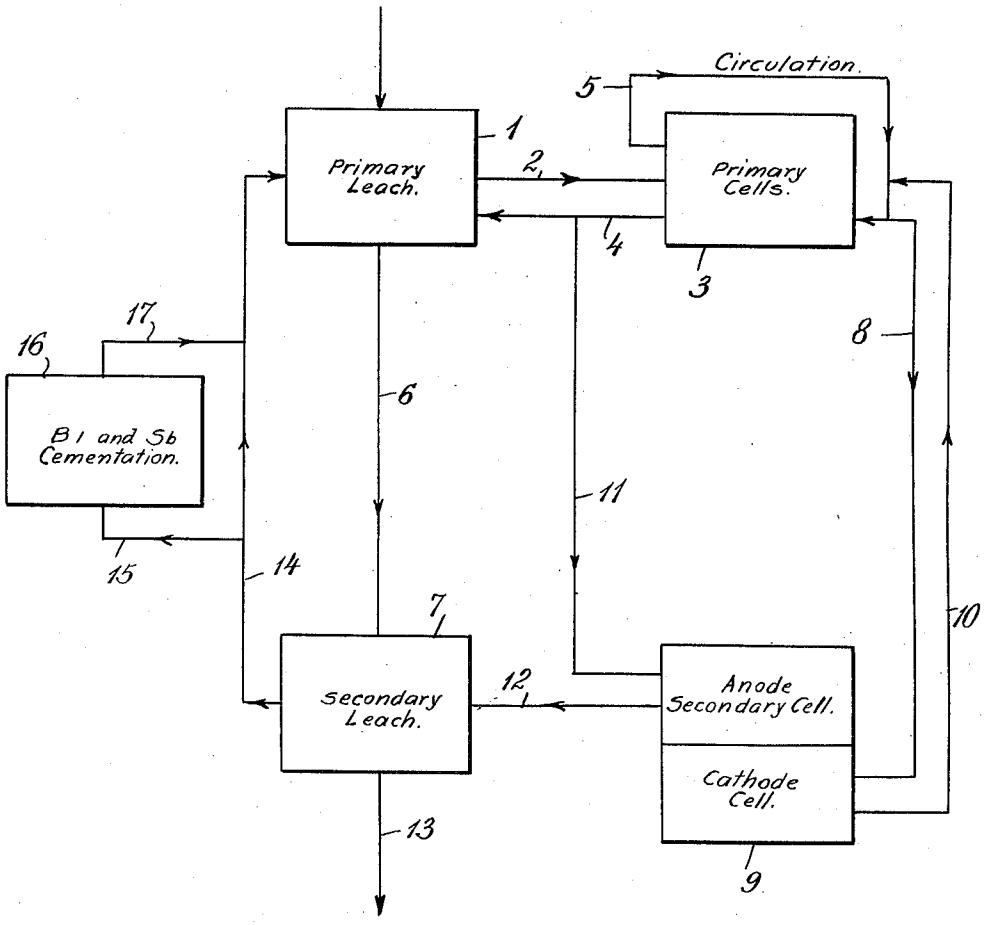
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METALLURGY OF TIN

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METALLURGY OF TIN.

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This invention relates to the recovery of tin from ores, concentrates and other materials in which the tin has been reduced to a metallic condition, and particularly to a cyclical method wherein the tin is leached from materials containing it and separated thereafter by electrolysis with regeneration of the leaching solution.

The metallurgy of tin as conducted heretofore requires concentration of the ore until it contains from sixty to sixty-five per cent. of tin before smelting is possible economically. In preparing concentrates containing tin in such high proportions twenty to thirty-five per cent. of the tin is lost in the tailings. This loss, which has been unavoidable heretofore, increases the cost of the recovered tin to a very material extent, but it has not been possible heretofore to avoid this loss because no methods have been available whereby the tin could be separated and recovered economically from low grade materials.

It is the object of the present invention to provide a relatively inexpensive and easily workable method whereby the ore or concentrates therefrom or other material containing tin even in relatively small proportions can be treated to recover the tin therefrom, and incidentally to separate it from impurities which are present in the raw material.

Other objects and advantages of the invention will be apparent as it is better understood by reference to the following specification in which the preferred embodiments of the invention are described.

In carrying out the invention it is essential that the tin or at least a portion thereof be reduced to the metallic form in the ore, concentrates or other tin-bearing material since the method herein described is not designed primarily to separate compounds of tin from the raw material. The reduction may be carried out in any usual or desired manner as, for example, by heating the tin-bearing material in the presence of a gaseous reducing agent. It is essential also that the tin-bearing material shall not be sintered to any substantial extent because the sintering would interfere with the subsequent leaching operation. The material delivered to the leaching plant should be in a granular condition, that is to say, in the physical form in which it comes from the crushing plant or concentrating mill. The reduction may be carried to a greater or less extent but as much as possible of the tin should be reduced since only metallic tin is dissolved in the primary process. It is possible, however, to separate tin sulphide from the raw material by a supplemental method hereinafter described.

The invention depends upon leaching the material containing reduced tin with a solvent which is capable of dissolving the tin. One example of a suitable solvent is a solution containing from twenty to twenty-five grams per liter of tin in the form of stannic chloride, one hundred grams per liter of iron in the form of ferrous chloride and twenty-five grams per liter of acid. Hydrochloric or sulphuric acids are preferred because these are relatively inexpensive and easily obtainable. The proportions of the several ingredients are those which in a particular instance gave the best results, but it is not essential that the proportions be adhered to strictly, and variations will occur in the operation of the method without affecting the results obtained to a serious extent.

In leaching an ore relatively free from acid soluble iron the iron content of the solution may decrease considerably below that of the example, for, as hereinafter explained, it is chiefly in leaching the less soluble forms of tin such as tin sulphide that the presence of iron becomes of particular value.

Likewise the limits of acid and tin concentration in the leaching solution may vary considerably, higher acid concentration sometimes being carried to make up for larger losses in the leaching operation and higher or lower stannic tin concentrations being carried depending on the ease of dissolution of the tin mineral and the concentration of tin desired in the solution going to the electrolytic deposition plant. This process also utilizes to good advantage a particular property of the solution herein employed, namely, the higher the stannic tin concentration in the leach solution, the greater the amount of tin that can be dissolved per unit

volume of leach solution and the less volume of solution that must be employed to leach the ore.

This invention will be better understood by reference to the flow sheet shown in the accompanying drawing, taken in conjunction with the following description:

The reduced tin-bearing material to be leached is held in an appropriate container 1 in contact with the leaching liquor. In practice, these materials are suitably agitated and the resulting solution passes through a line 2 to primary cells 3 where tin is electrodeposited. In cells 3 the leaching liquor is regenerated and a portion of it is returned through a line 4 to the primary leach 1. In practice, in order to facilitate the operation of the primary cells 3, part of the electrolyte is additionally circulated through the cells 3 and a line 5.

The residue from the primary leach (1) contains such materials as antimony, bismuth, tin sulphides, etc., which are removed in a suitable manner from container 1 through a line 6 to a secondary leach in container 7. The leaching solution for the secondary leach is derived from the primary leach solution. Part of the primary leach liquor is withdrawn from cells 3 through a line 8 and subjected to electrolysis in an ordinary cell 9 of the diaphragm type which is resistant to acid corrosion. The electrolysis results in the deposition of some tin and the regeneration of solution containing ferric chloride. The solution is then returned through a line 10 to the primary cells 3 and part of this solution is returned to the anode compartment of cell 9 through a line 11.

From the anode compartment of the secondary cell 9 the ferric chloride leach solution passes through a line 12 to the secondary leach container 7. Here the ferric chloride dissolves the antimony, bismuth and tin sulphides. The tailings, substantially free from tin, antimony and bismuth are discharged from the container 7 through an outlet 13.

The pregnant solution from the secondary leach (7) is returned to the primary leach (1) through a line 14. In practice, part of the solution flowing from the container 7 is by passed through a line 15 to a container 16 where the bismuth and antimony are cemented out on tin metal. The solution from container 16, free from antimony and bismuth, is returned to a line 14 through a line 17, from whence it passes to the primary leach 1.

Acid additions to the solutions can be made using either hydrochloric or sulphuric acid. Since sulphuric acid is as a rule much cheaper than hydrochloric acid this is the acid preferred. In this case it is usually desirable from time to time to add to the solution quantities of some appropriate chloride so as to maintain a chloride concentration in the solution of 10 grams per liter or over. The chloride has a number of advantages in promoting dissolution and eliminating hydrolysis of the tin as well as in some cases tending to give a more perfect and adherent tin deposit in the electrolysis.

Another particular advantage in using leach solution of the above character is embodied in its remaining an efficient leaching and electrolytic solution even after building up to saturation in ferrous iron. By carrying the iron in the solution at its full saturation value the necessity of discarding solution because of continued dissolution and contamination from iron compounds in the ore being leached is avoided. The iron sulphate builds up in the solution to a saturation value and thereafter any further iron dissolved from the ore precipitates again, either in the ore itself or subsequently.

The action of the solvent may be indicated as follows:

$$Sn+SnCl_4=2SnCl_2$$

and if any ferric chloride is present it will react as follows:

$$Sn+2FeCl_3=SnCl_2+2FeCl_2$$

The leaching may be carried out by percolation or agitation in any suitable container which is capable of holding the solvent. The mechanical features of the leaching equipment may be varied in accordance with well understood practice and do not affect the result which obviously is to dissolve the tin which is present in the raw material. The tin appears as stannous chloride in the solution which is delivered from the leaching plant. This solution will contain, for example, forty grams per liter of stannous chloride, one hundred grams per liter of ferrous chloride and fifty grams per liter of acid. The proportion of stannous chloride in the solution from the leaching plant will vary, of course, depending upon the practice followed, but it is preferable to so proportion the volume of solution used to the amount of tin present in the raw material that a solution containing about forty grams per liter of stannous chloride will be obtained.

The solution from the leaching plant is delivered to the electrolytic cells wherein the tin is separated. These cells may be of any of the well known types without diaphragms and provided with cathode plates of tin or other suitable metal. The anodes may be of graphite or any other corrosion-resistant anode material. The electrolyte is supplied continuously to the cells while curent is permitted to flow therethrough with the result that tin is deposited upon the cathode. The stannous chloride in the solution is thus converted into stannic chloride and ferric chloride is formed at the anode. The flow of solution is regulated, however, to convert

the ferric chloride immediately into ferrous chloride. The reactions may be indicated as follows:

$$SnCl_4+4FeCl_2=Sn+4FeCl_3$$
$$2SnCl_2+4FeCl_3=2SnCl_4+4FeCl_2$$

Consequently the solution leaving the cells will contain stannic chloride, ferrous chloride and acid, and if properly regulated the operation will result in the production of a solution containing from twenty to twenty-five grams per liter of stannic chloride, one hundred grams per liter of ferrous chloride and fifty grams per liter of acid. This, it will be noted, is the solution used originally in leaching the raw material, and consequently it can be returned to the leaching plant for the treatment of additional material. The net result of the operation is to dissolve approximately twenty grams of tin per liter of solution used from the raw material and to deposit it upon the cathode.

The ferrous chloride in the solution plays no part in the leaching operation, but in the electrolysis it acts as a depolarizer to reduce the cell voltage of 3.0 volts to 1.4 volts. The acid is used to prevent hydrolysis of the iron and tin chlorides and the proportion mentioned is high enough for that purpose, yet not sufficiently high to dissolve the cathode to any serious extent.

While it is not essential, it is preferable to employ a small amount of a colloid addition agent in the solution of electrolysis for the purpose of improving the character of the deposit at the cathode. Usually there is a sufficient amount of silicic acid derived from the ore or concentrate so that no extraneous material need be employed. However, the cathode deposit can be improved by the addition of a small amount of glue to the solution, particularly if it is deficient in silicic acid.

The method as described relates to the treatment particularly of materials containing tin in a metallic state. In practice, however, the reduced material will often carry as much as ten per cent of tin in the form of sulphide and the sulphide is not dissolved readily by stannic chloride. It is refractory also to most leaching agents. Consequently the tin sulphide, if present in the raw material, will be mostly left therein at the end of the leaching operation and will remain in the residue or tailings. My experiments have shown that it is possible and economical to leach the sulphide from the residue by the application of a modified method using a solution containing ferric chloride. The reaction is indicated as follows:

$$SnS+4FeCl_3=SnCl_4+4FeCl_2+S$$

The solution can be derived from the solution employed originally in the treatment of the raw material and recovered from the electrolysis. When such a solution is electrolyzed in a diaphragm cell ferric chloride is formed with high current efficiency. It can be produced also by passing chlorine gas into the required leach solution containing ferrous chloride. The solution as thus modified will contain, for example, twenty grams per liter of stannic chloride, sixty grams per liter of ferric chloride, forty grams per liter of ferrous chloride and fifty grams per liter of acid. This solution can be applied to the tailings from the previously leached material or to fresh raw material containing a large proportion of tin sulphide. The leaching can be carried on by percolation or agitation in accordance with well understood principles and will result in a solution containing, for example, fifty grams per liter of stannic chloride, one hundred grams per liter of ferrous chloride and fifty grams per liter of acid. This solution is subjected to electrolysis in an ordinary cell of the diaphragm type which is resistant to acid corrosion. Preferably it is diluted before it enters the cell by the addition of solution from the anode compartments thereof until the concentration in tin is reduced to about twenty-five grams per liter. The electrolysis results in the deposition of about five grams per liter of tin from the solution and the regeneration of the solution containing ferric chloride which was used as a solvent.

In carrying out the electrolysis some of the spent electrolyte from the cathode compartment is returned to the "head cells" to dilute the incoming solution from the leaching plant for the purpose hereinbefore noted. The remainder of the spent electrolyte from the cathode compartment flows through the anode compartments where the ferrous iron is oxidized to ferric iron, thus completing the cycle to produce the leaching solution.

As in the electrolysis as first described, it is desirable to have a colloid addition agent present, and unless there is sufficient silicic acid derived from the raw material it is desirable, though not essential, to add a small proportion of glue to the solution. This improves the quality of the cathode deposit.

An important feature of the method is that impurities present in the raw material such as iron, bismuth, arsenic, antimony, etc., remain therein during the initial leaching to separate metallic tin. Iron, if reduced to the metallic state or to the state of ferrous oxide, is soluble in the acid of the leach solution. However, as iron is one of the chief constituents of the solution, it may be carried at comparatively high concentrations and separated as crystallized ferrous chloride or sulphate, or a portion of the solution can be discarded from time to time to lower the iron concentration.

Metals such as bismuth and antimony are

below tin in the electro-chemical series and will not dissolve in the stannic chloride leach solution so long as any appreciable amount of metallic tin is present. Consequently by suitably controlling the operation, for example, by withdrawing the leaching solution when the metallic tin has been dissolved, bismuth and antimony will be retained in the residue or tailings with any tin sulphide if the latter is present. Bismuth and antimony are soluble in the ferric chloride leach and will be dissolved, therefore, when the residue is treated for the recovery of tin sulphide. The solution derived from the leaching of metallic tin is thus purified automatically and the tin deposited therefrom will be free from deleterious impurities.

When bismuth and antimony are present in the raw material and are recovered in the ferric chloride, leach, the solution can be electrolyzed and returned for further use until the concentration of antimony and bismuth is sufficiently high to permit recovery thereof by cementation on tin. Thus the ferric chloride solution from the electrolytic cells can be withdrawn at intervals and permitted to percolate over or otherwise contact with metallic tin, and the bismuth and antimony can be removed thus from the solution.

Since the solutions employed are regenerated continuously in conducting the operation, the cost of reagents for use therein is lowered materially. It is necessary only to add sufficient acid from time to time to maintain the necessary proportion thereof in the solution. Ferrous and ferric chloride are derived from the raw materials treated and the tin, of course, passes from the raw material through the solution to the cathode of the electrolytic cell. The method as described requires no complicated or unusual apparatus, and since only the acid need be transported to the place where the operation is conducted, the method is very economical. Moreover, only a relatively small amount of acid is required to make up for unavoidable losses in the solution.

Various changes may be made in the details of the operation and particularly in the proportions of the ingredients present in the solutions used without departing from the invention or sacrificing the advantages thereof.

I claim:—

1. The method of recovering tin from materials containing it, which comprises leaching the material with mixed solvents containing tin and iron compounds and acids, and electrolyzing the solution to deposit a portion of the tin therefrom and to regenerate the solvent.

2. The method of recovering tin from materials containing it, which comprises leaching the material with mixed solvents containing tin and iron compounds and acids which do not dissolve bismuth and antimony, electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent and recovering bismuth and antimony from the residue left by the solvent.

3. The method of recovering tin from materials containing it, which comprises reducing tin in the material to the metallic state, leaching the reduced tin from the material with mixed solvents containing tin and ferrous iron compounds and acids, and electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent.

4. The method of recovering tin from materials containing it, which comprises reducing tin in the material to the metallic state, leaching the reduced tin from the material with mixed solvents containing tin and ferrous iron compounds and acids, electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent further electrolyzing the solvent forming ferric iron, leaching the residue with the electrolyzed solvent containing a ferric iron compound and electrolyzing the second solution to deposit a portion of the tin and to regenerate the solvent.

5. The method of recovering tin from materials containing it, which comprises reducing tin in the material to the metallic state, leaching the reduced tin from the material with a mixed solvent containing a stannic salt, a ferrous salt and acids, and electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent.

6. The method of recovering tin from materials containing it, which comprises reducing tin in the material to the metallic state, leaching the reduced tin from the material with mixed solvents containing a stannic salt, a ferrous salt and acids, electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent, further electrolyzing the solvent forming ferric iron, leaching the residue with the electrolyzed solvent containing a stannic salt, a ferric salt and acids, and electrolyzing the second solution to deposit a portion of the tin and to regenerate the solvent.

7. The method of recovering tin from materials containing it, which comprises reducing tin in the material to the metallic state, leaching the reduced tin from the material with mixed solvents containing a stannic salt, a ferrous salt and acids, electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent, further electrolyzing the solvent forming ferric acid, leaching the residue with the electrolyzed solvent containing a stannic salt, a ferric salt and acids, separating antimony and bismuth from the second solution by cementation on tin and electrolyzing the second solution to deposit a portion of the tin and to regenerate the solvent.

8. The method of separating tin from materials containing it in the form of sulphide of tin, which comprises leaching the material with mixed solvents containing a stannic salt, a ferric salt and acids, and electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent.

9. The method of separating tin from materials containing it in the form of sulphide of tin, which comprises leaching the material with mixed solvents containing a stannic salt, a ferric salt and acids, separating antimony and bismuth from the solution by cementation on tin and electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent.

10. The method of separating tin from materials containing it, which comprises leaching successive portions of the material with mixed solvents containing tin and iron compounds and acids, and regenerating the solvent by electrolysis whereby a portion of the tin therein is deposited.

11. The method of separating tin from compounds containing it, which comprises subjecting successive portions of the material having tin in the metallic state to a mixed solvent containing a stannic salt and a depolarizing agent, and regenerating the solvent by electrolysis whereby a portion of the tin therein is deposited.

12. The method of separating tin from compounds containing it, which comprises subjecting successive portions of the material having tin in the metallic state to a mixed solvent containing a stannic salt, a depolarizing agent and acids, and regenerating the solvent by electrolysis whereby a portion of the tin therein is deposited.

13. The method of separating tin from compounds containing it, which comprises subjecting successive portions of the material having tin in the metallic state to a mixed solvent containing a stannic salt and a depolarizing agent, regenerating the solvent by electrolysis whereby a portion of the tin therein is deposited, separating tin sulphide from the residue by leaching with a mixed solvent containing a ferric salt, and regenerating the second solvent by electrolysis whereby a portion of the tin therein is deposited.

14. The method of separating tin from compounds containing it, which comprises subjecting successive portions of the material having tin in the metallic state to a mixed solvent containing a stannic salt and a depolarizing agent, regenerating the solvent by electrolysis whereby a portion of the tin therein is deposited, separated tin sulphide from the residue by leaching with a mixed solvent containing a ferric salt, separating antimony and bismuth from the second solution by cementation on tin and regenerating the second solvent by electrolysis whereby a portion of the tin therein is deposited.

15. In the cyclical leaching of tin ores and the like, the method of eliminating excess iron reacted with chemically by the constituents of the leach solution which constitutes maintaining the solution at a substantially saturated value of the combined form of iron least soluble in the leaching solutions employed.

16. A solvent solution suitable for leaching tin ores containing iron comprising a solution saturated with respect to ferrous sulphate and containing appropriate amounts of ferric iron, sulphuric acid and chloride ion.

17. The method of recovering tin from materials containing it which comprises leaching the material with a mixed solvent containing tin and iron compounds and sulphuric acid, and electrolyzing the solution to deposit a portion of the tin therefrom and to regenerate the solvent.

18. The method of recovering tin from materials containing it which comprises leaching the material with a mixed solvent containing tin and iron compounds and sulphuric acid which does not dissolve bismuth and antimony, electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent and recovering bismuth and antimony from the residue left by the solvent.

19. The method of recovering tin from materials containing it, which comprises reducing tin in the material to the metallic state, leaching the reduced tin from the material with a mixed solvent containing tin and ferrous iron compounds and sulphuric acid, and electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent.

20. The method of recovering tin from materials containing it, which comprises reducing tin in the material to the metallic state, leaching the reduced tin from the material with a mixed solvent containing a stannic salt, a ferrous salt and sulphuric acid, and electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent.

21. The method of recovering tin from materials containing it, which comprises reducing tin in the material to a metallic state, leaching the reduced tin from the material with a mixed solvent containing a stannic salt, ferrous salt and sulphuric acid, electrolyzing the solution to deposit a portion of the tin and to regenerate the solvent, leaching the residue with a similar solvent containing a stannic salt, a ferric salt and an acid, separating antimony and bismuth from the second solution by cementation on tin

and electrolyzing the second solution to deposit a portion of the tin and to regenerate the solvent.

22. The method of recovering tin from materials containing it, which comprises reducing tin in the material to a metallic state, leaching the reduced tin from the material with a mixed solvent containing a stannic salt, a ferrous salt and sulphuric acid, oxidizing the ferrous salt in the solution with chlorine to generate ferric salt, leaching the residue with the solvent containing a stannic salt, a ferric salt and an acid, separating antimony and bismuth from the second solution by cementation on tin and electrolyzing the second solution to deposit a portion of the tin and to regenerate the solvent.

23. The method of separating tin from materials containing it in the form of sulphide of tin, which comprises leaching the material with a mixed solvent containing a stannic salt, a ferric salt and sulphuric acid, and electrolyzing the solution to deposit a portion of the tin and regenerating the solvent.

In testimony whereof I affix my signature.

ELIAS ANTHON CAPPELEN SMITH.