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RECOVERY OF SELENIUM

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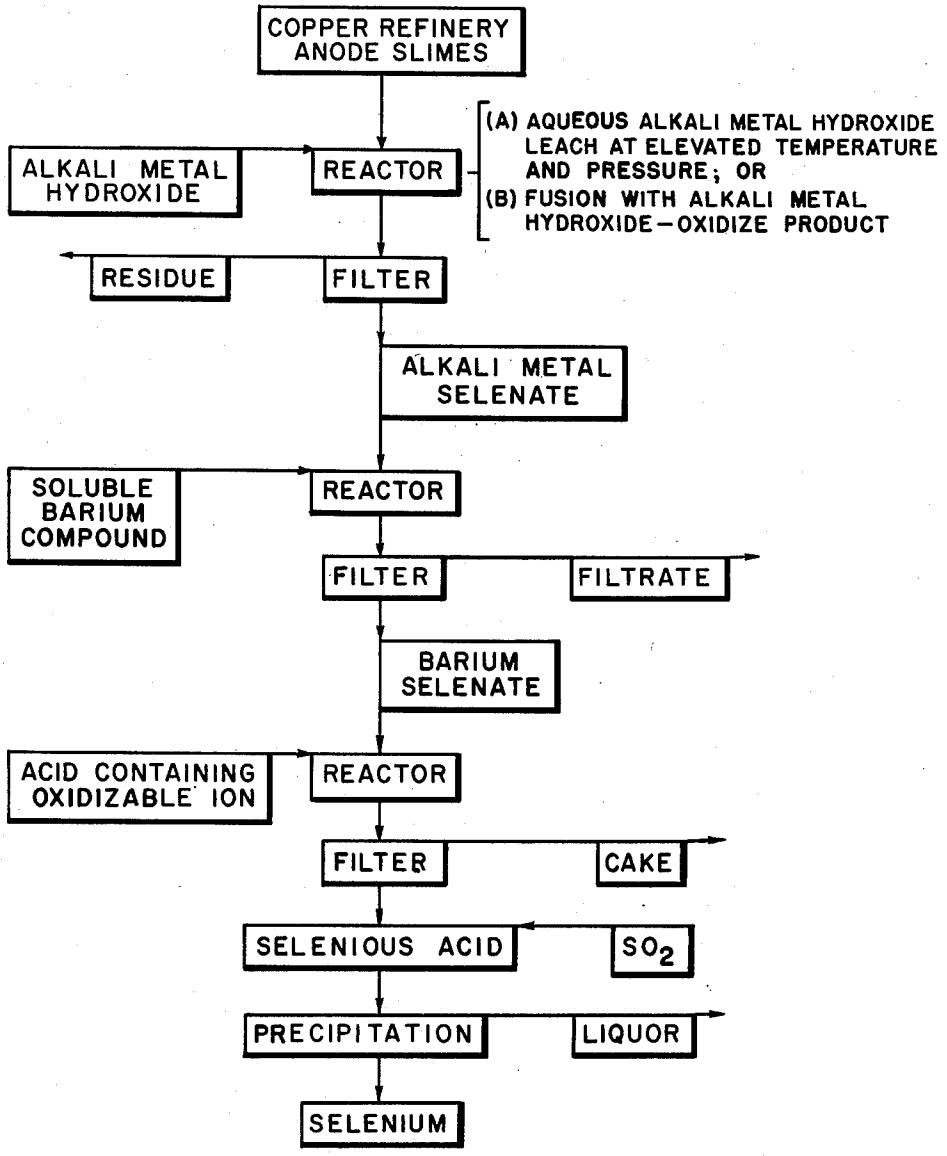

INVENTOR

LUTHER E. VAALER

BY C. T. Cross

ATTORNEY

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RECOVERY OF SELENIUM

Luther E. Vaaler, Columbus, Ohio, assignor, by mesne assignments, to Diamond Alkali Company, Cleveland, Ohio, a corporation of Delaware

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This invention relates to a new and improved process for the recovery of selenium from copper refinery anode slimes and/or other selenium-containing materials.

One of the primary commercial sources of selenium has been anode slimes produced in the electrolytic refining of copper. Copper refinery slimes originate during the electrolytic purification of relatively impure copper obtained by pyrometallurgical methods. In such a purification process, the impure copper is made the anode in an electrolytic cell. The impurities associated with the anode, including selenium, sink to the bottom of the cell and are collected as slimes.

While these slimes vary somewhat in composition, the following is a typical analysis wherein the quantities are expressed in terms of percent by weight:

Selenium	6.83
Tellurium	1.29
Gold	0.5
Silicon	0.9
Antimony	1.0
Iron	0.15
Arsenic	0.5
Magnesium	0.006
Lead	28.0
Tin	9.0
Bismuth	0.3
Nickel	0.8
Aluminum	1.3
Copper	11.0
Silver	23.0
Zinc	0.4
Titanium	0.006
Calcium	0.007

The prior art techniques of obtaining selenium from such slimes typically involve a sulfate roasting of the slimes, in some instances, followed by a caustic leach with subsequent use of HCl and sulfur dioxide to precipitate selenium metal. Roasting of the slime mixture, as usually carried out heretofore as an essential step, of course, involves certain difficulties in equipment maintenance and increases the costs of operation. Further, prior methods of selenium separation and recovery have not yielded a completely satisfactory solution to the problem providing an adequate supply of this important element.

It is, therefore, the principal object of the present invention to avoid difficulties encountered in the recovery of selenium, and to provide a new and improved method of obtaining selenium without the necessity of roasting the selenium-containing source material.

A further object is the provision of a new and improved method for separating substantially pure selenium from selenium containing materials.

A further object of the invention is the provision of a new and improved process for separating selenium from copper refinery anode slimes.

These and other objects and advantages of the invention will appear more fully in the following description.

This invention broadly comprises the successive treatment of a selenium-containing material, e. g., unroasted copper refinery anode slimes, with an alkali metal hydroxide, to form a soluble alkali metal selenate, thereafter forming an insoluble selenate and removing soluble impurities, oxidizing the insoluble selenate to a soluble selenate in solution, and precipitating selenium therefrom. Since perhaps the most common source of selenium is copper refinery anode slimes, particular reference to these slimes is made hereinafter, although it is to be understood that the invention contemplates the separation of selenium from various other source materials as well.

In the practice of this invention, copper anode slimes, e. g., unroasted slimes, are contacted with an alkali metal hydroxide, either, (I) in the form of a molten alkali metal hydroxide bath, or (II) in an aqueous leaching operation employing an alkali metal hydroxide aqueous solution at an elevated temperature and pressure. Preferably, the copper refinery anode slimes are first washed with hot water prior to contact with alkali metal hydroxide. Such a washing operation is not essential, but does substantially reduce the amount of alkali metal hydroxide necessary in the practice of the invention. In the practice of the invention, those skilled in the art will recognize that considerable economy of operation can be realized by recycling the unconsumed alkali metal hydroxide, either in the molten condition, or as an aqueous solution, after removal therefrom of insoluble materials.

I. USE OF MOLTEN ALKALI METAL HYDROXIDE AS EXTRACTANT

When the alkali metal hydroxide is employed in the molten form, its temperature generally may be varied from the temperature at which it melts to a maximum temperature dictated by the practical considerations of providing suitable high temperature resistant containing materials. Typical of such a temperature variance is the range from 320° C., e. g., the melting point of sodium hydroxide, to 800° C. A preferred temperature generally lies within the range from 550° to 650° C., 600° C. being the specifically preferred temperature at present.

In practice, the molten alkali metal hydroxide may comprise one or a mixture of alkali metal hydroxides. At times, the selenides in the slimes are oxidized to soluble selenites under the normal conditions existing during contact with the molten alkali metal hydroxide, i. e., via oxidation by atmospheric oxygen. However, at times it is desirable to incorporate one or more oxidation promoters in the molten caustic to facilitate oxidation of the selenides to selenates. Illustrative of materials which can be so employed are hydrazine (N_2H_2), cobaltimine ion ($Co(NH_3)_6^{+++}$), lead dioxide (PbO_2), chlorate ion (ClO_3^-), perchlorate ion (ClO_4^-), tellurate ($TeO_4^=$), peroxide, nickel dioxide (NiO_2), hypoiodate ($IO^=$), manganate ($MnO_4^=$), bromate (BrO_3^-), chlorite (ClO_2^-), periodate ($H_3IO_6^=$), hydroxylamine (NH_2OH), hypobromite (BrO^-), hypochlorite (ClO^-), ferrate ($FeO_4^=$), chlorine dioxide (ClO_2) and ozone (O_3).

The molten alkali metal hydroxide generally should be in contact with the selenium-containing slimes for a period sufficient to permit extraction of substantially all of the selenium. In practice, advantageous results have been obtained when this contact time is at least 30 minutes. Longer times up to about five hours are presently preferred. It will be appreciated that the extraction time in a specific application will also be influenced by the surface area of the fusion mixture, the passage of oxygen or air through the fusion mixture, and/or the presence or absence of an oxidation promotor such, for example, as those set forth in the preceding paragraph.

A convenient method of employing an oxidizing agent,

e. g., hydrogen peroxide, is by forming an aqueous alkaline solution from the selenium-containing extractant and introducing hydrogen peroxide until the desired oxidation to selenates is accomplished, e. g., typically five minutes or less at room temperature. The thus-obtained selenate is then treated further in accordance with this invention as will be described in detail hereinafter.

II. USE OF AQUEOUS SOLUTION OF ALKALI METAL HYDROXIDE AS EXTRACTANT

In the presently preferred practice of this invention selenium is extracted from anode slimes by an aqueous solution of an alkali metal hydroxide at an elevated temperature and pressure. Generally, the concentration of alkali metal hydroxide in the solution may vary from a small amount, e. g., 1% to an amount dictated by the solubility of the alkali metal hydroxide at the temperature employed, e, g., 85% sodium hydroxide at 200° C.

The temperature of the extractant solution desirably is in the range from 150°–250° C., preferably being between 175° and 225° C., e. g., 200° C. The total pressure, i. e., water vapor and other gas vapor pressure, should be maintained at a value less than 1000 p. s. i. in most instances. A pressure up to 500 p. s. i. is typical, a pressure of 100 p. s. i. or less being preferred at present. While the pressure can be varied, it is desirable that the partial pressure of oxygen be maintained at at least 60 p. s. i.

Extraction of selenium under the foregoing conditions is conducted until the selenium is substantially completely removed. In practice, the extraction time can, of course, be varied somewhat. However, an extraction time of at least a few hours, e. g., five hours, is preferred, a 24-hour extraction resulting in complete removal of selenium in all instances where an excess of alkali metal hydroxide is present over that necessary to react with the selenium and other substances present in the anode slimes.

The water-soluble selenate formed by either of the foregoing procedures after removal of any gold, iron, magnesium, bismuth, nickel, copper, silver, titanium, and calcium compounds, is then converted to an insoluble selenate and separated by filtration, centrifugation or the like, thus removing soluble impurities. In forming an insoluble selenate, it is preferred to treat the water-soluble alkali metal selenate with a water-soluble compound of a metal selected from the group consisting of barium, strontium, and radium. Generally, water-soluble salts of strontium and radium, e. g., strontium sulfate or radium sulfates, or water-soluble salts of barium are satisfactory. The preferred compound at present is a barium compound having a solubility in water equal to, or greater than the solubility of barium selenate.

Illustrative of suitable barium salts are barium chloride, which is preferred, barium chlorate, barium hydroxide, barium oxide and barium permanganates. Typical of barium salts which are not effective in the practice of the present invention are barium carbonate, barium chromate, and tribarium phosphate.

The desired reduction of the insoluble selenate, e. g., barium selenate, to a soluble selenite, such as barium selenite, can be accomplished by adding to the insoluble selenate an acidic solution containing an oxidizable ion, such as sulfuric acid, hydrochloric acid, or mixtures of sulfuric and hydrochlodic acids. In some instances hydroiodic acid and/or hydrobromic acid also may be used. Since barium sulfate is more insoluble than barium selenate, superior results are obtained in many instances using sulfuric acid which does not dissolve the barium but, on the contrary, precipitates an insoluble barium sulfate and forms a water-soluble selenic acid. On the other hand, when hydrochloric acid is used, barium chloride, chlorine, and water are formed, together with selenious acid.

While an acid treatment comprises the preferred method of obtaining the desired selenite by reduction of the insoluble selenate, i. e., either an oxidizable acid, or an acidic solution containing some oxidizable substance, including heating with agitation, cooling, and separation of undesired solid residues, the present invention also contemplates that the reduction may be accomplished in a neutral or alkaline solution containing a sufficiently strong reducing agent.

If sulfate ions are present in the selenite solution, barium will again be pecipitated and can be removed separately thus leaving a selenious acid solution. On the other hand, if no sulfate ions are present, the selenite-containing solution will comprise a barium selenite solution. In either event, the resulting solution is then contacted with sulfur dioxide to effect a reduction of the selenite and precipitation of selenium. Other reducing agents such as hydrogen and powdered zinc also may be used. Generally, the criteria for a suitable reducing agent are that it be sufficiently active to accomplish the desired reduction, that it stay in solution, and that it not react undesirably or combine with selenium.

Attention is now directed to the accompanying flowsheet, wherein there is schematically illustrated the recovery of selenium from copper anode slimes in accordance with the present invention. In the process illustrated, an alkali metal hydroxide, preferably sodium hydroxide, although the expression "alkali metal" as used throughout the specification and claims is intended to include other alkali metals as well, e. g., lithium, potassium, cesium, and rubidium, is added to anode slimes, e. g., unroasted slimes. This treatment comprises either an aqueous leaching operation at elevated temperature and pressure, a fusion treatment with molten alkali metal hydroxide. In either event, a water-soluble alkali metal selenate is to be formed.

To the water-soluble selenate, after removal therefrom of solids, is added a water-soluble barium compound and the thus-formed insoluble barium selenate is separated by filtration, the filtrate, which contains alkali metal hydroxide, being recycled if desired. To the barium selenate then is added an acid containing an oxidizable ion, e. g., sulfuric or hydrochloric acid, preferably a mixture of hydrochloric and sulfuric acids. The resultant solution is filtered, if necessary, and treated with sulfur dioxide to preceipitate metallic selenium.

In order that those skilled in the art may more completely understand the present invention and the preferred methods by which the same may be carried into effect, the following specific examples are offered:

Example I

PART A

Into a one-gallon autoclave, equipped with an agitator, is introduced 250 gms. of water-washed copper refinery anode slimes and 833 ml. of a 10% by weight aqueous solution of sodium hydroxide. This mixture is then heated at 200° C° for 4.6 hours under a total pressure (water vapor plus air) of 500 to 600 p. s. i. g. The autoclave is then opened and the contents are filtered and washed with water to yield 620 ml. of filtrate plus washings containing 24.2 gms. per liter of selenium, and 186 gms. of dried residue containing 1.18% selenium.

PART B

To portions of the filtrate obtained in accordance with part A are added amounts of barium chloride, in the form of a solution containing 250 gms. per liter of $BaCl_2 2H_2O$, using 5 ml. portions of the filtrate, so that successive solutions containing 2.0, 2.5, 3.0, 3.5, 4.0, and 6.0 moles of the barium salt are successively added for each mole of selenate present. Observation of the resultant mixtures indicates that complete precipitation of barium selenate is obtained only when the molar ratio of barium salt to selenate is 4.0 or higher.

PART C

To a 3.4 gm.-sample of a completely precipitated barium selenate of part B is added 40 ml. of 20% by volume HCl. The resultant mixture is heated to 155° F. for 25 minutes, cooled to room temperature, and the undissolved residue separated. Sulfur dioxide is added to the resultant liquor to precipitate selenium together with a trace of a white precipitate, i. e., barium sulfate. Heating the undissolved residue with concentrated hydrochloric acid and subjecting this mixture to sulfur dioxide causes no precipitation of selenium, thereby indicating complete extraction.

PART D

The procedure of part C is repeated except that sulfuric acid (20% by volume) is employed in lieu of the hydrochloric acid. Substantially pure red elemental selenium is obtained upon subjecting the resultant acid solution to contact with sulfur dioxide.

Example II

Into an autoclave equipped with an agitator is introduced a 120 gm.-sample of copper refinery anode slimes containing 6.83% by weight of selenium. There is then added 400 ml. of a 20% by weight aqueous solution of sodium hydroxide. Heat and pressure are then applied until a temperature of 200° C. and a total pressure (water vapor plus air) of 500 to 600 p. s. i. g. is obtained. These conditions are maintained for 22 hours.

The autoclave is then opened and the contents cooled. There results after filtering and washing with water 562 ml. of filtrate. The filter cake is washed with an additional 342 ml. of water and dried, weighing 62.5 gms. The filtrate, containing 97.5% of the originally present selenium, is then subjected to further treatment in accordance with the procedure of Example I, parts B, C, and D, with substantially the same advantageous results being obtained.

Example III

To 15 gms. of copper refinery anode slimes are added 45 gms. of sodium hydroxide. The mixture is fused at 600° C. for 5 hours, and cooled. The resultant mixture is then leached with hot water to yield 264 ml. of solution (sodium selenite). To insure conversion to a selenate, 10 ml. of this sodium selenite solution are then oxidized with a few drops of 30% hydrogen peroxide, and the excess peroxide is removed. To the thus-formed solution is added one gm. of barium oxide. The resultant precipitate, containing substantially all of the selenium, is then separated and treated further in accordance with the procedure of Example I, parts C and/or D, with substantially the same advantageous results being obtained.

It is to be understood that although the invention has been described with specific reference to particular embodiments thereof, it is not to be so limited, since changes and alterations therein may be made which are within the full intended scope of this invention as defined by the appended claims.

Similarly, while the invention has been described as being particularly applicable to the obtention of selenium from copper refinery anode slimes, other selenium-containing source materials also may be advantageously treated, e. g., lead chamber sludge from sulfuric acid plants, or vegetation concentrating selenium from the soil.

What is claimed is:

1. The method of separating selenium from a selenium-containing source material, said method comprising the successive steps of contacting said source material with an alkali metal hydroxide thereby to extract selenium from said source material as a soluble selenate, forming therefrom by the addition of a compound selected from the group of water soluble compounds of barium, strontium, and radium, an insoluble selenate, and separating soluble impurities, reducing the insoluble selenate by

the addition of a solution containing an oxidizable ion and precipitating substantially pure selenium therefrom by the addition of sulfur dioxide.

2. The method according to claim 1 wherein the alkali metal hydroxide is employed in the form of an aqueous solution.

3. The method according to claim 1 wherein the alkali metal hydroxide is molten.

4. The method according to claim 1 wherein the alkali metal hydroxide is dissolved in water and contact between the selenium-containing material and said alkali metal hydroxide is effected at an elevated temperature and pressure.

5. The method according to claim 1 wherein the water-soluble compound is a barium compound.

6. The method according to claim 1 wherein the water-soluble compound is barium oxide.

7. The method according to claim 1 wherein the water-soluble compound is barium chloride.

8. The method of separating substantially pure selenium from unroasted copper refinery anode slimes, said method comprising the successive steps of extracting selenium from said slimes with an alkali metal hydroxide at an elevated temperature to obtain a water-soluble alkali metal selenate, removing insoluble impurities, and contacting said alkali metal selenate with a water-soluble compound selected from the group consisting of compounds of strontium, barium, and radium, filtering the thus-obtained mixture to remove soluble material, and subjecting the thus-formed selenate to an acidic solution containing an oxidizable ion, thereby to form a selenite in solution, reducing the selenite and precipitating selenium therefrom by adding sulfur dioxide to the solution.

9. The method according to claim 8 wherein the alkali metal selenate is contacted with a barium compound.

10. The method of separating substantially pure selenium from unroasted copper refinery anode slimes, said method comprising the successive steps of extracting selenium from said slimes with an alkali metal hydroxide at an elevated temperature to obtain a water-soluble alkali metal selenate, removing insoluble impurities, and contacting said alkali metal selenate with a water-soluble compound selected from the group consisting of compounds of strontium, barium, and radium, filtering the thus-obtained mixture to remove soluble material, and reducing the thus-formed selenate by adding a solution containing an oxidizable ion thereby to form a selenite in solution, reducing the selenite and precipitating selenium therefrom by adding sulfur dioxide to the solution.

11. The method according to claim 10 wherein the selenate is reduced by admixture with sulfuric acid and hydrochloric acid.

12. The method according to claim 10 wherein the selenate is reduced by admixture with sulfuric acid.

13. The method according to claim 10 wherein the selenate is reduced by admixture with hydrochloric acid.

14. The method of separating substantially pure selenium from copper refinery anode slimes, said method comprising the successive steps of extracting selenium from said slimes with a molten alkali metal hydroxide under conditions which result in the formation of a water-soluble alkali metal selenate, removing insoluble impurities, and contacting said alkali metal selenate with a water-soluble compound selected from the group consisting of compounds of strontium, barium, and radium, filtering the thus-obtained mixture to remove soluble material, and subjecting the thus-formed selenate to an acidic solution containing an oxidizable ion, thereby to form a selenite in solution, reducing the thus-formed selenite and precipitating selenium therefrom by adding sulfur dioxide to the solution.

15. The method according to claim 14 wherein the alkali metal selenate is contacted with a barium compound.

16. The method of separating substantially pure sele-

nium from copper refinery anode slimes, said method comprising the successive steps of extracting selenium from said slimes with a molten alkali metal hydroxide under conditions which result in the formation of a water-soluble alkali metal selenate, removing insoluble impurities, and contacting said alkali metal selenate with a water-soluble compound selected from the group consisting of compounds of strontium, barium, and radium, filtering the thus-obtained mixture to remove soluble material, and reducing the thus-formed selenate by adding a solution containing an oxidizable ion thereby to form a selenite in solution reducing the thus-formed selenite, and precipitating selenium therefrom by adding sulfur dioxide to the solution.

17. The method according to claim 16 wherein the selenate is reduced by admixture with sulfuric acid and hydrochloric acid.

18. The method according to claim 16 wherein the selenate is reduced by admixture with sulfuric acid.

19. The method according to claim 16 wherein the selenate is reduced by admixture with hydrochloric acid.

References Cited in the file of this patent

UNITED STATES PATENTS

1,415,526	Chikashige et al.	May 9, 1922
1,945,074	Ralston	Jan. 30, 1934
2,048,563	Poland	July 21, 1936
2,084,394	Heberlein	June 22, 1937

OTHER REFERENCES

"Handbuch der Anorganischen Chemie," Gmelin, Aufl. 8, System Nr. 10, Selen, pages 84 and 85, page 267—bottom.