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CONTROL OF THE STATE OF THE SELENIUM IN ALKALI SLAGS

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This invention relates to control of the state of the selenium in an alkali slag containing same. More particularly, it relates to the recovery of selenium contained in selenium-bearing materials including the slimes, sludges, anode muds and similar material obtained from the electrolysis of copper contaminated with selenium, by a process involving the incorporation of the selenium into an alkali slag.

Heretofore, the slimes, sludges, anode muds and similar by-product material from the electrolysis of impure copper have been smelted with an alkali metal compound such as sodium hydroxide or sodium carbonate, together with an oxidizing agent such as sodium nitrate, with the objective of incorporating the selenium into a molten alkali slag in the form of sodium selenite. Thereafter, the slag was leached to dissolve its selenium content and the leach liquor treated with sulfur dioxide to precipitate and recover elemental selenium.

The prior practice was unsatisfactory and produced low and varying recoveries of selenium because, among other reasons, the amount and form of the selenium in the selenium-bearing material and in the slag were unknown variables and could not be determined except by laborious and time-consuming methods of analysis. Even if it were practical, as a commercial procedure, to delay the process pending the results of such methods of analysis, the results would not indicate reliably the amount of oxidizing agent required to form the selenite selenium under the conditions existing in the slag or during its formation.

Thus, for example, anode slimes and muds may contain up to 2% to 20% or more of selenium in more or less complex mixture with other elements including the noble or precious metals with the selenium present in the form of elemental selenium and selenides. For want of a better procedure, it has been the practice to add an amount of oxidizing agent, as dictated by prior experience, which was based upon a percentage of the weight of the material being smelted. As a result, alkali slags were produced which contained selenite selenium which varied not only in amount but also in proportion.

It has been found that while the selenium in a selenium-bearing material may be incorporated into the alkali metal slag in the selenide, selenite and selenate forms and that in these forms the selenium may be removed from the slag by aqueous leaching, nevertheless only the selenium in the selenite form is available for precipitation as elemental selenium in the subsequent sulfur dioxide precipitation step. Thus, in the prior practice, varying proportions of available selenium were obtained in the leach liquors, with the consequence that low and varying yields of elemental selenium were obtained from the process.

The principal object and advantage of the invention is to overcome the above-mentioned difficulties in the prior art. Another object is to provide a process in which the selenium in a selenium-containing alkali metal slag can easily be controlled to any desired form. These and other objects and advantages will become apparent from the following more detailed description of the invention.

In one aspect of the invention, the practice of the above-mentioned prior art is improved in that the selenium values in a selenium-bearing material, especially such materials as the slimes, sludges, anode muds, etc. from the electrolysis of copper containing selenium, are incorporated into a molten alkali slag of an alkali metal with an excess of an oxidizing agent in the slag to insure the presence therein of at least some selenate selenium, thereby assuring that any remaining selenium values in the slag are in the selenite form. A reducing agent then is added to the slag, preferably in incremental proportions, to reduce the selenate selenium to the selenite form.

It has been discovered also that the slag, as determined by the color of the solid slag, is an excellent indication of the state of the selenium contained therein. Thus, it has been found that a bright yellow colored slag indicates one in which all or substantially all of the selenium is present in the selenate form; that a bluish-gray color indicates a slag in which all or substantially all of the selenium is present as selenite; while a reddish-brown indicates a slag containing all or substantially all of the selenium as selenide. Upon reducing a yellow slag, its color changes gradually through yellowish-green to the bluish-gray color as more and more of the selenate selenium is converted to the selenite form. Upon continued reduction, the color changes from the bluish-gray through gray to the reddish-brown color as more and more of the selenite selenium is converted to the selenide form. Conversely, upon oxidizing a reddish-brown slag, a reversal of the above color sequence takes place, starting from the brown and passing through the bluish-gray to the yellow color as the selenium is oxidized progressively from the selenide through the selenite to the selenate form. As used herein and in the claims, references to the color of the slag refer to the color of the solid or solidified slag or sample thereof.

In another aspect, the invention comprehends a process for treating selenium-bearing materials by incorporating selenium from such materials into a molten alkali slag as an alkali metal compound of selenium and controlling the oxidation conditions in the slag to form a desired color therein in the range yellow to bluish-gray to reddish-brown. Thereafter, the selenium values in the slag may be recovered in any desired manner.

In the preferred mode of practicing the invention, the oxidation conditions in the slag are controlled to form a bluish-gray colored slag, after which the slag is leached and elemental selenium is precipitated from the leach solution with sulfur dioxide. For best results in the preferred mode, the selenium values in a selenium-bearing material are incorporated into an alkali slag of an alkali metal compound, using a sufficient excess of an oxidizing agent to insure the obtaining of a slag in which at least a part of the selenium values are in the selenate form, preferably as indicated by a yellow to a yellowish-green colored slag, thereby assuring that any remaining selenium values in the slag are in the selenite form. Thereafter, a reducing agent, preferably in incremental proportions, is added to the molten slag until a bluish-gray colored slag is obtained, as determined by a solidified slag sample. The invention also includes a process for the recovery of selenium from an alkali slag containing selenium in the form of an alkali metal selenate by introducing a reducing agent into a molten pool of slag to control the oxidation conditions therein to form the bluish-gray color. "Controlling the oxidation conditions" as used herein and in the claims, includes the use of either or both oxidizing agents and reducing agents.

In forming the slag, any alkali metal compound which yields an alkali slag or is itself alkaline may be used, such as, for example, an alkali metal carbonate, hydroxide or nitrate (the latter also being an oxidizing agent) or mixtures thereof. For reasons of economy, sodium

carbonate or sodium hydroxide or mixtures thereof are preferred. Any amount of slag-forming material may be used. In general, it is desirable to use a sufficient amount of such material to keep the total selenium content therein to a value below about 30%.

In controlling the oxidation conditions, any oxidizing or reducing agent may be used. For example, oxygen, oxygen-containing gases, sodium nitrate and the like may be used as the oxidizing agent, and carbonaceous material, including a hydrocarbonaceous material, such as carbon monoxide, natural gas, oil, coke, petroleum coke, etc., may be used as a reducing agent. In general, non-gaseous and particularly solid oxidizing or reducing agents are preferred, with sodium nitrate as the most preferred oxidizing agent and petroleum coke as the most preferred reducing agent.

For best results in controlling the oxidation conditions in the molten slag, a plurality of the samples of slag are taken in sequence, preferably periodically, during this step, to determine the color of the slag. Also, as indicated earlier, for best results the oxidizing agent and/or reducing agent or agents are added in incremental portions in conjunction with the sequential sampling to obtain the desired slag color. Thus, preferably, a sample is taken after an increment of such agent has been added and has been entirely or substantially entirely reacted.

In incorporating the selenium values in a selenium-bearing material into the alkali slag and in controlling the oxidation conditions in the slag, sufficiently high temperatures are used to smelt the charge and to provide a molten fluid slag. The temperatures required for such purposes will depend upon the nature of the charge. It has been found, however, that temperatures in the range of about 900–2200° F. are satisfactory in most cases.

The selenium values in the slag may be recovered in any desired manner, for example by leaching the slag and evaporating the leach liquor to recover a commercial selenium salt such as the selenide, selenite or selenate or mixtures thereof. The invention is most useful, however, for the production of elemental selenium using a reducing agent, particularly sulfur dioxide. For such purpose, the oxidation conditions in the slag are controlled to produce the bluish-gray color. The slag is then leached and elemental selenium is precipitated from the acidified leach liquor by introducing therein sulfur dioxide or a sulfur dioxide forming material.

The invention is further illustrated in the following examples in which the most preferred mode of practicing the invention is described. The examples, however, are submitted for illustration purposes only and the invention in its broader aspects is not limited thereto.

Example 1

The following process was tested on a plant scale in a refinery for a test period of two months, using during that time the entire production of the slimes, sludges, anode muds and similar by-product materials from the copper tankhouse. A typical analysis of the material used was as follows:

	Percent
Cu	20
Pb	5–22
Ag	30–45
Au	.5–1
Sb	4
As	6
Te	3
Se	3–8

Such material was leached with dilute sulfuric acid while blowing air into the leach vat to dissolve the copper as copper sulfate. The leached material was then filtered to remove the dissolved copper.

The filter cake was transferred to a reverberatory cupel furnace and smelted therein with sodium carbonate and sodium nitrate. Sufficient carbonate was used to incorporate the selenium into the resultant slag and to form a layer of molten slag in the furnace over the doré metal that was formed during the smelting. Sufficient nitrate also was used to insure the presence of selenate selenium in the slag. The excess oxidation was also indicated by the yellow to yellowish-green color of the solidified sample of the slag. In addition to the other advantages hereinafter noted, such overoxidation has the advantage of relatively rapidly and efficiently incorporating the selenium into the slag. Thereafter, the molten slag was skimmed from the doré metal and transferred to a slag furnace. The doré metal was further processed to recover the precious metal values therein.

In the slag furnace the slag was maintained in a molten, fluid condition. In most cases this was accomplished by maintaining the slag at a temperature in the range of about 1300–1800° F. While maintained in this condition, incremental amounts of petroleum coke were added and rabbled into the molten slag. After each increment of the coke had been all or substantially all consumed, the color of the slag, as determined by a solidified sample, was observed. The incremental additions of the petroleum coke were continued, the last few being diminishing increments, until the slag became a bluish-gray color as determined by the last solidified sample.

After the treatment with the petroleum coke was completed, the slag was removed from the slag furnace, cooled and then crushed and ground to a size which passed through a 100 mesh sieve. The ground slag was leached with water to dissolve its selenium values. The leach solution was adjusted to a pH value in the range 6–7 by the addition of appropriate amounts of a suitable acid to precipitate tellurium from the solution. The solution was then filtered. The filtrate was acidified and the selenium values precipitated therefrom as elemental selenium by bubbling sulfur dioxide through the filtrate. The elemental selenium was recovered from the solution by filtration. It was found that during the two-month test period, 95.88% of the selenium in the slag was available for precipitation as elemental selenium by sulfur dioxide.

These results are to be compared with those obtained in the same plant by the practice prior to the present invention. In the prior practice, the same general procedure was used except that a fixed percentage of nitrate, based upon the weight of the treated slimes, muds, etc., was used in the smelting. No reducing agent was used and, likewise, the determination of the color of the slag was not available for use. Also, a separate slag furnace was not used. In the prior practice, 74.5% of the selenium in the slag was available for precipitation as elemental selenium by the sulfur dioxide. It will be noted that the practice of the present invention resulted in an increase of the availability of the selenium in the slag from 74.5% to 95.8%—a difference of 21.3%, or a percentage increase of 28.3%.

The results in the following tests were obtained before the experiment described in Example 1 was made. A quantity of the slimes, sludges and anode mud from the copper refinery were treated as described in Example 1, using an excess of sodium nitrate. After the treatment with the nitrate, the slag was analyzed and found to have a total selenium content of 27.57% Se, of which 72.3% was in a form available for precipitation to elemental selenium by the use of sulfur dioxide. The color of the solid slag at this stage was yellowish-green. 200 gram samples of the thus prepared slag were remelted and to each sample was added the amount of petroleum coke indicated in the following tabulation. After the coke had been rabbled into each sample and had been consumed, the samples were cooled and the color of the solid slag was observed. An analysis of each sample as to total and available selenium content

was made. The results obtained are shown in the following table:

Example No.	Added Coke		Slag Analysis			Slag Color
	Grs.	Percent	Total Se	Available Se	Percent Availability	
2	1	0.5	26.38	22.45	85.2	light yellowish-green.
3	2	1.0	26.16	23.05	88.4	Do.
4	2½	1.25	26.48	25.40	95.9	bluish-gray.
5	3½	1.75	26.20	21.67	82.8	brown.
6	4	2.00	25.29	18.16	71.8	Do.

Alternative to the procedure of Example 1, the decopperizing step, if desired, may be dispensed with and the selenium-bearing material may be charged directly to the smelting furnace. The slag furnace also may be dispensed with and the conversion of the selenate to the selenite may be accomplished in the smelting furnace in the presence of the doré metal. Alternatively also, instead of over-oxidizing the slag, the nitrate or other oxidizing agent may be added, preferably incrementally, until the bluish-gray color is obtained in the presence of the doré metal. However, as indicated in Example 1, the preferred procedure is to incorporate the selenium into the slag, after which the slag is treated separately to adjust its selenium content to the desired state. In this preferred procedure the slag may be removed from the cupel furnace and sent to a slag furnace or the doré metal may be tapped from the cupel, after which the slag may be treated in the cupel.

It should also be pointed out that, as part of the technique in obtaining any desired color in the slag, a slight excess of oxidizing or reducing agent, as the case may be, may be used to take the color beyond the desired point and then adding small increments of reducing or oxidizing agent until the desired color is again reached. Such a procedure may be used to obtain what might be called a fine "end-point" or to correct an error when an excess of oxidizing agent or reducing agent has been used. Thus, until sufficient experience was had in the plant-size test referred to, a slight excess of petroleum coke was added to the first few slags to produce a brownish colored slag and the slag then was brought back to the desired bluish-gray color by the addition of handfuls of nitrate. Likewise, on several occasions in the latter stages of this test, an excess of the coke was accidentally added and the desired color was brought back by adding nitrate in the same manner.

What is claimed is:

1. A process for recovering selenium values from a selenium-containing material which comprises fusing said material with an alkaline compound of an alkali metal to obtain a molten selenium-containing slag, oxidizing the molten slag with a sufficient amount of an oxidizing agent to form a yellow to a yellowish-green colored slag as determined by a solidified slag sample, thereafter

introducing a sufficient amount of a reducing agent into the yellow colored slag to form a bluish-gray colored slag as determined by a solidified slag sample, thereby insuring the conversion of substantially all of the selenium values in the slag to the alkali metal selenite state, leaching the bluish-gray colored slag, and recovering selenium values from the leach solution.

2. A process for recovering selenium values from a selenium-containing material selected from the group consisting of slimes, sludges, anode muds and mixtures thereof produced in copper electrolysis which comprises smelting said material with an alkaline compound of an alkali metal and a sufficient amount of an oxidizing agent to obtain a molten selenium containing slag which is yellow to yellowish-green in color as determined by a solidified slag sample, thereafter adding a non-gaseous carbonaceous reducing agent in incremental portions to the molten slag to form a bluish-gray colored slag as determined by a solidified slag sample, thereby insuring the conversion of substantially all of the selenium values in the slag to the alkali metal selenite state, leaching the bluish-gray colored slag, and recovering selenium values from the leach solution.

3. A process according to claim 2 in which said alkaline compound of an alkali metal is selected from the group consisting of sodium carbonate, sodium hydroxide and mixtures thereof, said oxidizing agent is sodium nitrate, said reducing agent is petroleum coke.

4. A process according to claim 3 in which said reducing agent is introduced into said molten slag until the slag acquires a brownish color as determined by a solidified slag sample, and thereafter additional amounts of said oxidizing agent are added to said brownish colored slag to form said buish-gray slag color.

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