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ORE TREATMENT PROCESS

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This invention relates to ore treatment processes and more particularly to a process for treating ores containing zirconium and titanium.

One of the objects of the present invention is to provide an improved process for treating ores containing one of the metals zirconium and titanium to recover the zirconium and titanium content thereof in the substantially pure state.

Another object is to provide a method of sintering zirconium and titanium ores whereby the zirconium and titanium contents may be selectively converted into water soluble compounds substantially free of associated water soluble impurities.

Still another object is to provide an improved method of converting the oxide and silicate compounds of zirconium and titanium into water soluble alkali metal double fluoride compounds.

A further object is to provide an economically practical method of processing zirconium oxide and silicate ores to isolate therefom the zirconium content substantially free of associated metal impurities.

Other objects will be apparent as the invention is more fully hereinafter disclosed.

In accordance with these objects I have discovered that the highly refractory and chemically inert oxide and silicate compounds of the metals zirconium and titanium may be converted readily and easily into water soluble alkali metal double fluoride compounds by sintering the said oxide or silicate compound with an alkali metal double fluoride compound of a readily oxidized base metal such as, for example, an alkali metal double fluoride compound of one of the metals Fe, Ni, Co, Cr and Zn.

I have discovered that when the refractory metal oxide, reduced to small particle size, is intimately admixed with the double fluoride compound of the base metal, for example, with potassium ferric fluoride, and the mixture is heated to elevated temperatures approximating 700° C. the oxide and double fluoride react to form an alkali metal zirconium double fluoride and iron oxide. The reaction involved conforms essentially to the following equations:

(a) $4K_3FeF_6+3ZrO_2 \rightarrow 3K_2ZrF_6+2Fe_2O_3+6KF$

(b) $4K_3FeF_6+3(ZrO_2 \cdot SiO_2) \rightarrow 3K_2ZrF_6+2Fe_2O_3+6KF+3SiO_2$

Titanium oxide and silicate react in a similar manner with the alkali metal ferric fluoride to produce the double alkali metal titanium fluoride. Any of the double fluoride compounds of the other metals, above identified, may be substituted for the iron double fluoride without essential departure from the present invention. The alkali metal ferric fluoride, however, is the only such double fluoride that is readily available in sufficient quantity and at a price permitting use in the present invention at the present time.

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The compound potassium ferric fluoride

(K_3FeF_6)

is old and well known in the art and is best prepared by precipitation from aqueous solution. In this method, an aqueous solution of potassium fluoride, is acidified with sulfuric acid to a pH of about 4 and an aqueous solution of ferric sulfate then is slowly added with constant agitation of the solution until all of the fluoride present in the solution has been removed as alkali metal ferric fluoride precipitate. An excess of the ferric fluoride redissolves the double fluoride and should be avoided. After settling, decanting, and washing with clear water, the precipitated double fluoride may be air dried to free the same of water.

The double (alkali metal-ferric) fluoride compound thus obtained is a thermally stable compound having a definite melting point approximating 900° C. Nickel, cobalt, chromium, zinc, and many other base metals, form similar double fluoride compounds, as hereinbefore disclosed in Gmelin Handbook, vol. 8 (1926) on pages 60 and 72.

The double fluoride compounds of zirconium and titanium have heretofore been recognized and prepared by methods generally involving the formation of an acid zirconium fluoride solution and precipitation of the double fluoride salt by the addition of an alkali metal fluoride thereto. Heretofore in the art it has also been recognized that the wide difference in the relative solubilities of titanium and zirconium double fluorides, especially the potassium double fluoride, afforded an effective means for isolating the two elements from each other.

Heretofore in the art, however, it has not been recognized that the double fluorides of zirconium and titanium may be formed in the manner herein disclosed and that by the practice of this invention the zirconium and titanium content of the oxide and silicate ores of these metals may be selectively converted by a relatively simple roasting operation into water soluble alkali metal double fluoride compounds recoverable by a simple leaching operation from the ore residues substantially free of any of the metals and silica usually associated therewith in such ores.

As a specific embodiment of the practice of the present invention, but not as a limitation of the same, the adaptation of the above disclosed invention to the recovery of the zirconium content of zirconium oxide and silicate ores will be described. Each of the metals zirconium and titanium occurs widely in nature and in many ores zirconium and titanium are present together in such relative amounts as requires the practice of a complex chemical process to obtain either element free of the other even after separating the two metals from other metals associated with them in the ores.

The major zirconium ores, however, are known in the art as zircon and baddeleyite (or zirkite) which ordinarily contain a high percentage of zirconium and only small percentages of titanium. Zircon is essentially zirconium silicate

$$(ZrO_2 \cdot SiO_2)$$

of varying degrees of purity with the commercial grades averaging about 65% ZrO_2 balance silica and varying percentages of the oxides of iron, aluminum, titanium, calcium, and other metals, which frequently include rare earths and thorium. Baddeleyite is essentially an oxide ore of varying degrees of purity with the commercial grades averaging about 75% ZrO_2, balance silica, and substantially the same associated metals above mentioned in varying percentages.

Heretofore in the art, most ore treatment methods that have been proposed for the recovery of zirconium from either the oxide or silicate ore involve, first, an ore treatment step such as sintering, fusion, or acid treatment, which is designed to solubilize substantially all metal values present in the ore. This required the practice of a complicated series of chemical reaction steps designed to effect the removal of the associated solubilized impurities from the zirconium in solution to ultimately obtain some substantially pure zirconium compound, such as the oxide, chloride or sulfate. By the practice of the ore treatment step of the present invention the zirconium content of the zirconium ore only is solubilized and the practice of any complicated series of purification steps subsequently to obtain the elimination of associated impurities thereby is eliminated.

In accordance with the present invention, the zirconium ore is mixed with an alkali metal double fluoride salt of a base metal such as iron, in an amount relative to the ZrO_2 content of the ore to obtain one of the two reactions indicated in Equations *a* and *b* above, and the mixture is heated to elevated temperatures within the range 600–800° C. effective to obtain the double decomposition reaction indicated. The sintered mixture then is cooled to atmospheric temperatures, reduced to small particle size, and is leached with water, preferably hot water, to extract the water soluble double fluoride compounds of zirconium and titanium present therein, and the two compounds in aqueous solution thereafter are separated, one from the other, by recrystallization from aqueous solution in accordance with known practice based on the relative solubilities of the two compounds in water at different temperatures. The chemically pure double fluoride salts thus obtained thereafter may be converted into chemically pure oxide, chloride, sulfate and the like chemical compounds as may be desired by methods also old and well known in the art.

In the practice of the present invention on zirconium ores, it is generally economically impractical to attempt to recover any of the metal constituents present in the ore, except the zirconium. Usually the titanium content of the ore approximates 1% which makes it economically impractical to attempt to recover this element except as an unavoidable by-product. With this in mind, I have devised the following process which is designed to effect, in the most economically practical manner, the substantially complete recovery of the zirconium content of zirconium oxide and silicate ores with the minimum recovery of the titanium content of said ores. In this adaptation of the present invention, the ore in its finely ground condition is intimately admixed with potassium ferric fluoride in such relative proportions as is not over that empirically required in accordance with Equations *a* and *b* to convert all of the zirconium to double fluoride. This restriction limits the displacement reaction involved to the zirconium content of the ore.

The mixture is then compacted into suitable sized briquets or aggregates and the briquets or aggregates are heated, in any convenient manner, to a temperature approximating 700° C. This temperature is maintained for an extended time interval, usually approximating one hour, to obtain substantially complete reaction between the ferric fluoride compound and zirconium oxide in the ore. The sintered material, after cooling and crushing to small particle size, is then washed with hot water having a temperature approximating 100° C. and a volume approximately sufficient to dissolve all of the zirconium double fluoride present in the ore.

The potassium zirconium double fluoride has a solubility in pure water of about 1.4 grams per 100 grams H_2O at 15° C. and 25 grams per 100 grams H_2O at 100° C. By limiting the volume of the leach water to that theoretically required to obtain complete solution of the K_2ZrF_6 present in the sinter with the formation of a substantially saturated solution of the salt at the elevated temperature of the solution, I obtain a crystallizable solution of the double fluoride which, after filtering while hot, may be cooled naturally or artificially to 15° C. (or lower) to recover the zirconium salt present therein that is in excess of the solubility limit at the lower temperature.

I have found that whereas the solubility of the corresponding potassium titanium fluoride in pure water approximates 1.28 grams per 100 grams H_2O at 20° C., the solubility of this salt in concentrated solutions of the potassium zirconium fluoride is much lower than this, and that by limiting the amount of the ferric fluoride salt in the sinter mix to an amount less than that required to theoretically react with all of the ZrO_2 content, the major portion of the titanium oxide present in the ore usually remains unconverted to double fluoride even when present therein in amounts as high as 3%. By subsequently leaching with a volume of water at 100° C. forming a concentrated solution of the double zirconium fluoride the amount of the titanium double fluoride taken into solution is still further reduced, with the result that substantially pure zirconium double fluoride crystals are obtainable on the first crystallation from the leach solution. One or more subsequent recrystallizations of the double fluoride salt from pure water provides a double zirconium salt of a high degree of purity which subsequently may be converted by methods well known in the art to oxide, sulfate, chloride and the like compounds with little difficulty.

As a typical example of this procedure, about 1.9 parts (by weight) of the ore that contains

about 65% ZrO_2 is mixed with about 3.8 parts (by weight) of the potassium ferric fluoride, formed into briquets and heated in a muffle furnace to 700° C. for one hour. About 97% of the ZrO_2 present in the ore may be recovered as water soluble potassium zirconium double fluoride. Considerable variation in the percent recovery of zirconium results from varying the manner of forming the mixture into briquets or aggregates and in varying the relative particle sizes of the ore and ferric double fluoride, as one skilled in the art will recognize. Best results appear to be obtained by the use of ore and ferric fluoride sized to pass about 100 mesh screen which after mixing is moistened with water to form a stiff mud having a consistency permitting the same to be molded into small sized bricks. The particular size of the bricks may be varied widely without departure from the present invention as may also the method and mode of heating the same to the desired temperature of about 700° C. As the apparatus required forms no part of the present invention and is otherwise old in the art it will not be described. On any large scale production basis it is preferable to provide a continuous method of sintering wherein the briquets are fed continuously into one end of an elongated furnace and discharged from the other end. The time interval within the furnace being regulated to obtain the particular reaction time required with the size of brick employed.

I have found that I may lower the amount of the potassium ferric fluoride in the sinter mixture from the 3.8 parts, given above, to as low as 2.9 parts without materially lowering the percent recovery of the ZrO_2 content of the ore and to obtain as added advantages a lowered conversion of the titanium to double fluoride and materially lower costs of operation. As an example, by using 2.9 parts per 1.9 parts of ore (65% ZrO_2) the percent recovery of ZrO_2 as double fluoride salt approximates 92%, while the amount of titanium double fluoride formed is still further decreased, so that by using this ratio, substantially selective conversion of the Zr to double fluoride is obtained. This lower ratio of ferric salt to ZrO_2 approximates a one to one molecular weight ratio. The higher ratio approximates a 1⅓ to 1 ratio of salt to oxide as indicated in Equations *a* and *b*.

It is believed unnecessary to disclose the particular practice following in leaching the ore and in crystallizing the leach solution as such practice is old and well known in the art and may be practiced in a plurality of different ways without essential departure from the present invention as one skilled in the art will readily perceive.

Economic factors, however, dictate the necessity of the repeated use of the first leach water to leach successive batches of sinter, thereby to maintain the losses of the zirconium double fluoride (represented by the uncrystallized fraction therein) to a low constant. Thus by practicing the sintering operation in such manner as to limit the amount of titanium double fluoride formed to a low fraction percent, as hereinabove disclosed, a closed system of leaching may be evolved producing added economies of operation.

One of the major advantages of the present invention over processes heretofore proposed, lies in the feature of recovering the fluorine content of the double fluoride and in the leach waters, in the form of an alkali metal ferric fluoride, for return to the sintering step, thus forming a closed system affording added economies of operation.

In accordance with this feature of the present

invention, the substantially pure zirconium double fluoride crystals ultimately obtained are dissolved in pure water and the solution thus obtained is precipitated, in the heretofore known manner, with potassium hydroxide. The zirconium hydroxide thus obtained is washed free of potassium fluoride and converted to oxide by ignition to elevated temperatures or, alternatively the hydroxide may be redissolved in a strong mineral acid such as HCl or H_2SO_4 to form the chloride or sulfate zirconium salt, if desired. The wash waters, containing potassium fluoride, are collected, and after acidification of the same to a pH of about 4 the fluorine content of the wash waters is precipitated as potassium ferric fluoride by the addition thereto of ferric sulfate, as above described.

The first leach water after repeated re-use may be similarly treated for the recovery of the fluoride content therein, as the concentration of the potassium fluoride and titanium double fluoride therein becomes excessive for economic use. Alternatively, the zirconium content of the first leach water may, first, in major part be recovered by reducing the volume of the solution by evaporation at 100° C. until a concentrated potassium zirconium fluoride solution is obtained, which on cooling to 15° C. will crystallize out the double zirconium fluoride present therein in excess of the solubility limit at this lower temperature. In general, however, it will be found that the first leach water accumulates considerable amounts of potassium fluoride as well as of titanium double fluoride, and that in the practice of the alternative procedure the double zirconium fluoride crystals obtained will be contaminated to a greater or lesser degree by one or both of these impurities, requiring the practice of at least one recrystallization step to remove the same therefrom. Various combinations of these two procedures may be employed whereby the bulk of the zirconium content of the primary leach water may be recovered and purified and the major portion of the fluorine content converted to alkali metal ferric fluoride for return to the sintering step of the present invention.

The adaptation of the present invention to other zirconium ores and to titanium ores, for example, rutile or ilmenite, may be readily effected as one skilled in the art may perceive from the above disclosure. Due to the lower solubility of the titanium double fluoride considerably larger quantities of leach water must be employed than in the leaching of zirconium ores. In general, in the practice of the present invention on titanium ores containing low zirconium, all of the zirconium present in the ore will be concentrated in the leach water to be recovered therefrom after the major portion of the titanium has been separated therefrom.

It is believed apparent from the above disclosure that the present invention may be widely adapted and widely modified without essential departure therefrom and all such modifications and adaptations are contemplated as may fall within the scope of the following claims.

What I claim is:

1. The method of treating the group of compounds consisting of the oxide and silicate compounds of zirconium and titanium to render the zirconium and titanium content of said compounds water soluble, which comprises finely dividing the said compounds, mixing the same with an alkali metal double fluoride salt of a metal selected from the group of metals consisting of Fe,

Ni, Co, Cr and Zn and heating the mixture to a temperature within the range 600–800° C. for an extended time interval to convert the Zr and Ti into water soluble fluozirconate and fluotitanate compounds.

2. The method of treating the oxide and silicate compounds of zirconium and titanium to render the zirconium and titanium content of said compounds water soluble, which comprises finely dividing the said compounds, mixing the same with an alkali metal double fluoride salt of a metal selected from the group of metals consisting of Fe, Ni, Co, Cr and Zn forming the mixture into agglomerates and heating the agglomerates to a temperature within the range 600–800° C. for an extended time interval to convert the zirconium and titanium into water soluble fluozirconate and fluotitanate compounds.

3. The method of treating the group of compounds consisting of the oxide and silicate compounds of zirconium to convert the zirconium content of said compounds into water soluble alkali metal double fluoride compounds which comprises finely dividing said oxide and silicate compounds, mixing the said finely divided compounds with an alkali metal ferric fluoride salt, and heating the mixture to a temperature within the range 600–800° C. for an extended time interval.

4. The method of treating zirconium ores to recover the zirconium content thereof as water soluble compounds which comprises finely dividing the ore, mixing the same with an alkali metal double fluoride salt of a metal selected from the group of metals consisting of Fe, Ni, Co, Cr and Zn, heating the mixture to a temperature within the range 600–800° C. for an extended time interval, leaching the sintered mixture with water and recovering the zirconium from the leach water.

5. The method of solubilizing the zirconium content of ores containing the oxide and silicate compounds of zirconium which comprises finely dividing the ore, mixing the ore with an alkali metal ferric fluoride salt in an amount providing from one to one and one-third molecular weights of salt for each molecular weight of zirconium present in the ore, and heating the mixture to a temperature within the range 600–800° C. for an extended time interval approximating one hour.

6. The method of recovering the zirconium content of the oxide and silicate compounds of zirconium which comprises finely dividing the compounds, mixing the same with potassium ferric fluoride in an amount providing from one to one and one-third molecular weights of the fluoride for each molecular weight of zirconium present therein, heating the mixture to about 700° C. for an extended time interval, leaching the sinter with hot water, and recovering the zirconium from the said leach water.

7. The method of processing the group of ores consisting of the oxide and silicate ores of zirconium to obtain the zirconium content thereof substantially free from associated metal impurities, which comprises mixing the ore in its finely divided state with potassium ferric fluoride in the proportions providing from one to one and one-third molecular weights of double fluoride for each molecular weight of ZrO_2 present therein, forming the mixture into aggregates, heating the aggregates to about 700° C. for an extended time interval, cooling and crushing the heated aggregates, leaching the same with hot water, filtering the leach water while hot, cooling the leach water to a lower temperature to crystallize out the major portion of the potassium fluozirconate compounds present therein, separating the fluozirconate crystals from the leach water, and recrystallizing the said fluozirconate at least once from pure water to purify the same.

8. The method of claim 7, wherein the said leach water after separating the same from the fluozirconate crystals is reheated and re-used as a leach water on another batch of said heated aggregates.

9. The method of claim 7, wherein the fluorine content of the leach water and of all solutions used subsequently is conserved and recovered as potassium ferric fluoride for return to the sinter mixture.

10. The method of treating impure ZrO_2 to convert the same into substantially pure alkali metal fluozirconate compounds which comprises mixing the oxide with an alkali metal double fluoride salt of a metal selected from the group of metals consisting of Fe, Ni, Co, Cr and Zn, heating the mixing to 600–800° C. for an extended time interval, leaching the sintered mixture with hot water, filtering the leach water while hot and cooling the same to a low temperature to precipitate out the major portion of the fluozirconate compounds present therein, and recrystallizing the said fluozirconate crystals at least once from pure water to purify the same.

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