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PRODUCTION OF OXY COMPOUNDS OF TANTALUM AND COLUMBIUM FROM THE ORES

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Our invention relates to methods of recovering tantalum and columbium from the ores, and more particularly to processes for the leaching of tantalum and columbium ores.

The two metals, tantalum and columbium are closely associated in nature and practically all tantalum and columbium ores contain both tantalum and columbium minerals. Various methods of recovering these metals from the ores have been proposed in the past. Von Bolton, for instance, fused the ore with soda ash or other alkali metal salts and leached the fusion. By this method he obtained the compounds sodium tantalate and sodium columbate but the process is very complicated and expensive. We have found that both hydrofluoric and oxalic acids have leaching properties in respect of these ores but that, when used singly, they are relatively very weak. Hydrofluoric acid, however, has much stronger leaching properties than oxalic acid.

We have discovered, however, that an acid capable of decomposing tantalum or columbium ores such as hydrofluoric acid combined with an organic acid in which tantalum and columbium will dissolve, such as oxalic, tartaric, succinic or citric acids forms a very effective leaching reagent for tantalum and columbium ores and particularly so when conducted at a temperature of about the condensation point of steam. Similarly calcium fluoride and sulphuric acid in the presence of these organic acids may be used and while they act more slowly than the hydrofluoric acid they nevertheless give an equally effective leach over a longer period of time.

Our experiments have indicated that in the leaching solutions above mentioned, the hydrofluoric acid originally decomposes the ore (in which perhaps the oxalic acid assists to a slight degree) and subsequently the free oxalic acid holds the valuable constituents in solution. The solution, therefore, remains more concentrated in free hydrofluoric acid available to react upon the ore. It is the concentration of free hydrofluoric acid at any time which is an important factor in the extent of the leach.

In the case of the calcium fluoride and sulphuric acid combination the reaction

$$CaF_2 + H_2SO_4 \rightleftarrows CaSo_4 + 2HF$$

is in equilibrium and moves to the right with the consumption of hydrofluoric acid in reaction and volatilization. But owing to the formation of oxalic acid compounds of the tantalum and columbium, there will be less of the hydrofluoric acid consumed in the reaction and, consequently, hydrofluoric acid will be less rapidly generated by the action of the sulphuric acid upon the calcium fluoride. The effect of this combination is, therefore, slower than where hydrofluoric acid is directly used.

We have found experimentally that a combination of hydrofluoric acid with oxalic acid causes a much greater yield than the summation of the yields of both acids used singly. For example, from 100 grams of the ore, leaching with these two acids singly and then in combination, the quantities of reagent used in each instance being equivalent, we obtain the following results:

	Grams
Oxalic acid alone	16
Hydrofluoric acid alone	30
Combination of oxalic and hydrofluoric acids	72

In applying our invention we use at the beginning, for each 100 parts of finely ground ore 100 parts of a leaching solution containing for good results oxalic acid dissolved to the saturation point in a 50% solution of hydrofluoric acid. Heating to about 95° to 98° C. hastens the action of the leach. As exceptionally good results may be obtained by introducing steam directly into the solution and there condensing it, it is apparent that the above proportions will not hold good over a long period of steam condensation. It is also to be noted that the quantity of hydrofluoric acid mentioned is equivalent to the hydrofluoric acid available from 100 parts of calcium fluoride.

It is believed that the oxalic acid acts as a "solution link" for the tantalum and columbium oxides and that its function is not that of a mere solvent. The compounds resulting

from this leach apparently require free oxalic acid to hold them in solution, and as the concentration of free oxalic acid decreases, actual precipitation of the oxides from the solution occurs. An apparent break of the "solution link" takes place.

The leaching solution, of course, takes up not only tantalum and columbium but also iron, titanium, manganese and other impurities that may present. Tin in the form of SnO_2 is, however, not attacked by the acids and remains behind with the gangue. The solution becomes quite thick and syrupy but upon precipitation with ammonium hydroxide (NH_4OH) or other alkali the tantalum and columbium are precipitated but the iron, titanium, manganese and other impurities remain in the solution and are not precipitated.

As above pointed out, the decomposing properties of the hydrofluoric acid make it a very important factor in the extent of the leach. There should, therefore, be as much oxalic acid present as the solution will hold in order that the valuable constituents of the ore, in this case the tantalum and columbium, may be taken up in solution to the fullest extent. When the quantity of oxalic acid is substantially reduced, there is a very marked falling off in the yield.

It is believed that a large number of adsorbed carboxylic groups are necessary to hold the tantalum and columbium oxides in solution and that oxalic acid furnishes more of these groups with less additional weight to the molecule than any other carboxylic acid, while the group also will be directly attached to the molecule and not through a carbon chain. Succinic, tartaric and citric acids having a more complicated structure, all exhibit this property but to a less degree than oxalic acid. It may be also that more adsorbed groups may be necessary to hold the tantalum oxide in solution than in the case of the lighter columbium oxide.

It will be evident, furthermore, that several steps in the process which are hereinabove described as being simultaneous may be pursued separately. It is possible for instance to decompose the ores by subjecting them to the action of hydrofluoric acid as one step and then to dissolve the tantalum and columbium out of the decomposed ore by oxalic acid as a separate step.

Having thus described our invention what we claim is:

1. A leaching solution for tantalum and columbium ores comprising hydrofluoric acid and oxalic acid.

2. A leaching solution for tantalum and columbium ores comprising calcium fluoride and sulphuric acid in the presence of oxalic acid.

3. A leaching solution for tantalum and columbium ores comprising a combination of compounds adapted to generate hydrofluoric acid, and a carboxylic acid.

4. A leaching solution for tantalum and columbium ores comprising an acid adapted to decompose said ores and a carboxylic acid.

5. The process of producing oxy compounds of tantalum and columbium from the ores which comprises the leaching of said ores with a solution containing free hydrofluoric acid and free oxalic acid.

7. The process of producing oxy compounds of tantalum and columbium from the ores which comprises subjecting said ores to the action of hydrofluoric acid in the presence of a carboxylic acid.

7. The process of producing oxy compounds of tantalum and columbium from the ores which comprises subjecting said ores to the action of hydrofluoric acid in the presence of a carboxylic acid.

8. The process of producing oxy compounds of tantalum and columbium from the ores which comprises subjecting said ores to the action of calcium fluoride and sulphuric acid in aqueous solution in the presence of a carboxylic acid.

9. The process of producing oxy compounds of tantalum and columbium from the ores which comprises decomposing said ores by means of hydrofluoric acid and holding in solution the metal compounds resulting from decomposition by means of a carboxylic acid.

10. A process for the production of oxy compounds of tantalum and columbium from the ores which comprises the leaching of said ores with a solution containing hydrofluoric acid and a carboxylic acid while maintaining said solution at a temperature substantially equivalent to that of the condensation temperature of steam.

11. A process for the production of oxy compounds of tantalum and columbium from the ores which comprises the leaching of said ores with a solution containing hydrofluoric acid and a carboxylic acid while simultaneously condensing steam in the solution.

12. A process for the production of oxy compounds of tantalum and columbium from the ores which comprises the leaching of said ores with a solution containing compounds adapted to generate hydrofluoric acid and a carboxylic acid while simultaneously condensing steam in the solution.

13. A process for the production of oxy compounds of tantalum and columbium comprising the leaching of tantalum and columbium ores with a solution containing hydrofluoric acid and a carboxylic acid, followed by the precipitation out of the solution of the tantalum and columbium oxy compounds by the addition of an alkali thereby effecting a separation from iron and other constituents of said ores.

14. A process for the production of oxy compounds of tantalum and columbium com-

prising the leaching of tantalum and columbium ores with a solution containing hydrofluoric acid and a carboxylic acid, followed by the precipitation out of the solution of the tantalum and columbium oxy compounds by the addition of ammonium hydroxide.

15. A process for the production of oxy compounds of tantalum and columbium comprising the leaching of tantalum and columbium ores with a solution containing hydrofluoric acid and a carboxylic acid, while simultaneously condensing steam in said solution, and subsequently precipitating the tantalum and columbium oxy compounds out of the solution by the addition of ammonium hydroxide.

16. A leaching solution for tantalum and columbium ores consisting of oxalic acid dissolved to the saturation point in a 50% hydrofluoric acid solution.

In witness whereof, we have subscribed our names hereto this 15th day of May, 1926.

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