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HYDROMETALLURGICAL PROCESS

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This invention relates to hydrometallurgical processes. More particularly, the invention relates to hydrometallurgical processes involving the use of electrolytes containing a colloidally dispersed compound of molybdenum, and has for its principal object the provision of an improved method for the treatment of such electrolytes for the purpose of increasing their stability. In accordance with the method of the invention, colloidally dispersed compounds of molybdenum are separated from electrolyte solutions in which they are present, and the separated molybdenum compound may be recovered in marketable form.

The presence of colloidally dispersed compounds of molybdenum in certain electrolytes is objectionable. This is true especially in the case of electrolytes employed in hydrometallurgical (and other) processes involving oxidation or reduction reactions, because molybdenum compounds in colloidal form are susceptible to oxidation and reduction and interfere with efficient progress of the oxidation and reduction reactions sought to be carried out. For example, the presence of colloidally dispersed molybdenum compounds in the copper-bearing electrolytes employed in hydrometallurgical processes designed for the recovery of copper is objectionable both during purification of the electrolyte and during treatment of the purified electrolyte for the recovery of its copper content. The reactions occurring at these stages in the treatment of such electrolytes involve oxidation and reduction reactions the progress of which is impeded by the presence of colloidally dispersed molybdenum compounds.

In the recovery of copper from an oxidized copper ore, the ore is leached with a solution containing sulphuric acid to obtain a solution containing copper sulphate. The resulting copper sulphate solution also contains impurities such as nitrates and chlorides and sulphate of iron, and to eliminate certain of these impurities, particularly the chlorides, and to reduce others, especially the iron, the solution is subjected to a reducing or dechloridizing operation in the presence of metallic copper. If molybdenum is present in the solution during this dechloridizing operation, it is reduced to the form of a hydrated oxide corresponding to the formula $Mo_3O_8 \cdot 5H_2O$. This hydrated oxide of molybdenum is colored a deep blue and appears in the electrolyte in the form of a colloid. It is extremely sensitive to oxidation and acts as a reducer of nitric acid in solution, thereby itself becoming oxidized. Such a reaction sets in operation a train of oxidation and reduction reactions involving nitric acid, iron and molybdenum and rendering the solution unstable and highly corrosive to copper. Cathodes being deposited from such a solution are attacked and corroded by the solution. Moreover, cement copper, added to such a solution for the purpose of precipitating chlorides as cuprous chloride and for reducing ferric iron in solution, is attacked by the colloidally dispersed molybdenum and its effectiveness as an agent for accomplishing the purposes for which it is added is thereby diminished. As a result, the efficiency of the entire process for the recovery of copper is impaired.

It has been found that colloidal molybdenum compounds present in solutions such as described above carry a negative charge, and that by subjecting the electrolyte to a precipitation operation in the presence of a substance capable of effecting precipitation of the colloidally dispersed molybdenum compound, the molybdenum compound is precipitated in a form that is easily separated from the residual electrolyte. The precipitation may be effected by incorporating in the electrolyte containing the colloidal molybdenum compound a suitable colloid carrying a positive charge such, for example, as glue, or by the addition of a suitable coagulating agent, such, for example, as activated carbon. Upon precipitation of the colloidal molybdenum compound, for example, by means of glue, the resulting formed precipitate settles quickly from the solution and is easily separated therefrom. The precipitate is composed of glue or decomposition products of glue, molybdenum oxide, impurities such as silica, and small amounts of substances included in entrained electrolyte. The precipitate contains the molybdenum in fairly concentrated form, and it is easily converted to a marketable molybdenum product.

As illustrative of the manner in which the method of the invention is carried out, it is described below in connection with the treatment of an electrolyte employed in the hydrometallurgical treatment of oxidized copper ores for the recovery of copper. The copper ore is leached with a solution containing sulphuric acid, usually in the form of spent electrolyte from the electrolytic cells in which metallic copper is recovered, and the copper sulphate solution (or electrolyte) thus obtained ordinarily contains the

following ingredients about in the concentration ranges indicated:

	Grams per liter
Copper	20 to 70
Sulphuric acid	70 to 5
Nitric acid	1/10 to 10
Iron	1/2 to 10
Molybdenum	3/10 to 8
Chlorine	1/100 to 3/10

In addition, the electrolyte may contain impurities such as sodium, potassium, lead, tin, aluminum, managanese, selenium, tellurium, arsenic and antimony. The presence or absence of these impurities, however, does not appear to have any influence on the effectiveness of the method of the invention. The molybdenum, at this stage of the process, is in true solution in the electrolyte.

The electrolyte from the leaching operation is introduced into a suitable purification vessel and is agitated in the presence of a reducing agent such as cement copper. The primary function of the copper is to reduce the iron in solution to the ferrous form and to effect elimination of the bulk of the chlorides by precipitation as cuprous chloride. In addition, however, the copper effects conversion of molybdenum in the solution to the form of a hydrated molybdenum oxide corresponding to the formula $Mo_3O_8 \cdot 5H_2O$, which appears in colloidal form in the electrolyte. The occurrence of the reaction by which this colloidal molybdenum compound is formed does not depend upon the presence or absence of copper sulphate or sulphuric acid. Substantially the same colloidal molybdenum compound is formed whenever a reducing reagent such as copper is brought in contact with a solution containing molybdenum in oxidized form, whether or not the solution also contains copper sulphate or sulphuric acid.

The metallic copper employed as the reducing material is separated from the electrolyte, and a suspension of glue in water is incorporated in the resulting reduced electrolyte containing the colloidally dispersed molybdenum compound. The strength of the glue suspension and the amount that is employed depends upon the amount of colloidally dispersed molybdenum compound in the electrolyte undergoing treatment. Preferably the electrolyte is agitated during incorporation of the glue suspension in order to effect thorough dissemination of the glue throughout the electrolyte. The glue brings about precipitation of the colloidal molybdenum compound in a form that is easily separated from the electrolyte.

To effect separation of the thus precipitated molybdenum compound from the residual electrolyte, the electrolyte is introduced into a suitable settling or thickening vessel. In the settling or thickening vessel, the precipitate settles readily and completely from the solution. Clarified electrolyte from which the precipitate has settled is withdrawn from the upper portion of the settling or thickening vessel, and settled precipitate is withdrawn together with a portion of the electrolyte from the bottom thereof. The withdrawn precipitate is filtered, centrifuged, or otherwise treated to effect substantially complete separation of the precipitate from accompanying electrolyte. If desired, the settling operation preceding the filtration or centrifuging operation may be omitted, but it is advantageous when handling large volumes of solution.

The separated precipitate contains molybdenum in the form of an oxide that is easily treated to convert it to a marketable molybdenum product.

The electrolyte, after separation of the precipitate, is introduced into an electrolytic cell where it is electrolyzed in the usual manner for the recovery of its copper content. The spent electrolyte from the electrolyzing operation is returned to the leaching operation for the purpose of utilizing its sulphuric acid content in the extraction of copper from a further quantity of ore.

It has been found that the electrolyzing operation proceeds more efficiently when employing as the electrolyte a solution from which molybdenum has been separated in the manner described above than when an electrolyte from which molybdenum has not been removed is employed. It has also been found that in a cyclic operation such as described above, the treatment of the electrolyte for the elimination of the molybdenum lowers the molybdenum content of all of the electrolyte employed in the process and thereby increases the efficiency with which the purification operation preceding the molybdenum precipitation operation proceeds. The method of the invention, therefore, contributes materially to the efficiency and economy of the copper recovery process.

Various modifications may be made in carrying out the process of the invention. As it has been described above, the process of the invention involves the use of glue as the agent capable of effecting precipitation of the colloidal molybdenum compound, but other agents are available for accomplishing this purpose, such, for example, as activated carbon. The specific process described above for the recovery of copper from copper ores involves the use of metallic copper as the reducing material employed in purifying the electrolyte solution and in effecting conversion of the molybdenum in solution to the form of a colloidally dispersed compound of molybdenum, but other reducing agents, such as sulphur dioxide either in gaseous or in liquid form, may be employed, either alone or in combination with metallic copper.

It is apparent that the method of the invention, although particularly well adapted to use in connection with hydrometallurgical processes for the treatment of copper ores, is not limited in its utility to such processes. It may be employed equally well in other processes where it is desired to increase the stability of electrolytes rendered unstable by the presence of molybdenum, and may be employed also in processes for the recovery of molybdenum from solutions in which it is present.

I claim:

1. In a hydrometallurgical process for the recovery of copper in which an oxidized copper ore is leached with sulphuric acid and a solution comprising copper sulphate and containing a colloidally dispersed molybdenum compound is obtained, the improvement which comprises subjecting the copper sulphate solution to a precipitation operation in the presence of activated carbon to effect precipitation of the colloidally dispersed molybdenum compound, agitating the solution during the course of the precipitation operation, and separating the precipitated molybdenum compound from the residual solution.

2. A hydrometallurgical process for the recovery of copper from an oxidized copper ore

containing molybdenum which comprises leaching the ore with a solution containing sulphuric acid to obtain a solution containing copper sulphate and dissolved molybdenum, subjecting the resulting copper sulphate solution to a reducing operation in the course of which the dissolved molybdenum is converted to the form of a colloidally dispersed compound of molybdenum, thereafter subjecting the solution to the action of a substance capable of effecting precipitation of the colloidally dispersed compound of molybdenum, thereby to precipitate the molybdenum compound, separating the precipitated molybdenum compound from the solution, and treating the resulting clarified solution for the recovery of its copper content.

3. A hydrometallurgical process for the recovery of copper from an oxidized copper ore containing molybdenum and iron which comprises leaching the ore with a solution containing sulphuric acid to obtain a solution containing copper sulphate, dissolved molybdenum, and ferric iron, subjecting the resulting copper sulphate solution to the action of metallic copper to reduce the ferric iron to the ferrous form and to convert the dissolved molybdenum to the form of a colloidally dispersed compound of molybdenum, thereafter subjecting the solution to the action of activated carbon to effect precipitation of the colloidally dispersed compound of molybdenum, separating the precipitated molybdenum compound from the solution, and subjecting the resulting clarified solution to an electrolytic operation for the recovery of its copper content.

4. A hydrometallurgical process for the recovery of copper from an oxidized copper ore containing molybdenum and iron which comprises leaching the ore with a solution containing sulphuric acid to obtain a solution containing copper sulphate, dissolved molybdenum, and ferric iron, subjecting the resulting copper sulphate solution to the action of sulphur dioxide to reduce the ferric iron to the ferrous form and to convert the dissolved molybdenum to the form of a colloidally dispersed compound of molybdenum, thereafter subjecting the solution to the action of activated carbon to effect precipitation of the colloidally dispersed compound of molybdenum, separating the precipitated molybdenum compound from the solution, and subjecting the resulting clarified solution to an electrolytic operation for the recovery of its copper content.

5. The method of increasing the stability of a copper sulphate electrolyte containing nitric acid, dissolved iron, and a colloidally dispersed compound of molybdenum which comprises subjecting the electrolyte to the action of activated carbon to effect precipitation of the colloidally dispersed molybdenum compound, and separating the precipitated molybdenum compound from the electrolyte.

6. The method of recovering molybdenum from solutions containing a colloidally dispersed compound of molybdenum which comprises subjecting the solution to the action of glue to effect precipitation of the molybdenum compound, separating the precipitated molybdenum compound from the residual solution, and treating the separated precipitate for the recovery of its molybdenum content.

7. The method of recovering molybdenum from copper sulphate solutions containing dissolved molybdenum which comprises subjecting the solution to the action of a reducing agent to convert the molybdenum to the form of a colloidally dispersed compound of molybdenum, subjecting the resulting solution to the action of a substance capable of effecting precipitation of the colloidally dispersed compound of molybdenum, thereby to precipitate the molybdenum compound, and separating the precipitated molybdenum compound from the residual solution.

8. The method of recovering molybdenum from a sulphate solution containing dissolved molybdenum which comprises treating the solution with a reducing agent of the class consisting of cement copper and sulphur dioxide to convert the molybdenum to the form of a colloidally dispersed compound of molybdenum, subjecting the resulting solution of the actions of a substance capable of effecting precipitation of the colloidally dispersed compound of molybdenum, thereby to precipitate the molybdenum compound, and separating the precipitated molybdenum compound from the residual solution.

9. The method of recovering molybdenum from a solution of a copper salt containing dissolved molybdenum which comprises treating the solution with a reducing agent of the class consisting of cement copper and sulphur dioxide to convert the molybdenum to the form of a colloidally dispersed compound of molybdenum, subjecting the resulting solution to the actions of a substance capable of effecting precipitation of the colloidally dispersed compound of molybdenum, thereby to precipitate the molybdenum compound, and separating the precipitated molybdenum compound from the residual solution.

10. The method of recovering molybdenum as set forth in claim 8 in which the agent for precipitating the colloidally dispersed molybdenum compound is activated carbon.

11. The method of recovering molybdenum as set forth in claim 9 in which the agent for precipitating the colloidally dispersed molybdenum compound is activated carbon.

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