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ORE TREATMENT PROCESS

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This invention relates to ore treatment processes and more particularly to a method of treating the ores of zirconium and titanium to recover the zirconium and titanium content thereof.

One of the objects of the invention is to provide an economically practical method of processing the oxide and silicate ores, concentrates, residues and the like materials containing at least one of the elements zirconium and titanium to recover the zirconium and titanium content thereof substantially free of associated impurities.

Another object is to provide a method of selectively solubilizing the zirconium and titanium content of oxide and silicate compounds of zirconium and titanium.

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

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

In accordance with these objects I have discovered that the zirconium and titanium content of the oxide and silicate compounds of these elements may be converted into water soluble alkali metal double fluoride salts by heating the said compounds while in admixture with an alkali metal silico-fluoride compound to elevated temperatures within the range 600 to 800° C.

Heretofore in the art, water soluble alkali metal double fluoride compounds of zirconium and titanium have been known and various methods of separating the zirconium and titanium from each other and from associated impurities utilizing these double fluoride salts have been proposed. Heretofore in the art, however, these compounds have been prepared by forming a concentrated acid fluoride solution of zirconium and titanium and precipitating the double fluoride salt from this solution by the addition of an alkali metal fluoride thereto. This method of preparation normally resulted in the formation of water soluble fluoride salts of associated impurities and required the use of a large number of recrystallizations of the double fluoride salt from aqueous solutions to obtain a purified zirconium or titanium double fluoride product.

In accordance with the present invention the zirconium and titanium present in the oxide and silicate compounds of these elements are converted directly into the double fluoride compounds by a double decomposition or displacement reaction without concurrent conversion of associated metal impurities into water soluble fluoride salts, with the result that these double fluoride compounds may be dissolved in water away from the associated impurities and subsequently may be separated one from the other by recrystallization methods heretofore known in the art.

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In the adaptation of the invention to any particular zirconium or titanium-containing raw material, the process may be widely modified to obtain a plurality of results, as one skilled in the art will recognize. As one specific embodiment of the invention, however, I will describe the adaptation of the invention to the treatment of a zirconium silicate ore known in the art as zircon. This ore consists essentially of zirconium silicate ($ZrO_2 \cdot SiO_2$) containing varying percentages of associated impurities principally calcium, aluminum, iron and other heavy metals, titanium and frequently thorium and some of the rare earth metals. The commercial grade of this ore usually averages about 65% ZrO_2, 1 to 3% TiO_2, 30% SiO_2, 3% Al_2O_3, 1% Fe_2O_3, balance calcium and miscellaneous impurities.

In accordance with the present invention, this ore is ground to fine particle size passing 60 to 100 mesh screen and is mixed with an alkali metal silicofluoride, such as potassium silicofluoride, in an amount providing approximately the proportions conforming to the following equation:—

$$K_2SiF_6 + ZrO_2 \cdot SiO_2 = K_2ZrF_6 + 2SiO_2$$

or one molecular weight of the alkali metal silicofluoride for each molecular weight of zirconium (or zirconium calculated as oxide) present in the ore.

The mixture is then agglomerated into aggregates, such as by compaction or by moistening with water to a stiff mud and molding into small sized bricks, and the aggregates are heated in any convenient manner to a temperature approximating 700° C. for an extended time interval, usually approximating one hour. Following this heating, the aggregates are cooled and are crushed to fine particle size and the fine sized material is leached with water, heated preferably to temperatures approximating 100° C., the volume of the water being limited with respect to the amount of zirconium double fluoride present in the sintered material to obtain substantially complete extraction of the zirconium double fluoride with the formation of a saturated solution of the double fluoride salt at the temperature of the water.

The solubility of the zirconium double fluoride approximates 25 grams per 100 grams of H_2O at 100° C., and about 1.4 grams per 100 grams H_2O at 15° C.

The hot saturated solution of the double fluoride salt thus obtained is separated from the insoluble materials present therein, as by filtering, and the clear solution is cooled to 15° C. (or below) to cause the crystallization therefrom of the zirconium double fluoride salt in excess of the solubility limit at this lower temperature.

Following crystallization, the mother liquor is drained off, and is either reheated and re-used to leach a succeeding batch of sinter, or is evaporated to a lesser volume, depending upon the fluotitanate content thereof, at which a second crystallization of fluozirconate can be obtained therefrom. The fluozirconate crystals thus obtained are redissolved in hot water and recrystallized therefrom one or more times or until substantially pure fluozirconate crystals are obtained.

In the practice of this invention on zirconium ores, it is preferable from an economic viewpoint, to adapt the process to convert the zirconium content only to double fluoride leaving the major portion of the titanium unconverted to double fluoride inasmuch as the amount of titanium present is so low as to make it economically impractical to attempt to recover it except as an unavoidable residue. To accomplish this result, I have found that the amount of the silico-fluoride employed should be substantially less than that theoretically required to convert all of the zirconium content to fluozirconate, the amount of this decrease being dependent upon the amount of titanium present in the ore. As an example, where the ZrO_2 and TiO_2 percentages in the ore are, respectively, 65% and 1%, the use of the theoretical amount of the silicofluoride may be expected to be distributed between the zirconium and titanium in about the ratio of 65 to 1, inasmuch as the heats of formation of these compounds are closely similar. This results in a small loss in the zirconium recovery, that normally is less than the titanium percentage. By using 10% less than the theoretical amount the zirconium loss will be higher, but the amount of titanium unconverted will be greater proportionately. In general, by adjusting the relative proportions of silicofluoride to ZrO_2 to obtain under best operating conditions an extraction of about 95% of the zirconium from the ore, I find that the amount of the titanium that is converted to double fluoride approximates 25% of that present in the ore, where the total TiO_2 does not exceed 3%. Thereafter by employing in the first leach operation a volume of water at 100° C. that is sufficient to dissolve substantially all of the fluozirconate to produce a saturated solution, I find that the solubility of the fluotitanate in this solution is considerably less than that given for fluotitanate in pure water (1.28 grams/100 grams H_2O at 20° C.) and that the bulk of the fluotitanate is undissolved. In this way, I find that with zircon ores containing as high as 3% TiO_2 I can obtain substantially pure fluozirconate by crystallization directly from the leach solution and highly purified fluozirconate crystals in only one recrystallization operation. This contributes markedly to the economies of the present invention.

The fluozirconate product of the above process is a desirable product of manufacture and has wide utility in the art but, if desired, may

be converted to oxide or to the chloride or sulfate salt in accordance with known methods. As the economies of the present invention are favored by the return of the fluorine content of the fluozirconate to the sintering operation, I prefer to convert the fluozirconate first to hydroxide by dissolving the fluozirconate in water and precipitating the solution with caustic alkali (KOH) and after separating the hydroxide from the alkali metal fluoride solution for ignition to oxide or solution in HCl or H_2SO_4 to form the chloride or sulfate salt, the fluorine content of the solution is precipitated as potassium silicofluoride in accordance with any of the known chemical procedures. I prefer, however, to add sulfuric acid and an active form of silica such as diatomaceous earth which in presence of the potassium fluoride solution react to form sparingly soluble potassium fluosilicate which is separated from the solution. The alkali metal fluosilicate product thus obtained is returned to the sintering step of the present invention. In this manner unavoidable fluorine losses in the process may be economically replaced.

The sintering of the ore-silicofluoride mixture may be performed in a plurality of different ways without essential departure from the invention. On any large scale production basis a continuous method of sintering is economically more practical than any other method. I have found that the greatest economies result from the use of an elongated muffle furnace heated by gas burners throughout the major portion of its length to the desired sintering temperature of about 700° C. and by providing means, such as a moving car bottom hearth to progressively move the sinter aggregates through the furnace said means allowing the required time interval at temperature for the reaction involved to proceed to completion. This particular furnace and means for feeding the sinter mixture through the furnace forms no part of the present invention.

In the adaptation of the present invention to the oxide ores of zirconium, such as baddeleyite or zirkite, substantially the same practice is followed as above described with the silicate ore, the amount of the silico-fluoride employed being about one molar weight for each molar weight of ZrO_2 present in the ore.

As one specific improvement of this invention I have found that by the addition of an alkali metal basic compound, such as the oxide, hydroxide, carbonate or sulfate, to the sintering mixture in substitution for part of the silicofluoride I may lower the amount of silicofluoride employed as much as 20 to 25% without substantially lowering the amount of zirconium recovered from the sinter. The exact explanation for this is not apparent at this moment, but the alkali metal basic compound may function to maintain the fluorine as fluoride during the high temperature heating that normally tends to be lost by thermal decomposition of the silicofluoride. On the other hand the strongly basic oxide may function to neutralize the strongly acidic silicon dioxide liberated during the double decomposition reaction and tend to inhibit the reverse reaction forming zirconium silicates. Whatever the true explanation may be my experiments have indicated that a sinter mixture containing 75–80% of the theoretical amount of silicofluoride and an amount of K_2O chemically equivalent to 20 to 25% of the ZrO_2 contained in the ore, is substantially as effective as one containing 100% the theoretical amount of silicofluoride, insofar

as zirconium recovery as fluozirconate salt is concerned.

In the adaptation of the present invention to titanium ores substantially the same procedure hereinabove disclosed is followed, with the difference that the lower solubility of the fluotitanate requires the use of larger volumes of water with the result that the zirconium double fluoride salt usually concentrates in the leach water. At the present time, the adaptation of the present invention to even high grade titanium ores does not appear economically practical except for the production of titanium compounds of extreme purity.

Having hereinabove described the invention generically and specifically and given one specific example of the practice of the same it is believed apparent that the same may be widely varied without essential departure therefrom and all such are contemplated as may fall within the scope of the following claims:

What I claim is:

1. The method of producing a soluble akali metal double fluoride which comprises heating a compound of the class consisting of the oxides and silicates of the elements zirconium and titanium while in admixture with an alkali metal fluosilicate salt to a temperature within the range 600–800° C. for an extended period of time and recovering the alkali metal double fluoride of said element so produced.

2. The method of producing a soluble alkali metal double fluoride which comprises heating a compound of the class consisting of the oxides and silicates of the elements zirconium and titanium while in admixture with an alkali metal fluosilicate salt and an alkali metal basic compound to a temperature within the range of 600–800° C. for an extended period of time and recovering the alkali metal double fluoride of said element so produced.

3. The method of producing a soluble alkali metal double fluoride which comprises heating a mixture consisting of equal molar weights of a compound of the class consisting of the oxides and silicates of the elements zirconium and titanium and an alkali metal fluosilicate salt to a temperature within the range 600–800° C. for an extended period of time and recovering the alkali metal double fluoride of said element so produced.

4. The method of producing a soluble alkali metal double fluoride which comprises heating a zirconium compound of the class consisting of the oxides and silicates while in admixture with an alkali metal fluosilicate salt and an alkali metal basic compound, said admixture containing for each molar weight of said compound 80% to 100% of one molar weight of the said salt and from a small amount up to an amount chemically equivalent to 25% of the ZrO_2 present in said compound of said basic compound, to a temperature within the range of 600–800° C. for an extended period of time and recovering the alkali metal double fluoride of said element so produced.

5. The method of selectively converting the major portion of the zirconium content of impure zirconium oxide and silicate compounds to water soluble fluozirconate compounds which comprises mixing the impure zirconium compounds with an alkali metal silicofluoride salt in

the relative proportions providing not over one molar weight of the silico fluoride salt for each molecular weight of zirconium oxide present in the said impure compounds and heating the mixture of a temperature within the range 600 to 800° C. for an extended time interval.

6. The method of claim 5, wherein the amount of said silicofluoride salt is less than the amount specified by an amount theoretically approximating that of the titanium present in the impure zirconium compound.

7. The method of claim 5, wherein the amount of said silicofluoride salt is less than the amount specified by as much as 20% and wherein an alkali metal compound in an equivalent percentage displaces the said salt.

8. The method of claim 5, wherein the said impure zirconium compound comprises a zirconium ore.

9. The process of recovering zirconium from zirconium ores which comprises finely dividing the ore, admixing the ore with an alkali metal silicofluoride salt in an amount providing about one molar weight of silicofluoride for each molar weight of zirconium present therein, heating the mixture to a temperature approximating 700° C. for an extended time interval, cooling and crushing the heated product to small particle size, and treating the small particle sized heated product with water to dissolve out the water soluble alkali metal zirconium double fluoride compounds present therein.

10. The method of claim 9, wherein the said water in the last step of the process is heated to a temperature approximating 100° C. and the volume of the water is limited to that providing a highly concentrated solution of the said zirconium double fluoride and wherein the said hot concentrated solution after separating the same from the insoluble material present therein is cooled to a lower temperature to obtain a crystallization of the said zirconium double fluoride that is in excess of the solubility limit at the lower temperature.

11. The method of claim 9, wherein the solution obtained in the last step is subjected to crystallization to separate therefrom the dissolved zirconium double fluoride salts present therein, and wherein the said salts are recrystallized from pure water at least once to purify the same.

12. A process for the extraction of zirconium from its ores which comprises sintering the ore mixed with an alkali metal silicofluoride salt in an amount providing about one molar weight silicofluoride for each molar weight of zirconium present in the ore, the sintering temperature being within the range 600 to 800° C., digesting the sintered ore with hot water to extract therefrom the water soluble fluozirconate compounds present therein, crystallizing the said fluozirconate compounds from said leach water, and recrystallizing the fluozirconate compounds at least once from pure water to purify the same.

13. The method of claim 12, wherein the fluorine content of the leach water and fluozirconate compounds is recovered as alkali metal silicofluoride salt and returned to the sintering step of the process.

14. The method of claim 12, wherein the silicofluoride is displaced in an amount up to 20% by an alkali metal basic compound.

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