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2,970,036

METHOD OF RECOVERING CUPRATE ANIONS FROM THEIR METAL SALT SOLUTIONS

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This invention relates to the recovery of cuprate anions from metal salt solutions which contain them, and to the preparation of an anion exchange material which will enable their recovery.

Explanatory of the present invention, it has heretofore been proposed to treat oxidized copper ores with sodium hydroxide. The use of sodium hydroxide as a leaching agent for such ores is primarily occasioned by the fact that these ores frequently contain substantial amounts of limestone, rendering an acid leaching process inappropriate due to the fact that the acid largely exhausts itself in reacting with the limestone. There may be other reasons why an acid leaching process may be inappropriate for a particular ore containing recoverable copper.

When ores of this character are leached with sodium hydroxide we have ascertained that sodium cuprate (Na_2CuO_2) is produced and have succeeded in isolating sodium cuprate by ion exchange methods and determining its existence from assays and spectrometric methods. The resulting leached solution may be regarded as a highly diluted solution of sodium hydroxide containing sodium cuprate, the copper of which it is proposed to recover by producing a much more concentrated electrolyte containing sodium cuprate from which the copper can be recovered by electrolysis.

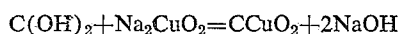
The present invention is largely predicated upon the discovery that cellulose preferably in a relatively pure form such as cotton fibers, batting, linters, and the like, if properly treated becomes an ideal ion exchange medium for the cuprate anion.

In accordance with the present invention, the cellulose employed is initially prepared by regenerating it to hydroxyl form. This is accomplished by passing a sodium hydroxide solution through cotton. In lieu of sodium hydroxide, potassium hydroxide might be used, but sodium hydroxide is preferable from the economical standpoint. After passing the hydroxide through the cotton the cotton is thoroughly washed with distilled water or de-mineralized water until the effluent is neutral to litmus paper, it being desirable to remove all of the free hydroxide from the cotton which may then be regarded as being in the hydroxyl form of cotton. To identify such regenerated cotton in the following equations it may be assumed to have the following formula, cotton being represented by the symbol C:



This material thus obtained becomes an ideal anion exchange medium for cuprate (CuO_2) anions.

Assuming that there is obtained from leaching oxidized copper ores with sodium hydroxide a highly dilute electrolyte containing sodium hydroxide and sodium cuprate, this electrolyte is then passed through the regenerated cotton and the following reaction probably occurs:



As above indicated the OH anion associated with the cotton is exchanged for the cuprate (CuO_2) anion and

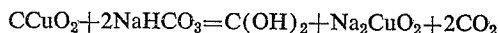
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the cuprate anion is adsorbed by the cotton. The sodium cation combines with the OH anion given up by the cotton to form sodium hydroxide and remains in the effluent. This sodium hydroxide can be thus recovered and held available for future leaching processes. We have determined that if a sodium hydroxide leaching solution containing 75.0 grams of copper is passed through a plug of cotton regenerated as above described, that approximately 67.13 grams of copper will be adsorbed by the cotton thus obtaining on the cotton approximately 89.5% of the copper present in the solution.

Recycling of the feed solution through the cotton may be necessary to effect as large an adsorption or deposit of the copper on the cotton as is commercially practicable.

The point at which adsorption of the cuprate anion on the cotton is complete can be determined to some extent by the color of the cotton and the color of the effluent leach solution. The cotton becomes dark blue in color and the feed solution may be recycled until there is very little bleeding of the color in the effluent. Another manner in which to determine when the adsorption of the cuprate anion on the cotton is complete is to assay the effluent solution periodically and recycle until the effluent is sufficiently barren that recycling is no longer economical.

The next step in the procedure is to obtain the adsorbed copper from the cotton and to retain it in a solution of sufficient concentration that it is suitable for copper recovery by electrolysis. This is accomplished by eluting or dissolving the cuprate anion from the cotton with a solution of sodium bicarbonate. The probable reaction that occurs is as follows:



The cuprate anion is thus exchanged for the hydroxyl anion in the sodium bicarbonate and the hydroxyl anion is retained or held by the cotton. The cuprate anion combines with the sodium of the sodium bicarbonate to form an ionized solution of sodium cuprate in water. The sodium bicarbonate solution is preferably a saturated solution although the use of a saturated solution is not essential. By using a saturated solution the effluent is of sufficient concentration to be suitable for copper recovery by electrolysis. The volume of the solution obtained by eluting the cuprate anion from the cotton may be as little as one-tenth of the volume of the original leach solution. Practically all of the copper adsorbed on the cotton can be removed by eluting with the sodium bicarbonate solution, and as the above formula indicates, the cotton has been restored to its regenerated or hydroxyl condition and is available for immediate re-use with additional leach solution enabling the process to be repeated. Consequently, it will be appreciated that the regenerated cotton used as an ion exchange medium may be produced in either of two ways.

(1) By treating cotton in its natural state with a sodium hydroxide solution; or

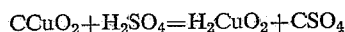
(2) By treating cotton which has adsorbed the cuprate anion with sodium bicarbonate solution.

The eluate solution obtained as a result of treating the cotton having the adsorbed cuprate anion with sodium bicarbonate solution contains a sufficiently concentrated amount of sodium cuprate which is suitable as an electrolyte for the electrolytic deposition of copper.

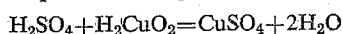
Before the hydroxyl form of the cotton obtained as a result of passing sodium bicarbonate solution through it is reused it should be thoroughly washed with distilled or demineralized water until the effluent becomes neutral to litmus paper. The eluate containing the more concentrated solution of sodium cuprate after electrolysis will of course contain sodium hydroxide which is stored for future use as a leaching reagent.

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In lieu of using sodium bicarbonate as an elutriant or solvent for the cuprate anion other chemical elutriants may be used such as sulphuric acid or sodium bisulphate. Sulphuric acid is an economical and practical elutriant for the cuprate anion. The probable equation is as follows:



The H_2CuO_2 (cupric acid) in a solution with an excess of sulphuric acid present undergoes the following reaction:



The resulting electrolyte is a mixture of copper sulphate, water, and an excess of sulphuric acid and is a conventional electrolyte for the electrolytic deposition of copper. The cotton in this method of treatment is in the sulphate form and is then treated with sodium hydroxide leach solution to convert the cotton back to the hydroxyl form and thus prepare it for the adsorption of cuprate anions.

The concentration of hydroxyl ion in the leach solution is far in excess of the stoichiometric quantity of OH required to exchange it for the quantity of SO_4 present on the cotton after thorough washing with water.

In treating cotton having the adsorbed cuprate anion thereon with either of the elutriants, sodium bicarbonate, sulphuric acid or sodium bisulphate, recycling of these elutriants may also be necessary to effect a complete withdrawal of the cuprate anion from the cotton.

From the above-described procedure it will be appreciated that we have developed an inexpensive, but nevertheless highly efficient ion exchange medium for cuprate anions, to wit, inexpensive cotton in its hydroxyl form obtained from treating it with a solution of a strong hydroxide such as sodium hydroxide. The solution used for this purpose need only be a 5% solution.

Furthermore, we have demonstrated that a sodium hydroxide solution containing sodium cuprate on being passed through that medium, will have its cuprate anion exchanged for the hydroxyl anion on the cotton. This deposited cuprate anion can thereafter be eluted from the cotton by treating the cotton with a saturated solution of sodium bicarbonate, thus obtaining an effluent of small volume and containing pure sodium cuprate.

The above-described process has an additional important advantage, namely a purification of the cuprate from the leach solution. For example, when 71 grams of copper have been adsorbed by the cotton and 69 grams of copper removed therefrom assays show that the effluent from eluting with sulphuric acid was quite pure in copper sulphate and well below the maximum tolerances for zinc, lead, and iron in the electrolyte; thus an assay of the elutriant showed as follows:

Zn, .005 gm.; Zn/liter=.0005% Zn.

Pb only trace (not determinable with ordinary assay procedure).

Fe, 0.1 gm.; Fe/liter=.01% Fe.

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The zinc, lead, and iron in the crude or original ore may amount to as much as 2% Zn, 2% Pb, and 8% Fe. We suspect that the iron obtained in the assay of the elutriant is due to organic iron present in the cotton, and if this is true, re-use of the same cotton should cause this iron to be practically completely eliminated.

Various changes may be made in the steps of the method without departing from the spirit and scope of the invention as defined by the appended claims.

We claim:

1. The method of producing a concentrated copper electrolyte from an alkaline solution containing cuprate anions which comprises contacting said solution with cotton in its hydroxyl form thereby selectively adsorbing the cuprate anions onto the cotton, and subsequently treating the cotton containing the adsorbed cuprate anions with an elutriant selected from the group consisting of sodium bicarbonate, sulphuric acid, and sodium bisulphate to obtain said concentrated electrolyte.

2. The method of producing a concentrated copper electrolyte from an alkaline solution containing cuprate anions which comprises contacting said solution with cotton in its hydroxyl form thereby selectively adsorbing the cuprate anions onto the cotton, and subsequently treating the cotton containing the adsorbed cuprate anions with an elutriant containing sodium bicarbonate to obtain said concentrated electrolyte.

3. The method of producing a concentrated copper electrolyte from an alkaline solution containing cuprate anions which comprises contacting said solution with cotton in its hydroxyl form thereby selectively adsorbing the cuprate anions onto the cotton, and subsequently treating the cotton containing the adsorbed cuprate anions with an elutriant containing sulphuric acid to obtain said concentrated electrolyte.

4. The method of producing a concentrated copper electrolyte from an alkaline solution containing cuprate anions which comprises contacting said solution with cotton in its hydroxyl form thereby selectively adsorbing the cuprate anions onto the cotton, and subsequently treating the cotton containing the adsorbed cuprate anions with an elutriant containing sodium bisulphate to obtain said concentrated elutriant.

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