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## (54) Recovery of tungsten values from tungsten-bearing materials.

(57) A method of recovering tungsten values from a high grade tungsten bearing ore or concentrate such as scheelite or wolframite includes the steps of roasting, without fusion, the ore or concentrate in the presence of a reactive composition selected from the group of an alkali metal chloride, an alkali metal carbonate and mixtures thereof and extracting the water-soluble tungsten values from the roasted product, e.g. by water leaching. The reactive composition is preferably an alkali metal carbonate on its own.

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THIS invention relates to the recovery of tungsten values from tungsten bearing ores or concentrates.

Tungsten is generally found in nature in scheelite type ores and wolframite type ores. These two ores differ substantially in their chemical composition being a calcium tungstate and an iron-manganese tungstate, respectively. Consequently, different processes have generally been used to recover the tungsten values from each type of ore. In the case of scheelite ores, the classical prior art process is to treat the ore with hydrochloric acid to produce insoluble tungstic acid. The tungstic acid is taken up in an ammonia solution to produce ultimately ammonium paratungstate (APT). Wolframite on the other hand is usually decomposed by fusing the ore with sodium hydroxide/sodium carbonate which extracts the tungsten as sodium tungstate. The cooled fused product is leached with water to extract the soluble sodium tungstate. Similarly, this may be treated with hydrochloric acid to precipitate tungstic acid which is taken up in an ammonia solution to produce APT.

British patent specification No. 1,089,913 describes a process for recovering tungsten values from both scheelite and wolframite type ores or concentrates. This process comprises fusing powdered scheelite and/or wolframite tupe ores or concentrates with a fluxing mixture of sodium carbonate, sodium chloride and sodium nitrate (which mixture also contains, in the case of the starting material containing calcium, at least sufficient siliceous material to form calcium silicate therewith), leaching the cooled, fused material with water and separating a tungsten-bearing alkaline leach liquor from water-insoluble impurities, acidifying the separated leach liquor and adding thereto sufficient of the fluoride or hydrofluoric acid to form, with any silicon and phosphorus present, compounds which are substantially insoluble in organic media, extracting the thus-treated material with an organic solution comprising an organic amine capable of forming a water-insoluble organic amine tungsten complex to transfer tungsten from the aqueous to the organic phase, separating the phases, treating the separated organic phase, with aqueous ammonia to form a water-soluble ammonium tungstate, and separating the aqueous phase containing ammonium tungstate from the organic phase. This process involves, as an essential step, the fusion of powdered scheelite and/or wolframite type ores or concentrates with a mixture of sodium carbonate and sodium chloride. Indeed, it is stated in the specification that a fluid melt should be produced. Typical temperatures at which the fusion take place are 698°C to 825°C.

Fox U.S. Patent Specification No. 3,800,025 describes a process of extracting tungsten values from low grade tungsten ores which includes the steps of roasting a particulated tungsten-containing ore in a water containing atmosphere in the presence of sodium chloride and at least one of the reagents selected from sodium carbonate and sodium phosphate at a temperature in the range of about 600°C to about 900°C for about 1 to 3 hours, water leaching the resulting calcines to dissolve soluble tungsten values and filtering. This process is restricted in application to low grade tungsten ores and requires a water containing atmosphere for its operation. Moreover, relatively high roast temperatures and relatively low amounts of sodium reactant are generally used.

According to the present invention, there is provided a process for recovering tungsten values from a high grade tungsten-bearing ore or concentrate including the steps of roasting without fusion the ore or concentrate in the presence of a reactive composition selected from an alkali metal chloride, an alkali metal carbonate and mixtures thereof, and extracting water-soluble tungsten values from the roasted product. It is essential to the process that roasting takes place without general fusion, that is the mix of material and flux must not form a fluid melt during roasting. The fact that a melt is not produced confers a much greater flexibility in process design and can result in energy savings. The roasted product is an easily handleable material.

The tungsten values in the roasted product will be in the form of water-soluble alkali metal tungstate. This product may thereafter be treated in known manner to recover the tungsten values as tungsten metal. For example, the tungsten values may be water leached from the roasted mixture and the leach liquor then treated in the manner described in British patent specification No. 1,089,913. These treatment steps are essentially an application of chemistry known in the art.

The alkali metal for both the chloride and the carbonate will invariably be sodium.

The tungsten-bearing ore or concentrate is a high grade one, i.e. one containing at least 20 percent by weight tungsten as tungsten oxide ($WO_3$). Such materials will generally be of the schellite or wolframite type and may contain up to 80,5 percent tungsten as tungsten oxide.

The reactive composition may be an alkali metal chloride, an alkali metal carbonate or a mixture thereof. It is a particularly preferred feature of the process that the reactive composition consists solely of an alkali metal carbonate such as sodium carbonate. It has surprisingly been found that excellent tungsten recoveries, at relatively mild temperatures can be achieved using sodium carbonate alone.

The roasting temperature will vary according to the nature of the ore or concentrate being treated and the type and quantity of reactive composition present. The important point is that a temperature must be chosen which will not result in fusion of the ore or concentrate taking place but will yet be high enough for the desired reaction to take place in a reasonable time. As a general rule temperatures in the range 600° to 800°C will be used. For wolframite ores, lower temperatures down to 500°C can be used and good extractions still obtained. When the recoveries are low then the roasted product, after filtration, can be dried and remixed with reactive reagent and then re-roasted. This can be continued until as much of the tungsten as desired has been extracted from the ore. The re-roasting of ore to increase the tungsten extraction may be used particularly with scheelite ores.

The amount of reactive composition present during roasting will also vary according to the nature of the ore or concentrate. There should be at least sufficient sodium present to combine with all the tungsten to form sodium tungstate. It has been found, however, that a stoichiometric excess of sodium is generally necessary when the ore being treated is a wolframite ore.

The roasting must take place for a sufficient time to convert as much as possible of the tungsten to sodium tungstate. The roasting time is typically up to 120 minutes, although for many ores no particular advantage has been found by heating for a period of longer than 60 minutes.

Where necessary, depending on the ore composition and/or type of heating equipment being used, the reactive composition may also contain a suitable oxidising agent such as sodium nitrate. Such an oxidising agent is particularly useful where wolframite ores or concentrates are being treated. Where the tungsten-bearing ore or concentrate also contains a substantial quantity of calcium it may be desirable in some cases to include finely divided silica in the reactive composition. The silica reacts with the calcium to form tricalcium silicate which is subsequently readily separable from the sodium tungstate.

The tungsten-bearing ore or concentrate and the reactive composition will generally both be provided in finely divided state and will be intimately mixed prior to roasting. After roasting, the product may be leached with water. It has been found experimentally that one leach and a replacement wash under appropriate conditions are generally sufficient. The fact that there is no fusion during roasting means that leaching may take place on the roasted product as such without subjecting that product to a crushing or like step. Moreover, leaching may take place while the roasted product is still hot.

After leaching, the leach liquor is treated by commonly known methods to remove impurities such as aluminium, magnesium, phosphorous, silicon, antimony, arsenic and molybdenum.

After the first purification step, the filtrate may be further purified by treatment with a fluoride or hydrofluoric acid. The adequately purified solution is then subjected to a conventional solvent extraction procedure. The tungsten contained in the organic phase may be extracted with ammonium hydroxide to provide an aqueous ammonium tungstate solution.

Tungsten metal powder may be produced from the ammonium tungstate by known methods.

Various scheelite and wolframite ores and mixtures thereof were treated by the process of the invention using various reactive compositions, ratios of ore to reactive composition and at different roasting temperatures. In all these experiments the ore and reactive composition was in finely divided or particulate form and was roasted as a mixture. After roasting, the sodium tungstate was leached with water, the residue separated from the leach liquor by filtration and washing and the leach liquor treated in the manner generally described above to recover the tungsten values. The results of the experiments are given in the Tables below.

<u>Experiments 1 to 4:</u> The ore used was a wolframite ore containing 68,1% tungstic oxide; the reactive composition was sodium carbonate and the roast temperature was 650°C.

TABLE 1

| Experiment | Ore (g) | $Na_2CO_3$ (g) | Nature of Roasted Product | %Tungsten Extraction |
|---|---|---|---|---|
| 1 | 25 | 25 | Powdery | > 99 |
| 2 | 40 | 20 | " | > 99 |
| 3 | 40 | 10 | " | 88 |
| 4 | 50 | 8 | " | 62 |

The stoichiometric ratio of tunstic oxide ($WO_3$) content to the reactive composition is about 2,2.

These experiments illustrate the importance of having a stoichiometric excess of sodium present and the excellent recoveries which can be achieved using sodium carbonate above. The roasted product, of a powdery nature, was easily handleable and could be subjected directly to leaching, and while still hot.

Experiments 5 to 8: The ore used was a scheelite ore containing 74,8% tungstic oxide, the reactive composition was sodium carbonate; and the roast temperature was 650°C for experiments 5 and 6 and 800°C for experiments 7 and 8.

TABLE II

| Experiment | Ore (g) | $Na_2CO_3$ (g) | Nature of Roasted Product | % Tungsten Extraction |
|---|---|---|---|---|
| 5 | 40 | 10 | Powdery | 16 |
| 6 | 50 | 8 | " | 15 |
| 7 | 300 | 48 | " | 23 |
| 8 | 300 | 53 | " | 25 |

It will be noted that the tungsten extractions are relatively low. The reason for this is that a less than the stoichiometric quantity of sodium carbonate was required to prevent fusion taking place. The roasted product was powdery and could be directly leached, and while still hot. The leached residue, after drying, can again be roasted in the presence of sodium carbonate and leached to increase the tungsten extranction. This can be repeated as often as desired to extract as much of the tungsten as possible.

Experiment 9:

Ores were roasted at various temperatures using various ratios and reactive compositions to ore. The reactive composition in each case contained 1 part sodium carbonate to 0,67 parts sodium chloride. The results of these experiments are set out in Table III.

TABLE III

| Ore/Flux Weight Basis | Roast Temperature | Nature of Roasted Product | % Tungsten Recovery |
|---|---|---|---|
| Wolframite (68,7% $WO_3$) | | | |
| 1/1,67 | 500 | Powder | 71 |
| 1/1,25 | 500 | " | 76 |
| 1/1,0 | 500 | Sticky Powder | 64 |
| 1/1,0 | 550 | Lumpy | 81 |
| 1/0,75 | 550 | " | 61 |
| 1/0,50 | 550 | " | 60 |
| 1/0,25 | 550 | " | 48 |
| Scheelite (71,4% $WO_3$) ($SiO_2$ present) | | | |
| 1/1,67 | 500 | Powder | 32 |
| 1/1,25 | 500 | " | 24 |
| 1/1,0 | 500 | " | 36 |
| 1/0,5 | 500 | " | 19 |
| 1/0,75 | 550 | Sticky Powder | 22 |

In all the above experiments the roasted product could be subjected directly to leaching with water, and while hot. The powdery roasted product was easily handleable.

## Experiment 10

In this experiment a scheelite concentrate containing 74,8% of $WO_3$ and a wolframite concentrate containing 68,1% $WO_3$ were mixed 1 : 1 by weight and the mixture was mixed with sodium carbonate in the proportion of 1 part of sodium carbonate to four parts of the mixture. Roasting was conducted at 650°C for four hours.

Thus 300 g of scheelite, 300 g of wolframite and 150 g of sodium carbonate were mixed and roasted. The theoretical stoichiometric amount of sodium carbonate was 98 g. The percentage extraction of tungsten was 58%.

## Experiment 11

The residue from experiment 10 was again mixed with sodium carbonate and roasted at 650°C and two tests conducted with different amounts of sodium carbonate. The results are given in table 1V.

### TABLE 1V

| Residue (g) | $Na_2CO_3$(g) | Theoretical Stoichiometric $Na_2CO_3$ | Percentage Extraction of W | Overall % Extraction |
|---|---|---|---|---|
| 70 | 30 | 14,4 | 71 | 90 |
| 10 | 30 | 2,1 | 86 | 95 |

The overall tungsten extraction is 90 and 95 percent at residue: $Na_2CO_3$ ratios of 7:3 and 1:3. The particular ratio chosen will depend on the particular economic circumstances under which any process operates at any given time.

As far as the applicant is aware, this is the first process which has been found to be suitable for treating mixtures of scheelite and wolframite. The latter acts to reduce the tendency of scheelite to form a sticky product.

CLAIMS

1.
A method of recovering tungsten values from a high grade tungsten bearing ore or concentrate including the steps of roasting, without fusion, the ore or concentrate in the presence of a reactive composition selected from the group of an alkali metal chloride, and alkali metal carbonate and mixtures thereof and extracting water-soluble tungsten values from the roasted product.

2.
A method according to claim 1 in which fusion is prevented by controlling the amount of reactive composition used.

3.
A method according to claim 1 or claim 2 wherein the reactive composition is a mixture of an alkali metal chloride and an alkali metal carbonate.

4.
A method according to claim 1 or claim 2 wherein the reactive composition consists solely of an alkali metal carbonate.

5.
A method according to any one of the preceding claims wherein the alkali metal is sodium.

6.
A method according to any one of the preceding claims wherein the roasting takes place at a temperature in the range 500°C to 800°C.

7.
A method according to any one of the preceding claims wherein the water-soluble tungsten values are extracted from the roasted product by leaching with water.

8.
A method of claim 7 wherein the roasted product is leached while it is hot.

9.
A method of any one of the preceding claims wherein the ore is a scheelite ore and the roast temperature is in the range 600°C to 800°C.

10.
A method according to claim 9 wherein the roasted product is, after extraction of water-soluble tungsten values therefrom, roasted in the presence of the reactive composition and further water-soluble tungsten values then extracted therefrom.

11.
A method according to any one of claims 1 to 9 wherein the ore is a wolframite ore and the roast temperature is in the range 500°C to 800°C.

12.
A method according to claim 11 wherein the amount of reactive composition used is such that a stoichiometric excess of sodium is present in relation to the tungsten oxide in the ore.

13.

A method according to any one of claims 1 to 9 wherein the ore is a mixture of wolframite and scheelite.

14.

A method according to claim 12 wherein the roasted product is, after extraction of water-soluble values therefrom, roasted in the presence of a reactive composition and further water-soluble values are extracted from the thus roasted product.

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# EUROPEAN SEARCH REPORT

Application number

EP 79 30 2549

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim |
|---|---|---|
| X | FR - A - 992 821 (ADMINISTRATION-SEQUESTRE DES RÖCHLING'SCHE EISEN- U. STAHLWERKE)<br>* Whole patent *<br>-- | 1-8 |
| X | US - A - 2 187 750 (O.F. MARVIN)<br>* Page 1, column 1; claims *<br>-- | 1-14 |
| A | US - A - 2 394 362 (B. BURWELL) | |
| A | US - A - 2 501 952 (C.G. MAIER) | |
| A | US - A - 3 256 057 (B. BURWELL) | |
| A,D | US - A - 3 800 025 (J.S. FOX) | |
| A,D | GB - A - 1 089 913 (A.G.E. ROBIETTE)<br>---- | |

CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)

C 22 B 34/36

TECHNICAL FIELDS SEARCHED (Int.Cl. ³)

C 22 B 34

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| The Hague | 01-02-1980 | JACOBS |

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