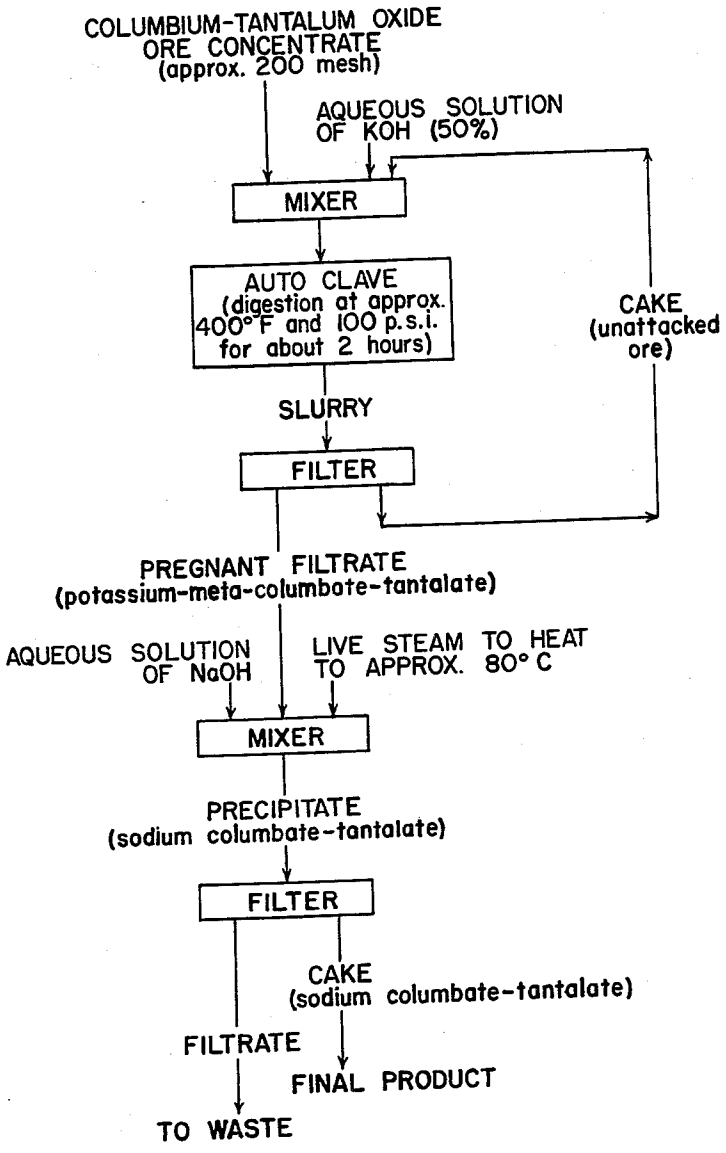
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PROCESS FOR RECOVERING COLUMBIUM AND TANTALUM FROM ORES AND ORE CONCENTRATES CONTAINING SAME

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PROCESS FOR RECOVERING COLUMBIUM AND TANTALUM FROM ORES AND ORE CONCENTRATES CONTAINING SAME

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This invention relates to metallurgical processes for the recovery of columbium and tantalum from ores and ore concentrates in which these metals are found, and, in particular, to processes for recovering columbium and tantalum in the form of substantially pure compounds which may be used for various purposes, especially the production of the metals as such.

Columbium has become important as a strategic material in the field of high temperature metallurgy, particularly as an alloying ingredient in the production of super alloys for jet aircraft and the like, such, for example, as heat-resistant alloys based on nickel and/or cobalt and containing chromium and one or more strengthening ingredients, for example, titanium, zirconium or aluminum. The addition of a small amount of columbium has a marked beneficial effect on the resistance to creep of such alloys at elevated temperatures. Moreover, columbium is particularly useful as a carbide stabilizer in stainless steel. Thus, a process which will recover columbium easily and substantially free from impurities, such as iron, manganese, titanium, tungsten, and silicon, is highly desirable.

The most important source of columbium and tantalum at the present time is ore containing the minerals columbite and tantalite, although ores containing other columbium-tantalum minerals are known and becoming increasingly available.

The ore is generally available as a high grade columbite-tantalite concentrate containing about ten times as much columbium oxide (Cb_2O_5) as tantalum oxide (Ta_2O_5), the main impurity being iron. Chemically, it is often given the broad designation $FeO(Cb,Ta)_2O_5$, even though other impurities than iron are present, for example SnO_2, TiO_2, and MnO_2. An analysis of a typical concentrate shows about 66.10% Cb_2O_5, 7.30% Ta_2O_5, 18.53% FeO, and 1.84% SnO_2, 2.00% TiO_2, 1.48% MnO_2.

Attempts at solubilizing the columbium-tantalum values have not been satisfactory in the past, although potassium hydroxide has been successfully employed in a fusion procedure requiring high temperatures and complicated treatment of the fusion product.

In accordance with this invention, I have found that an aqueous solution of potassium hydroxide may be employed as a digestant under conditions of heat and pressure to break down the ore materials and yield salts of columbium and tantalum which may be relatively easily recovered. In addition, I have found that the reactants can be proportioned to yield a potassium columbate-tantalate which is soluble in the digestant solution, so as to be readily separable from insoluble waste materials, and that too much of the KOH will result in the formation of insoluble potassium columbate-tantalate salts.

A principal object of the invention is to provide a new and relatively simple process for recovering columbium and/or tantalum values from ore and ore concentrates containing same.

Another object is to provide such a process which will yield an exceptionally high purity compound useful as a source of columbium and tantalum metals.

Additional objects and features of the invention will become apparent from the following detailed disclosure and the accompanying drawing, the single FIGURE of which is a flow sheet indicating the presently preferred procedure in detail.

While, broadly speaking, the invention is concerned with the breaking down of refractory types of columbium-tantalum ore materials, such as those containing the minerals columbite, tantalite, fergusonite, samarskite, and euxenite, by digestion thereof with KOH, a highly important aspect is the obtaining of a particular, soluble, potassium columbate-tantalate salt by limiting the quantity of KOH employed. X-ray diffraction analysis has indicated that the particular salt desired is potassium-meta-columbate-tantalate, and that its production, as against other potassium columbates-tantalates which are insoluble in the leach solution, e.g. potassium-pyro-columbate-tantalate, depends upon the ratio between the potassium hydroxide in the digestant and the columbium-tantalum oxides in the ore material.

I have found that the reason ratio range is critical, so far as solubility of the resulting columbium-tantalum salt is concerned, is because excess potassium hydroxide at an elevated temperature reacts with the soluble potassium-meta-columbate-tantalate formed, to produce potassium columbate-tantalate salts (particularly potassium-pyro-columbate-tantalate) which are insoluble in the leach liquid.

The theoretical reaction between a columbite-tantalite ore material and potassium hydroxide is:

$$Fe(CbO_3,TaO_3)_2+2KOH \quad 2K(CbO_3,TaO_3)+Fe(OH)_2$$

The theoretical ratio for the reaction is two moles of the potassium hydroxide to one mole of the oxides. However, at this ratio, the solution isn't strong enough to yield an economic recovery in digestion of reasonable duration. Thus, an excess must be used. In accordance with preferred practice, the allowable excess prior to formation of such insoluble compounds as potassium-pyro-columbate-tantalate provides the upper limit of the range of ratios permissible.

Digestion of the raw ore material is ordinarily carried out in an autoclave at a temperature of about 400° F. and a pressure of about 100 p.s.i. The temperature and pressure may be varied somewhat depending upon the nature of the ore, the more refractory ores benefitting by higher temperatures. The time will also vary somewhat, depending both upon the nature of the ore and the ratio of KOH to the ore, the lowest possible ratio being, of course, the theoretical 2 to 1 mentioned above. A period of from one to three hours in the autoclave is generally sufficient to accomplish a satisfactory breaking down of the ore material, given a satisfactory excess of the KOH reactant.

The character of the digestion product, as pointed out hereinbefore, will depend largely upon the ratio of KOH to the columbium and tantalum oxides contained by the ore, as will the recovery procedure following the digestion stage. Where insoluble potassium columbates-tantalates are formed by utilizing too much of the KOH reactant, it will be necessary to treat the resulting slurry for their separation from the insoluble waste materials

present, as, for example, by filtering and by treating the resulting filter cake with a mineral acid, to solubilize the iron, manganese, and other waste materials and to hydrolyze the potassium columbate-tantalate to hydrated columbium-tantalum oxides. The resulting oxide slurry can then be treated by known procedures, such as solvent extraction, to obtain separated and purified columbium and tantalum oxides.

The purity of the oxides so obtained, however, is not exceptionally high. Moreover, the procedure is expensive. It is much preferable to control the KOH-oxides ratio to insure the formation of the soluble potassium-meta-columbate-tantalate, as previously indicated.

I have found that a workable ratio of KOH to the combined columbium-tantalum oxides in the ore material is substantially within the molar range of from a ratio of about 4.47 to 1 to a ratio of about 5.26 to 1, while best results in most instances will be had with a ratio of about 4.72 to 1, all as is indicated by the table of typical test results appearing hereinafter.

In connection with the above, it should be noted that various factors have an influence upon workability near the upper limit of the specified workable range. Temperature and time variations, purity of the water and reagents, and the columbium-tantalum ratio and total composition of the ore all have an effect upon the results. Thus, higher temperatures and prolonged time of treatment tend to lower recovery, while increased purity of water and reagents tend to raise the recovery. Increase in the ratio of columbium to tantalum tends to increase recovery, as does also high iron and low manganese, tin, and similar impurities.

When the quantity of KOH exceeds the workable range noted above, breaking down of the ore by digestion with KOH will yield insoluble potassium columbate-tantalates not susceptible of recovery by the simple and advantageous procedure about to be described nor of yielding the exceptionally pure product otherwise obtainable. Accordingly, the percent recovery from any given run of an ore or ore concentrate through the autoclave will not be particularly high, although repeated runs will succeed in removing substantially all the columbium-tantalum present.

When digestion has been such as to yield a soluble potassium tantalate, as is preferred, the digested slurry is filtered and the resulting pregnant filtrate solution is treated with a soluble sodium compound (NaOH, NaCl, etc.), preferably by mixing the filtrate solution with an aqueous solution of the sodium compound while introducing steam to heat the mixture, thereby producing a precipitate of sodium columbate-tantalate, which is insoluble so long as an excess of sodium ions is maintained during the precipitation step.

The precipitate is filtered and the resulting filter cake washed with a dilute solution of the sodium compound to yield a sodium columbate-tantalate product of exceptionally high purity. If desired, this product can be subjected to hydrolysis with a mineral acid (preferably nitric) and to further treatment in known manner to yield separate, exceptionally high purity oxides for further treatment to produce the metals.

Typical laboratory procedures and results upon which this invention is based are as follows:

A Nigerian concentrate containing about 73.4% in the aggregate of Cb_2O_5 and Ta_2O_5 (66.1% Cb_2O_5, 7.3% Ta_2O_5, 18.53% FeO, 1.84% SnO_2, 2.0% TiO_2, 1.48% MnO) was ground to substantially minus 200 mesh. Given amounts of the ground ore were mixed with a solution comprising about 50% by weight of potassium hydroxide, the amount of solution used in each instance being dependent upon the molar ratio of anhydrous KOH to the combined columbium-tantalum oxides in the ore. Each mixture in turn was put into a high pressure autoclave and digested at a pressure of about 100 p.s.i. (gauge reading) and a temperature of about 400° F. The respective mixtures were treated for various times ranging from 1 hour to 3 hours. The digested material was filtered and washed, the filtrate and cake washings being allowed to cool and then being treated by the addition of an excess of the stoichiometric ratio of NaOH, to bring down a precipitate of sodium columbate-tantalate.

The results obtained are given in the following table:

Ore (gm.)	KOH (85% gm.)	Water (cc.)	Molar Ratio KOH–Ore	Time (hrs.)	Percent Extraction
100	118	100	7.06:1	1	0.0
125	118	100	5.65:1	1	0.0
150.4	100	100	4.72:1	2	66.67
150	100	100	4.72:1	2	67.7
150	100	100	4.72:1	1	66
108	56	50	3.27:1	3	0.0
130	91	91	4.47:1	3	52.3
130	97	97	5.26:1	3	52.3
130	94	94	5.13:1	3	52.2

Thus, while KOH digestion of a columbium-tantalum ore is useful with unrestricted ratio of KOH to the columbium-tantalum oxides in the ore above the theoretical necessary to produce a optassium columbate-tantalate, it is much preferable, from the standpoint of overall processing, to restrict the ratio substantially in accordance with the above results, which indicate the extent of solubility of the potassium columbates-tantalates produced by the digestion.

Whereas this invention is here disclosed with particular reference to specific procedures, it should be understood that various modifications may be made without departing from the essential inventive concepts.

I claim:

1. In a process for recovering columbium and tantalum from columbium-tantalum oxide ores and ore concentrates, the step of digesting such an ore or ore concentrate under superatmospheric pressure with a hot aqueous solution of potassium hydroxide, to break down the ore or ore concentrate and form a potassium columbate-tantalate salt, the potassium hydroxide being present within a ratio range of from a ratio of about 4.47 moles thereof to 1 mole of the combined columbium-tantalum oxides to a ratio of about 5.26 to 1, and the digestion product being a slurry in which the potassium columbate-tantalate salt is dissolved.

2. The process of claim 1, wherein the ratio range is about 4.72 to 1.

3. A process for recovering columbium and tantalum from columbium-tantalum oxide ores and ore concentrates, comprising digesting such an ore or ore concentrate under superatmospheric pressure with a hot aqueous solution of potassium hydroxide, to break down the ore or ore concentrate and form a potassium columbate-tantalate salt, the potassium hydroxide being present within a ratio range of from a ratio of about 4.47 moles thereof to 1 mole of the combined columbium-tantalum oxides to a ratio of about 5.26 to 1, and the digestion product being a slurry in which the potassium columbate-tantalate salt is dissolved; treating said slurry to separate the liquid phase from the solid phase; and precipitating sodium columbate-tantalate of exceptionally high purity from said slurry by introducing thereinto an excess of the stoichiometric amount of sodium ions.

4. The process of claim 3, wherein the ratio range is about 4.72 to 1.

5. In a process for recovering columbium and tantalum from columbium-tantalum oxide ores and ore concentrates, the step of digesting such an ore or ore concentrate under superatmospheric pressure with a hot aqueous solution of potassium hydroxide, to break down the ore or ore concentrate and form a potassium columbate-tan-

talate salt, the potassium hydroxide being present in at least the stoichiometric amount required for the reaction.

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