UNITED STATES PATENT OFFICE.

CHARLES MORRIS JOHNSON, OF AVALON, PENNSYLVANIA, ASSIGNOR TO CRUCIBLE STEEL COMPANY OF AMERICA, OF PITTSBURG, PENNSYLVANIA, A CORPORATION OF NEW JERSEY.

TREATMENT OF ORES.

964,870. Specification of Letters Patent. Patented July 19, 1910.

No Drawing. Application filed January 31, 1910. Serial No. 541,014.

To all whom it may concern:

Be it known that I, CHARLES MORRIS JOHNSON, residing at Avalon, in the county of Allegheny and State of Pennsylvania, a citizen of the United States, have invented or discovered certain new and useful Improvements in the Treatment of Ores, of which improvements the following is a specification.

My invention relates to the treatment of certain ores of certain metals, and particularly to treatment of the ores of tungsten and like metal, and the first object of my improvement is to obtain by a simple and economical process the oxid of tungsten or like metal, and having obtained such oxid, as a second step, to prepare the oxid by reduction for use in steel-making, without separation of the dross with which the oxid as I obtain it is mixed, which dross has in earlier operations been removed preparatory to steel-making, for it has been supposed that such removal was essential to success.

Certain of the ores of tungsten, namely, wolframite ($MnFeWO_4$) and hübnerite ($MnWO_4$), have in prior processes of producing tungsten oxid been subjected to an operation of fusion. I have found that by the acid operation, which I am now about to describe, I can obtain the desired oxid without the greater expense involved in the fusion operation. I take the mineral in its concentrated form—either one of the ores already named or another tungsten ore, for example sheelite ($CaWO_4$) or iron tungsten ore ($FeWO_4$)—that is, in the form in which it is known to the trade as "concentrate." With the concentrated ore will be a certain amount of dross, consisting largely of silica derived from the rock in which the ore is found. I charge a quantity of such ore into a retort, preferably a vitrified clay kettle, together with a chlorin-affording substance. This chlorin-affording substance will preferably be a relatively small quantity of an alkaline chlorate (chlorate of sodium or chlorate of potassium) the ratio of chlorate to ore being about 1 to 100. To this charge I add hydrochloric acid, preferably in the commercial form known as muriatic acid, in the ratio of about 125 to 150 pounds of mineral to 111 pounds of 20° acid. While the ensuing reaction is in progress I maintain the temperature of the kettle and its content at about 90° C. This I preferably accomplish by surrounding the kettle with a wooden jacket, and supplying the intervening chamber with injected steam. I preferably also cover the kettle during the operation with a wooden cover. The desired reaction will be completed after an interval of from 10 to 18 hours, at the end of which period the liquid is decanted from the solid residue and that residue is washed in water. The washing is continued until the soluble constituents are removed. That is to say, in the case of wolframite, until the wash-water contains but a slight trace of manganese, or in the case of sheelite (which also may be used) until the wash-water contains but a small quantity of calcium. This residue consists of tungstic acid mixed with insoluble dross, which ordinarily will largely consist of silicic acid or silica. This product may now be variously treated, according to the end which I desire to obtain. For example, it may be treated with ammonia water and the tungstic acid thus by solution separated from the dross, or it may be treated, dross and all, together as follows: Heretofore in the production of tungsten steel and steel including in its composition a content of metal of similar character with tungsten, it has been considered necessary to charge into the crucible, together with the other steel-making ingredients, the tungsten or similar metal in metallic state, practically free of dross or adulteration, and heretofore in the manufacture of tungsten steel the common practice has been to employ tungsten of from 95 to 98% purity. The production of metallic tungsten of such purity was accomplished heretofore at very considerable expense, and at an expense which adds appreciably to the price of the tungsten steel. I have found it unnecessary to bring the tungsten ingredient of the crucible charge to such degree of purity as has heretofore been thought necessary, and I have found on the contrary that tungsten adulterated with substances contained in the native rock, after such refining operation as I have found to be sufficient, may be employed in the crucible charge, and that the tungsten steel produced is of good marketable quality. The adulteration will, as is indicated in the foregoing part of the specification, be notably silica which as has been said is present in the matrix or rock in which the tungsten ores lie, and the product of my refining

operation will contain tungsten, together with an adulteration which may amount to as much as 20 per cent., or even more, and this adulteration will consist to a large extent at least of silica. The silica and such other adulterants as remain will be separated from the metal in the crucible by slagging off, in the progress of the crucible operation.

Describing now the further operation, I take the insoluble residue of the acid treatment hereinbefore described, and after washing it, dry it and submit it in the presence of a reducing agent to a temperature sufficient to effect the reduction of the tungsten oxid. To explain, the residue from the acid reaction will contain the tungsten in the form of oxid or acid; and the object of this second reducing step is to effect the reduction of that oxid to metallic tungsten. To this end, the residual substance of the acid reaction is, while maintained in the presence of a reducing agent, brought to a temperature sufficient to effect the reduction of the tungsten oxid. This step of my operation will preferably be effected in a furnace, and according to a method of operation particularly described in a co-pending application of mine, filed June 19, 1909, Serial No. 503,112, for method of reducing metallic oxids. When the operation of reduction shall have been carried out, and the charge of the reducing furnace shall have been cooled down and withdrawn, that charge will consist of metallic tungsten in finely divided form, somewhat caked, mechanically combined with dross or adulteration which, as above explained, will to a large extent consist of silica. The tungsten content of the resulting product will ordinarily be about 80 per cent. of the whole, though in thus stating what the percentage ordinarily is in practice, I do not mean to limit myself to any ratio.

If the particular ore treated be sheelite in commercial form, the silica content of the resulting product will be particularly great; if the ore treated be wolframite or iron tungsten ore, the dross will consist in part of silica, and there will be a very appreciable quantity of iron—in the case of the iron tungsten ore, as much as 7 per cent.; if the ore be wolframite, there will be some small quantity of manganese in the dross. It will be understood that iron, if present, will be brought to metallic state at the same time with the reduction of the tungsten, and that such iron content will be clear gain in the crucible charge. It will thus be observed that the silicon present and in the form of silica forming an adulterant with the commercial ore, instead of being separated from the tungsten before the latter is charged into the crucible (which separation can be effected only at relatively great expense), is allowed to remain and to be charged with the tungsten into the crucible, where it is removed as an incident to the steel-making operation, and at relatively small expense. The eradication of silicon in this manner is possible, because it is present in the crucible charge in the form of the oxid, silica, mechanically mixed with the tungsten, and in this form it is slagged out unchanged.

I have particularly referred in describing my process to the manufacture of tungsten steel, and to the preparation of minerals in which tungsten occurs. It will of course be understood that I do not limit myself to the specific ores named, nor to a process which involves the use of tungsten only; for my invention is applicable to the refinement of ores of other metals, of like character with tungsten, as a preliminary operation, preparing the metal as it is found in the ore for its introduction into the charge of the crucible or other metal-reducing furnace.

I claim as my invention:

The herein described process of treating an ore of tungsten or like metal adulterated with silica-containing rock, which consists in submitting the ore to the action of hydrochloric acid in the presence of a chlorin-affording substance and without removal of the silicon content submitting the residue from such reaction to the action of a reducing furnace.

In testimony whereof, I have hereunto set my hand.

CHARLES MORRIS JOHNSON.

Witnesses:
SUE B. FRITZ,
BAYARD H. CHRISTY.