

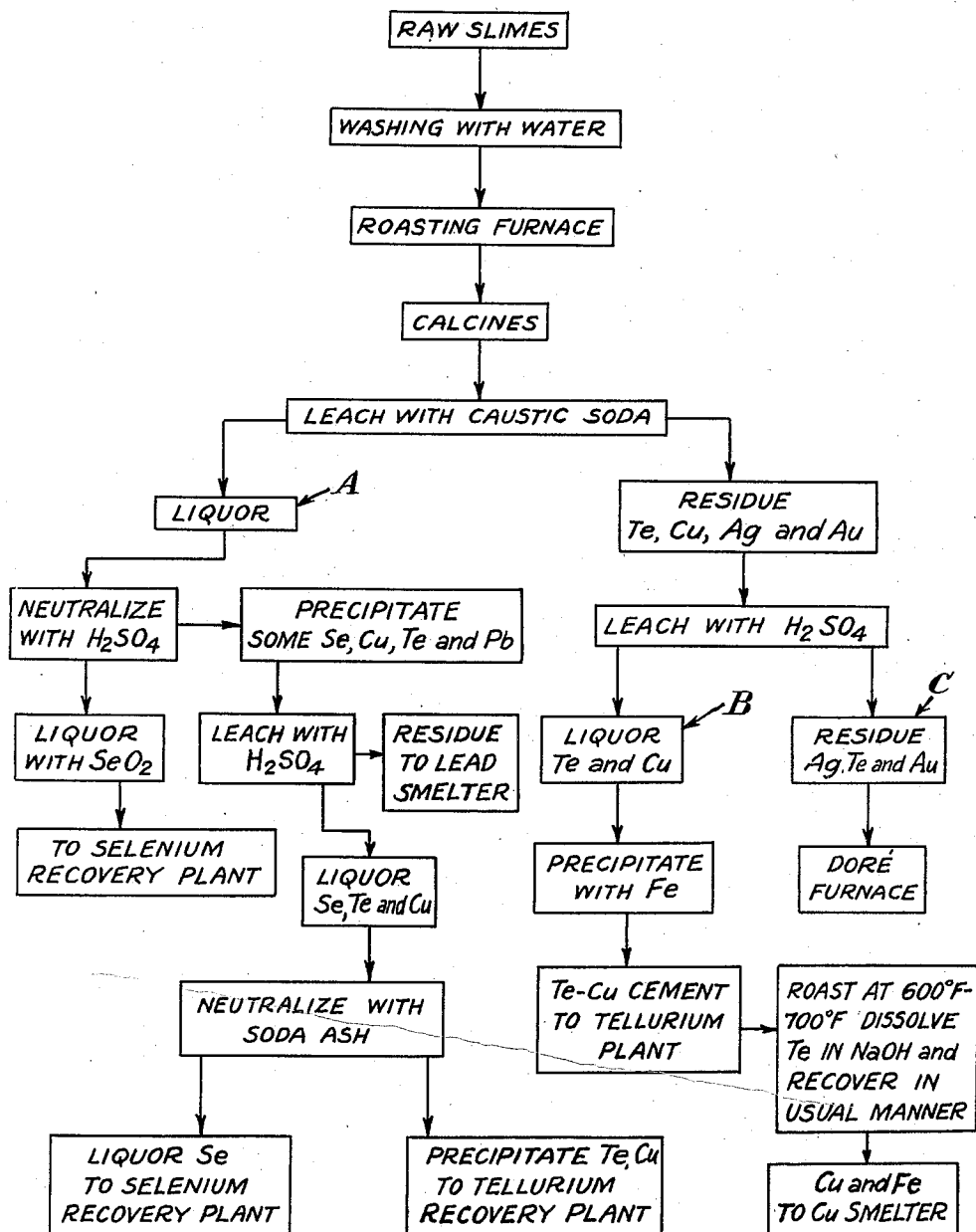
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2,084,394

ART OF REFINING METALS

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ART OF REFINING METALS

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This is an invention for the treatment of slimes produced in the electrolytic refining of copper and, more particularly, the invention relates to the removal from the slimes of impurities such as selenium and tellurium.

The invention has further reference to a novel method or sequence of steps involving roasting of the slimes under controlled conditions in order to put the selenium and tellurium in such form that they may be eliminated before or with the removal of the copper.

Various other objects, advantages and features of the invention will become apparent from the following detailed description.

The invention further resides in the method, features and novel series of steps of the character hereinafter described and claimed.

For an understanding of the invention, reference is to be had to the following description and to the sheet of drawings which constitutes a diagrammatic representation of the novel series of steps of the invention.

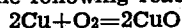
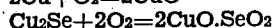
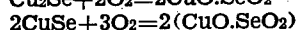
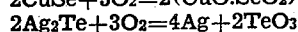
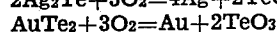
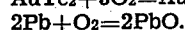
Only small amounts of selenium and tellurium are eliminated in the furnace operation of making anodes. During the electrolysis selenium and tellurium pass, with other impurities including the precious metals and some copper, into the slimes. When treating these slimes for the reclamation of the precious metals, small amounts of selenium and tellurium do not complicate the treatment as practiced by the usual methods, substantially such as described by L. Addicks "Copper Refining" (First Edition McGraw Hill Book Company, Inc., 1921) on page 119. But when the amounts of selenium and tellurium are appreciable, they cause considerable difficulty when treated this way, and if it is intended to recover selenium and/or tellurium as commercial by-products, the recoveries are low.

The roast-leach process heretofore practiced involves roasting of the slimes to make copper soluble and then leaching with sulphuric acid to eliminate the copper. Some of the selenium and tellurium are volatilized in the roasting and are partially recovered in the flue system; some are dissolved in the acid leach and as this solution is either returned to the tankhouse, or used to manufacture bluestone, selenium and tellurium are harmful and must be eliminated.

I have made a careful study of the constitution of tankhouse slimes which is described in "Metall und Erz" for 1933, vol. 30, pages 363-366 entitled "Ueber die Entfernung von Selen und Tellur aus Kupfer-Electrölysen-Schlämmen". The most important constituents are metallic

copper, cuprous selenide (Cu_2Se), cupric selenide (CuSe), silver telluride (Ag_2Te), lead, silver and gold.

From my observations, when conducting the roasting in accordance with my invention at a temperature between 600 and 800° F., I find that the following reactions take place:



The completeness of these reactions depends very much upon the handling of the roasting furnace and after a practical roast, according to my method, the selenium in the calcines should be present principally as $2\text{CuO} \cdot \text{SeO}_2$ or $\text{CuO} \cdot \text{SeO}_2$ and the tellurium as TeO_3 .

In accordance with my invention and in order to accomplish a satisfactory calcine, I first thoroughly wash the slimes free of sulphuric acid and copper sulphate. After drying, the material is carefully roasted preferably at 600-680° F. with or without rabbling and preferably in a muffle roasting furnace, the best results having been obtained when the greatest heat is applied to the bottom of the muffle, and the draft being regulated to withdraw rapidly any fumes produced. When working with fresh slimes, I find that it is only necessary to heat them sufficiently to start the reaction which is indicated by the glowing of the slimes. This reaction progresses through the entire mass and when this has ceased, the roasting is completed. The rate of glowing can be controlled by regulation of the draft to control the amount of fresh air allowed to come in contact with the slimes. I find that when the slimes are roasted in thin layers, the best results are obtained because the danger of overheating is avoided. Layers of about one inch thick roast satisfactorily, but I do not wish to be limited to this thickness as the thickness will vary with the kind of slimes being treated. When the slimes are not fresh, i. e., such as have become oxidized, I find that more heat must be applied.

A satisfactory roast may be judged by the amount of sulphuric acid insoluble copper in the calcines which should be less than 0.3%. The slimes calcine should also have a yellow green color, thus indicating a mixture of green copper selenites and yellow tellurium tri-oxides.

After roasting, the calcines are leached with a solution of caustic soda for the purpose of dissolving the selenium. A solution containing

from 2½ to 10% of Na(OH) is suitable. Sufficient heat is applied to bring the mass to the boiling point. The amount of caustic soda used depends upon the amount of selenium and lead in the material, as some lead is also soluble. The liquor from this operation is neutralized with sulphuric acid, producing a second liquor containing selenium dioxide and a precipitate containing small amounts of copper and tellurium, some selenium, and the lead soluble in the caustic. Under roasting conditions, when the temperature is maintained at 600° F.-800° F. only small amounts of copper and tellurium will appear on neutralization. A larger amount of lead is dissolved by the caustic soda and appears in the leach liquor. The selenium liquor is worked up in the usual way for the production of metallic selenium. The precipitate is treated with sulphuric acid producing a third liquor and a residue containing lead which is transferred to a lead smelter. This liquor is neutralized with soda ash and filtered. The filtrate contains selenium and is combined with the liquor mentioned above which is used for the production of metallic selenium; the precipitate contains tellurium together with a trace of copper, this precipitate being transferred to the tellurium plant.

The residue from the original caustic soda leach contains, besides the copper and precious metal values of the original slimes, the remainder of the tellurium. This is treated with sulphuric acid which dissolves the copper and the larger part of the tellurium. I next precipitate copper and tellurium from this solution with metallic iron and separate the copper from the tellurium by roasting at 600° F.-700° F., the tellurium being dissolved with a caustic soda solution. The residue from the acid treatment above is treated in the Doré furnace in the usual way.

Example.—Raw tankhouse slimes were carefully roasted for 2¼ hrs. at an average temperature of 633° F. (max. 670° F. min. 610° F.) the charge being about one inch thick and was rabbled thoroughly at 10-15 minute intervals. During this period no fumes were observed. The roasted material was then leached with caustic soda and sulphuric acid, as described above, with the following results:

	Contents, grams			Distribution percentage		
	Cu	Se	Te	Cu	Se	Te
Material.....						
Raw slimes.....	20.7	5.2	5.6	100	100	100
Calcines.....	20.7	5.13	5.6	100	98.6	100
NaOH liquor (A on chart).....	0.10	5.12	---	.5	98.4	Tr.
H ₂ SO ₄ liquor (B on chart).....	20.6	3.9	99.5	---	69.7	---
Final leach residue (C on chart).....	---	---	1.67	---	---	30.3

It will be noted that the content of the selenium and tellurium in the roasted calcined slimes is such that substantially all of the selenium originally present in the copper slimes is still present. The selenium is present as copper selenite and tellurium as tellurium trioxide, as above mentioned.

If the roasting should be conducted below 570° F., silver is oxidized and will go into solution with sulphuric acid when it is used to eliminate the copper contained in the slimes; also telluride will be oxidized according to the equation $2\text{Ag}_2\text{Te} + 3\text{O}_2 = 2(\text{AgO} \cdot \text{TeO}_2)$ which is soluble in caustic soda and consequently considerable amounts of tellurium will be soluble when it is

used to dissolve the selenium and thus contaminate this solution.

The invention as heretofore described involves the steps of roasting the slimes while maintaining them in a predetermined temperature range and then leaching the calcines with caustic soda. This is preferred practice but it shall be understood that the invention is not to be thus limited. Thus, the roasting of the slimes while maintaining the temperature thereof in the range set forth in this specification, i. e., 600° F.-800° F. is an advantageous first step over the prior art process of roasting the copper slimes and then leaching them with H₂SO₄. When the process herein described is used, there is less expensive Doré operation because the selenium and tellurium are eliminated and the greater proportion of the copper is recovered in the tankhouse instead of in the Doré slag.

While some slimes give a satisfactory result with a single roast and caustic soda leach, I find that when the slimes are not fresh, or when the selenium content is high—as for instance 20%, a second roast under the same conditions as mentioned above, and leaching again with caustic soda, further increases the extraction of selenium.

While the invention has been described with respect to certain particular preferred examples which give satisfactory results, it will be understood by those skilled in the art after understanding the invention, that various changes and modifications may be made without departing from the spirit and scope of the invention and it is intended therefore in the appended claims to cover all such changes and modifications.

What is claimed as new and desired to be secured by Letters Patent is:

1. In the art of treating copper slimes containing selenium and tellurium, the step which consists in roasting the copper slimes at about 600° to about 700° F. and somewhat above substantially out of contact with heating gases and with intermittent rabbling, to form copper selenite and tellurium trioxide but at a temperature not to decompose or break down substantially these compounds.

2. In the art of treating copper slimes containing selenium and tellurium, the step which consists in roasting the copper slimes while disposed in thin layers at about 600° to about 700° F. and somewhat above substantially out of contact with heating gases and with intermittent rabbling, to form copper selenite and tellurium trioxide but at a temperature not to decompose or break down substantially these compounds.

3. In the art of treating copper slimes containing selenium and tellurium, the steps which consist in roasting the copper slimes to produce a selenite and tellurium tri-oxide, and leaching the resulting calcines with caustic soda.

4. In the art of treating copper slimes, the step which consists in leaching the calcined copper slimes containing a selenite and tellurium tri-oxide with caustic soda to obtain a liquor containing mainly selenium and a residue containing the precious metals and substantially all of the tellurium and copper of the original slimes.

5. In the art of treating copper slimes containing selenium and tellurium, the steps which consist in roasting the copper slimes while maintaining the temperature thereof in the range 600° F.-800° F., and leaching the calcined copper slimes with caustic soda to obtain a liquor con-

taining mainly selenium and a residue containing the precious metals and substantially all of the tellurium and copper of the original slimes.

6. In the art of treating copper slimes, the steps which consist in leaching the calcined copper slimes containing a selenite and tellurium trioxide with caustic soda to obtain a liquor containing mainly selenium and a residue containing the precious metals and substantially all of the tellurium and copper of the original slimes, and leaching said residue with sulphuric acid to obtain a liquor containing tellurium and copper.

7. In the art of treating copper slimes, the steps which consist in leaching the calcined copper slimes containing a selenite and tellurium trioxide with caustic soda to obtain a liquor containing mainly selenium and a residue containing the precious metals and substantially all of the tellurium and copper of the original slimes, leaching said residue with sulphuric acid to obtain a liquor containing tellurium and copper, and precipitating tellurium and copper from said liquor.

8. In the art of treating copper slimes, the steps which consist in leaching the calcined copper slimes containing a selenite and tellurium trioxide with caustic soda to obtain a liquor containing mainly selenium and a residue containing the precious metals and substantially all of the tellurium and copper of the original slimes, leaching said residue with sulphuric acid to obtain a liquor containing tellurium and copper, treating said liquor with metallic iron to precipitate tellurium and copper therefrom, and roasting said precipitate to separate the copper from the tellurium.

9. In the art of treating copper slimes, the steps which consist in leaching the calcined copper slimes containing a selenite and tellurium trioxide with caustic soda to obtain a liquor containing mainly selenium and a residue containing the precious metals and substantially all of the tellurium and copper of the original slimes, neutralizing said liquor with sulphuric acid to precipitate a mixture containing selenium, tellurium and lead, and leaching said mixture with sulphuric acid to thereby obtain a liquor containing selenium and tellurium.

10. In the art of treating copper slimes, the steps which consist in leaching the calcined copper slimes containing a selenite and tellurium trioxide with caustic soda to obtain a liquor containing mainly selenium and a residue containing the precious metals and substantially all of the tellurium and copper of the original slimes,

neutralizing said liquor with sulphuric acid to precipitate a mixture containing selenium, tellurium and lead, leaching said mixture with sulphuric acid to obtain a liquor containing selenium and tellurium, leaching said residue with sulphuric acid to obtain a liquor containing tellurium and copper, and precipitating tellurium and copper from said last named liquor.

11. In the art of treating copper slimes containing selenium and tellurium, the steps which consist in roasting the copper slimes while maintaining the temperature thereof in the range of 600° F.-800° F., leaching the calcined copper slimes with caustic soda to obtain a liquor containing mainly selenium and a residue containing the precious metals and substantially all of the tellurium and copper of the original slimes, neutralizing said liquor with sulphuric acid to precipitate a mixture containing selenium, tellurium and lead, leaching said mixture with sulphuric acid to obtain a liquor containing selenium and tellurium, leaching said residue with sulphuric acid to obtain a liquor containing tellurium and copper, and precipitating tellurium and copper from said last named liquor.

12. In the art of refining metals, the steps which consist in treating a liquor containing tellurium and copper with metallic iron to precipitate tellurium and copper therefrom, and roasting said precipitate to prepare it for leaching out the copper from the tellurium.

13. In the art of refining metals, the steps which consist in treating a liquor containing tellurium and copper with metallic iron to precipitate tellurium and copper therefrom, roasting said precipitate to separate the copper from the tellurium and dissolving the tellurium in a caustic soda solution.

14. In the art of treating copper slimes, the steps which consist in subjecting the copper slimes containing selenium and tellurium to successive roasting operations while maintaining the temperature thereof in the range 600° F.-800° F., and, after each roasting operation, leaching the resulting calcines with caustic soda.

15. In the art of treating copper slimes containing selenium and tellurium, the step which consists in roasting the copper slimes at above approximately 600° F. substantially out of contact with heating gases and with intermittent rabbling until substantially all of the selenium originally present in the copper slimes is present as copper selenite and the tellurium is present as tellurium trioxide.

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