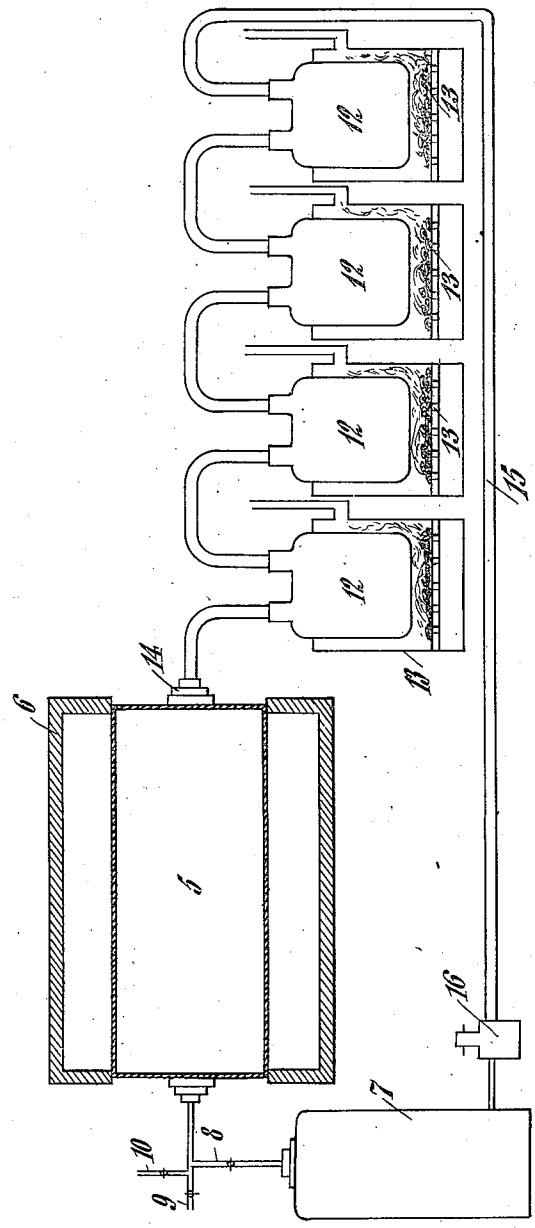
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PROCESS OF RECOVERING METALS.

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PROCESS OF RECOVERING METALS.

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To all whom it may concern:

Be it known that I, ALEXANDER L. DUVAL D'ADRIAN, a citizen of the Republic of France, and a resident of Washington, county of Washington, and State of Pennsylvania, have invented certain new and useful Improvements in Processes of Recovering Metals, of which the following is a specification.

Heretofore in the production of the oxides or salts of chromium, zirconium, vanadium, uranium, cobalt, silver, or nickel from their ores, disadvantages have been encountered in obtaining the oxides or salts, free from the iron that may be present in the ores, or in the residues, or free from other impurities, or in the separation of one or more metallic compounds from a group.

The object of my invention is to provide a process by means of which the oxides or salts such as chlorides, of chromium, zirconium, vanadium, uranium, cobalt, silver, or nickel, may be readily obtained from their respective ores or from residues containing chromium zirconium, vanadium, uranium, cobalt, silver, or nickel, by means that are simple and efficient and commercially practicable.

In order to carry out my invention, I will describe the same in the light of one embodiment, and more particularly refer by way of example, to the treatment of chromium ore, and the obtaining of chromium oxide from the ore, with the understanding, however, that parts of this process may be applied to the treatment of zirconium, vanadium, uranium, cobalt, silver or nickel, with, however, certain modifications which will hereinafter appear.

In carrying out my process, for the purpose of obtaining chromium oxide practically free from iron or other impurities, I take the chromium ore as it comes from the mines, and grind it very finely into powdered form. This chromium ore is usually called chromite. The object of grinding the ore into finely powdered form, is to get as large a surface as possible so that it may be readily treated as hereinafter described. This powdered chromium ore is then mixed with sawdust and with molasses, or with a starch and water mixture, or any other suitable organic compound may be used, adapted to serve as a binder. The preferable proportions are about as follows, as an example:

Chromium ore in 100 parts; sawdust in 15 parts, and the binder in 5 parts.

This mass is then formed into bricks or blocks. These bricks or blocks are then placed in a furnace having a closed muffle, and heated. The heating to which the bricks or blocks are subjected, first carbonizes the sawdust and the binder. Thereby the particles of the chromium ore are separated from each other by spaces filled with gases, and by the carbonized particles, by reason of which the bricks or blocks become of a porous character, and a large surface of exposure of the chromium ore is obtained after the sawdust and binder have been carbonized. Chlorine gas is then injected into the furnace. The chlorine gas penetrates the blocks or bricks and acts on the ore. The chlorine gas is injected through a tube from a suitable storage tank. The muffle during the introduction of the chlorine gas, is brought to a temperature at which the evolution of the iron chloride commences. It is advantageous to maintain the muffle temperature between approximately 450° C. and 1000° C., depending upon the ores to be treated. It is here to be noted that various chromium ores, even from the same mine, require variations in the treatment with respect to the temperatures. The iron of the chromium ore sublimes at about 450° C., though some iron chloride is formed at temperatures below this. It is preferable not to go beyond 1000° C. because chromium chloride sublimes at about 1065° C. The chlorine gas combines with the iron in the chromium ore, and forms iron chloride which passes out of the furnace, flowing through a pipe line. This pipe line may be made transparent by the use of glass or the like, or may be provided with some transparent window so that the contents flowing through the pipe may thereby be visible and may be inspected. This iron chloride passes through the pipe in the form of a thick vapor of a brown color. The passing of the chlorine gas is continued until no further considerable iron chloride passes through the tube or

exhaust pipe which may be readily determined by inspection. In some cases, it is preferable to inject a slight amount of steam either into the muffle by means of a separate tube, or through the same tube with the chlorine gas. This steam acts to form a certain amount of chloride of iron containing six molecules of water ($FeCl_3 6(H_2O)$), which very readily volatilizes, namely at a temperature of about 280° to 285° C. The injection of the chlorine gas is continued until the brown vapor practically ceases, whereupon it is shut off. It may be mentioned that when the brown vapor stops, practically all the iron of the ore has been combined with the chlorine gas, and carried off in the form of iron chloride. This may be conducted to cooling vessels whereby it may be condensed into a marketable article, by the utilization of temperatures below about 450° C.

The heating operation is continued for about fifteen minutes or more, to assist in driving off any iron chloride which may be in the muffle, and air is passed through the muffle to eliminate as much as possible any chlorine gas present in the muffle. It is preferable to use moist air. The air also brings about the combustion of the carbon particles. The remaining content of the muffle is composed of chromium oxide with some chromium chloride, and small amounts of silica or other impurities, but practically free from iron.

After the chromium oxide has thus been obtained practically free from iron, the chromium oxide and any chromium chloride remaining in the furnace are taken out of the furnace and the chromium oxide is freed from the chromium chloride by dissolving out the chromium chloride in a manner well known to the art.

For commercial purposes, it is preferable to use a rotary muffle kiln or muffle furnace. In the use of a rotary furnace, no molding of the ore is necessary. This is due to the agitation to which the ground ore is subjected by the rotation of the furnace and the consequent production of new surfaces of contact of the particles of the ore with the gas in the muffle. In the use of a rotary furnace, the ore in finely powdered form is mixed with carbon and then heated and subjected to the action of the chlorine gas for the elimination of the iron from the ore. It is not always necessary to use the carbon It has been found, however, that with the use of carbon, lower temperatures may be utilized as the presence of carbon facilitates and makes more rapid the action of the gas. The treatment of the contents of the muffle is carried out as above described. The remaining chromium oxide with chromium chloride such as remains in the furnace, is treated as above described, namely by dissolving out the chromium chloride in a manner well known to the art. Whatever silica remains here, as also in the furnace before mentioned, may be removed by processes well known in the art, as for example, by hydrofluoric acid.

The process as above described, is based upon the regulation of the temperatures during the passage of the chlorine gas through the furnace and its coming into contact with the ore, it being important to so regulate the temperatures that only a selective volatilization and subliming will take place, that is, such temperatures as will cause the iron to combine with the chlorine gas to from iron chlorides and will practically sublime or distill only the iron chlorides. In other words, fractional sublimation or distillation is obtained.

If desired, this selective temperature method may be replaced by another method which utilizes temperatures higher than 1000° C. or 1065° C. at which latter temperature chromium chloride is formed and sublimes, and which carries out the process until all of the materials in furnace are volatilized and sublimed in the form of chlorides. In this process, temperatures are utilized from 450° C. upwards.

In the accompanying drawing I have disclosed a typical apparatus by means of which the present process may be sucessfully practiced. In this drawing 5 designates the rotary muffle kiln or furnace having an outer wall or shell 6 of refractory material. To one end of the rotary kiln a chloride gas storage tank 7 is connected through the medium of the pipe 8, which is coupled to a pipe 9 for supplying air under pressure, and to a steam supply pipe 10. A suitable gas pipe fitting or connection is provided between the gas supply pipe and the end of the rotary kiln. A series of condensers 12 are connected in series to each other, each condenser being arranged in conjunction with a heating chamber 13. The first condenser in the series is connected by a gas tight fitting 14 to the other end of the rotary kiln, while the last condenser in the series is connected by a pipe 15 with a pump 16, which creates a partial vacuum in the several condensers and draws the chlorine gas entering the condensers from the furnace through the said pipe 15, and returns the same to the storage tank 7 through the pipe connection 17 between said tank and the pump 16. It will be understood that the drawing is simply illustrative of one possible construction of apparatus which may be employed in the practice of my improved process on a commercial basis.

It will be readily appreciated that various other alternative constructions might be employed. Thus, as hereinafter noted, instead of providing the single condenser 12, a

plurality of groups of condenser units may be utilized, and such groups of units connected in series with each other whereby a succession of condensations will occur in each condenser group.

Above the temperature of 1065° C. the chromium oxide is transformed into a chloride and is sublimed at or above this temperature, and practically all the rest of the materials are transferred into chlorides and are volatilized and sublimed. During the time that the ore is subjected to the temperatures ranging from the initial temperature of 450° C. and then through the various temperature up to 1065° C. and above 1065° C. the vapors or sublimates are conducted from the furnace into condensers. These condensers are arranged in series, that is, the first condenser is in communication with the furnace and thereafter each following condenser communicates with the one preceding. These condensers are maintained at different temperatures. The first condenser, or in case more than one is desired to be used, then the first condenser or the first group is maintained at one constant temperature, and this temperature is higher than any of the other temperatures in any of the other condensers. The temperature of the first condenser or group of condensers is selected to bring about the deposit of chromium chloride. If chromium chloride is maintained at a temperature less than 1065° C.. it will deposit. For this reason the first condenser or the first group of condensers which has for its object to bring about the deposit of the chromium chloride, are maintained at a temperature between 460° to 500° C. All substances which maintain their subliming at temperatures below 500° C. will flow from the first group of condensers to the next or number two group. This number two group of condensers is maintained at a temperature below 450° C. but above 220° C. It is within this range of temperatures that iron chloride deposits in the form of $FeCl_3$. The other substances which keep on subliming, pass off or continue into the number three group of condensers. This third group of condensers is maintained at a temperature below 57° C. and above 40° C. This range of temperatures brings about the deposit of various silicon chlorides, as per example, $SiCl_3$ below 145° C., $SiCl_4$ below 57° C., and Si_3Cl_8 below 210° C. Certain substances, as for instance $FeCl_36(H_2O)$ are carried off from these condensers into a next group, and this last group is kept at temperatures below 37° C., whereupon the $FeCl_36(H_2O)$ deposits.

I have spoken of groups of condensers for each step, but it is clear that in some cases, one condenser may take the place of a group. The advantage, however, of more than one condenser for each step is that in the first condenser of a group, for instance at the step wherein it is desired to deposit chromium chloride, perhaps not the entire quantity of chromium chloride will deposit, and part of the chromium chloride will be carried off with the remaining chlorides, and deposited in a subsequent unit of the same group. Similarly, in the second step where iron chloride is deposited, parts of the iron chloride may pass off from the first condenser of this group and will deposit in a subsequent unit of the same group. Similarly, in the subsequent steps it is preferable to use two or more condensers.

It will therefore be seen that by the various groups of condensers regulated at temperatures which control the condensation and deposit, all the various chlorides which have passed out of the furnace will be individually isolated.

The chromium chloride deposited in the first condenser or a group of condensers, is then treated in a manner well known to the art to secure chromium or its compounds, as for instance chromium oxide. Similarly, the other chlorides may be utilized. Such portions of chlorine gas as come from the muffle and pass through the condensers, may be collected and recovered.

In carrying out the process, it must be remembered that ores from the same mine are different in their characteristics and that it has been found desirable to select portions of the ore desired to be treated and subject them to a preliminary test to ascertain their characteristics. When this preliminary test has been completed and the characteristics of the ore have been ascertained, then one of the above two methods of treatment may be employed as above described. Some ores will be better treated with a selective volatilization, others with a complete volatilization and a selective condensation.

I have referred to the use of chromium ore, but it is clear that other ores may be treated in a similar manner.

In regard to vanadium and uranium, it has been found that the complete volatilization and selective condensation method is usually more advantageous.

Vanadium ores may contain in addition to vanadium, uranium, lead, silica, iron, barium and other constituents, and by selective condensation vanadium, uranium, silica and iron can be separated. In the case of zirconium ores which may contain silica, iron and titanium, the zirconium titanium, silicon and iron can be similarly separated. In case of cobalt ores, which, in addition to cobalt, usually contain nickel, silver, iron, arsenic, antimony and silicon, these may be all selectively condensed, or the cobalt ore may be first roasted to remove arsenic and antimony, and then the cobalt, nickel, silver,

iron and silicon, selectively condensed. I have spoken of ores, but it is clear that residues may be similarly treated.

In the case of a cobalt ore or a residue containing cobalt, it is necessary in carrying out the above described methods, to remember and be guided thereby, that cobalt chloride sublimes at temperatures about 700° C. Silver chloride sublimes at temperatures about 800° to 900° C. and nickel chloride sublimes at temperatures about 600° to 700° C. Arsenic and antimony is usually separated by roasting and arsenic chloride distills at temperatures below about 130° C. The different antimony chlorides distill at various temperatures above about 102° C. and below about 225° C. The iron chloride as heretofore, sublimes at about 450° C. and the $FeCl_3 6(H_2O)$ distills at below about 37° C. The silica chlorides distill at temperatures as follows:

$SiCl_3$ below about 145° C.
$SiCl_4$ below about 57° C.
Si_3Cl_8 below about 210° C.

In the case of vanadium ores or residues, the several vanadium chlorides distill at above about 126½° C. and below about 154° C. Uranium chloride distills below about 750° C. The iron chloride and $FeCl_3 6(H_2O)$ distill as heretofore stated. Silica chlorides distill as heretofore stated. The lead chloride sublimes at about 861° to 954° C. and the barium chloride is left as an acid.

In the case of zirconium ores or residues, titanium chloride distills at below about 136½° C. The silicon chlorides and iron chlorides as heretofore, and the zirconium chloride at 400° C.

Among the ore residues that I have treated are speiss. I have also treated metal alloys for the separation of the metals, composing the same.

I believe my methods are also applicable to the treatment of slags and mattes.

Reference is herewith made to my pending application Serial No. 336,260, filed November 7, 1919, of which this is a divisional application.

I have described the above as embodiments of my invention but it is clear that changes may be made therein without departing from the spirit and scope of the invention as defined in the appended claims.

I claim:

1. The process of obtaining chromium, zirconium, vanadium, uranium, cobalt, silver, or nickel in the form of chlorine compounds from their respective ores, or from residues containing chromium, zirconium, vanadium, uranium, cobalt, silver, or nickel, which consists in subjecting an ore or residue to a heat treatment at successively higher temperatures in the presence of chlorine gas to form chlorides, and then selectively condensing the chlorides at different temperatures to separately deposit the chlorides of the metal or metals of the ore or residue being treated.

2. The process of obtaining chromium, zirconium, vanadium, uranium, cobalt, silver, or nickel in the form of chlorine compounds from their respective ores, or from residues containing chromium, zirconium, vanadium, uranium, cobalt, silver, or nickel, which consists in mixing the ore with carbon, heating the ore or residue in the presence of the carbon, then subjecting the ore or residue and carbon to further heat treatment at successively higher temperatures and to the simultaneous action of chlorine gas, to thereby form chlorides and volatilize and sublime the same, and then removing the chlorides.

3. The process of obtaining chromium, zirconium, vanadium, uranium, cobalt, silver, or nickel in the form of chlorine compounds from their respective ores, or from residues containing chromium, zirconium, vanadium, uranium, cobalt, silver or nickel, which consists in heating the ore or residue at successively higher temperatures in the presence of chlorine gas to form chlorides, and selectively condensing the chlorides.

4. The process of obtaining halogen compounds of the metals from ores or residues, comprising subjecting the same at successively higher temperatures to the action of halogen gas, and selectively condensing the halogen compounds at different temperatures to recover the same.

5. The process of obtaining chlorides of the metals from ores or residues comprising subjecting the same at successively higher temperatures to the action of chlorine gas, and selectively condensing the chlorine compounds at different temperatures to recover the same.

6. The process of obtaining chlorides of the metals from ores or residues, comprising finely grinding the same, mixing carbon therewith to promote the subsequent action of chlorine gas on the metal-content of the mixture, subjecting the mixture at successively higher temperatures to the action of chlorine gas, and selectively condensing the chlorine compounds at different temperatures to recover the same.

In testimony that I claim the foregoing as my invention, I have signed my name hereunder.

ALEXANDER L. DUVAL d'ADRIAN.