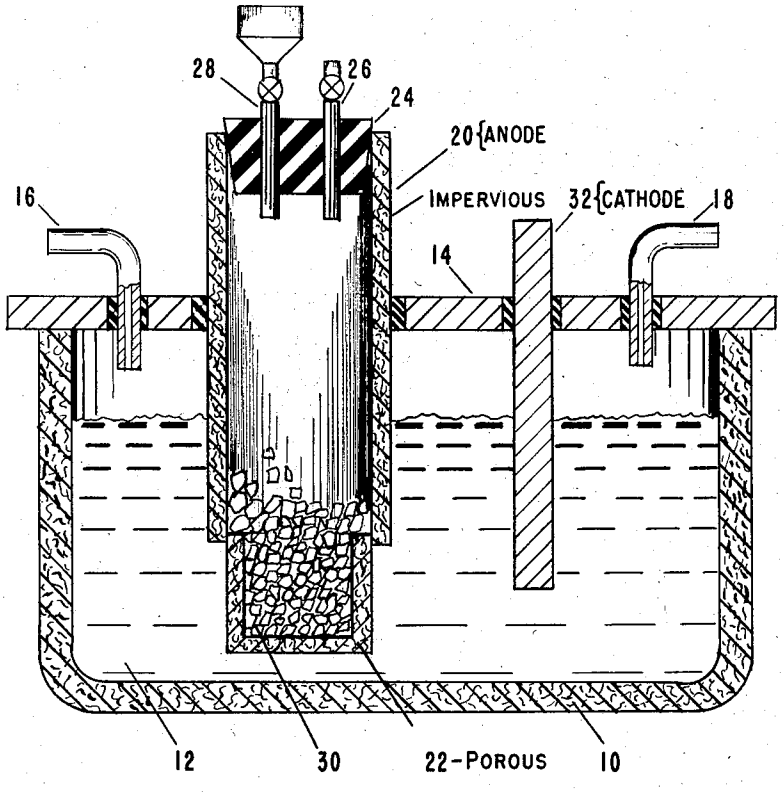
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PREPARATION OF FUSED SALT ELECTROLYTES

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PREPARATION OF FUSED SALT ELECTROLYTES

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This invention relates to the production of anhydrous chlorides of various metals and to the subsequent recovery of the metal by a fused salt electrolysis of the chloride. More particularly, it relates to a novel procedure whereby an oxide containing compound of the metal to be recovered is converted into an oxygen-free chloride of the metal and the oxygen-free chloride is thereafter converted to the desired metal by electrolysis in a fused salt electrolyte.

Numerous processes have been described in the prior art for producing metals from oxygen-containing metal compounds such as the oxides, carbonates, nitrates, and various salts of organic acids such as oxylates and the like, since the metal oxides are relatively inexpensive and are generally easy to prepare in relatively pure form from such oxygen containing compounds. These processes include thermal as well as electrochemical procedures. One electrochemical approach which has been extensively attempted has been an electrolysis in a suitable fused salt electrolyte employing an anode formed of a mixture of the metal oxide and carbon. Such electrolytes have been formed of one or more alkali metal chlorides or one or more alkaline earth chlorides or mixtures of one or more alkali metal chlorides and one or more alkaline earth metal chlorides. Invariably, these attempts have failed when attempted on a commercial scale because most of the chlorine formed by electrolysis at the anode escapes as a gas instead of reacting with the metal oxide constituent of the mixture to form the metal chloride necessary for the success of the operation. A further disadvantage of this prior art method arises from the necessity for obtaining the required electrical conductivity in the anode. This is met by providing a large excess of carbon in the mixture, with the resulting decrease in the amount of metal oxide in the mixture available for reaction with the chlorine evolved, as well as later contamination of the bath by the excess carbon. Since this prior art approach employs materials which are relatively inexpensive, and which are readily prepared, the method remains economically attractive in spite of the technical difficulties previously encountered in adapting it to commercial production.

I have discovered a method which is free from the disadvantages of the prior art methods and a novel means for carrying out my method whereby the advantages of a reactive oxide anode can be retained. Instead of relying on a self supporting electrically conductive mixture of metal oxide and carbon to serve as the anode, I provide a charge container in the form of a hollow non-reactive conductive reaction tube one end of which is adapted to be closed by a porous disc and the other end of which is adapted to be connected to a source of a chlorinating gas.

Various chlorinating agents may be employed to effect the chlorination of the oxidic metal compound, among which may be mentioned anhydrous hydrogen chloride, carbon tetrachloride, phosgene and elemental chlorine. In the case of chlorine, the reaction requires the presence

of carbon in the charge. In the case of the other chlorinating agents, the carbon may be eliminated from the chlorinizable mixture.

In accordance with my method, the reaction tube is immersed in a fused salt bath, with the porous disc end well below the surface of the fused salt, and the hollow tube is filled with a charge of oxygen containing metal compound with which carbon may be admixed if desired and then the charge is chlorinated by means of the chlorinating gas. The metal chloride formed is carried out of the tube through the porous disc in the stream of excess chlorinating agent and other gaseous products formed by the reaction into the fused salt bath surrounding the porous portion of the charge containing reaction tube, wherein the metal chloride dissolves.

In this aspect of my invention, the hollow-non-reactive conductive tube serves merely as a reaction chamber in which the following reaction is caused to take place between a suitably proportioned mixture of metal oxide with carbon or graphite and a chlorinating agent, such as elemental chlorine (Equation 1) or a metal oxide and a chlorinating agent such as hydrogen chloride (Equation 2):

$$M_xO_y+yC+yCl_2\rightarrow M_xCl_{2y}+yCO \quad (1)$$

$$M_xO_y+2yHCl\rightarrow M_xCl_{2y}+yH_2O \quad (2)$$

Where x and y are integers and M is any metal whose oxide or readily decomposed oxygen containing compounds are adapted to be treated in the manner described.

The metal chloride, at the temperature of the reaction, is carried out of the reaction chamber along with any gaseous products produced and any excess or unreacted chlorinating gas. The several products may be readily separated from one another in any convenient fashion. To recover the desired metal from the metal chloride so produced, various known techniques may be employed. For instance, the metal chloride may be decomposed by electrolyzing the fused salt bath surrounding the reaction tube after the metal chloride has dissolved therein. Preferably this fused bath is pumped to a conventional fused salt electrolytic cell and electrolyte is returned to surround the reaction chamber and to be replenished with metal chloride evolved in the continuing chlorination.

In another aspect of my invention, the reaction tube itself serves as the anode in an electrolysis which may be carried out during or subsequent to the chlorination reaction. In this embodiment, the reaction tube is immersed in a fused salt bath so that, as the metal oxide is chlorinated, the metal chloride formed passes out of the porous disc and directly into the fused salt bath as previously described. The fused bath surrounding the hollow tube serves to protect the tube and its contents from the effect of air, oxygen, or any other undesirable reactive environment, and also functions to maintain the temperature of the reaction tube and its contents within close limits. The resulting salt bath, which comprises the original salt bath plus the metal chloride which has passed out of the reaction tube may be directly electrolyzed to recover the metal by suitably constructing the reaction apparatus.

In a preferred aspect of my invention, there may be added to the charge in the hollow tube a small amount of an extraneous salt, usually an alkali metal chloride, in which the metal chloride dissolves as it forms during the chlorination reaction so that the metal chloride dissolved in the alkali metal chloride passes on into the fused bath in the form of a molten mixture instead of as a vapor. The reaction may be represented as follows:

$$xMCl_y+zNaCl\rightarrow Na_zM_xCl_{(xy+z)} \quad (3)$$

The advantages of operating in the manner previously described are at once evident. First, the desired electrical

conductivity is provided by the hollow anode and as a result, instead of proportioning a mixture of oxide and carbon to produce the required conductivity, the mixture may be proportioned from the standpoint of the optimum chemical conversion to metal chloride with little or no excess of any of the reactants. By effecting contact between the metal oxide and the chlorinating agent within the confines of the hollow anode, instead of on the exterior surface of the anode, as in the prior art, the chlorinating agent is afforded ample opportunity to react with metal oxide in an efficient manner. Other advantages will become apparent from the following description.

In the accompanying drawing, the figure represents a sectional view of a preferred apparatus for carrying out my method.

As shown in the drawing, a refractory crucible **10** serves as the container for a fused salt bath **12**. The crucible is provided with a cover **14** having an inlet **16** and an outlet **18** through which gases may be admitted to or vented from the space above the fused bath in order to control the atmosphere above the bath. Means (not shown) are provided for maintaining the temperature of the salt bath above the fusion temperature of its components. Cover **14** is provided with additional openings through which one or more reaction chambers or electrodes may be inserted. In the figure, one such chamber and one such electrode are shown identified as **20** and **32** respectively.

Reaction chamber **20** is formed of any suitable material, and is preferably constructed of graphite. When the tube **20** is to serve as a reaction chamber in which the chlorination is effected, it is merely required to possess the necessary structural strength and chemical inertness to the materials in contact with it. When the tube **20** also functions as an electrode, in an electrolytic cell, it is required to possess a sufficient conductivity to satisfy the electrical conditions imposed on it. In either instance it has been found that commercial graphite is suitable and a cylindrical, elliptical, rectangular or other shaped hollow configuration may be employed. The lower end of tube **20** is closed with a porous plug **22** of graphite, carbon or ceramic composition. The upper end of tube **20** is closed by a plug **24** provided with inlet means **26** for admitting a halogenating agent such as chlorine gas and means **28** schematically showing an arrangement for replenishing the solid portion of the reaction mixture in the element **20**.

Within element **20** there is shown a charge consisting of briquettes **30** of the oxide or decomposable oxygen containing compound of the metal to be produced with or without a carbonaceous reducing agent. The briquettes are preferably formed by mixing together finely divided carbon such as —325 mesh (Tyler Standard) lampblack with —200 mesh metal oxide in substantially stoichiometric proportions. These ingredients may be formed into briquettes or pellets with any suitable binder, methyl cellulose, molasses, and water each having been found suitable.

To facilitate the removal of the metal chloride formed by the reaction conducted in chamber **20** as a liquid rather than in vapor form, it has been found advantageous in some cases, to include a small amount of at least one alkali metal halide or alkaline earth metal halide in the charge. The additional halide is chosen from those halides in which the metal chloride, formed by chlorination of the metal oxide, dissolves.

When the apparatus is employed for carrying out the electrolytic aspect of my process, one or more cathodes **32** are suspended in fused bath **22** which is comprised of one or more alkali halides or alkaline earth halides or mixtures of same. With most of the metals amenable to the practice of my invention, I prefer to form the bath of sodium chloride or eutectic mixtures of sodium chloride and other chlorides of the alkali or alkaline earth

metals, since such baths are economical and are composed of materials readily commercially available in the desired purity.

Both the electrolytic and non-electrolytic processes constituting my invention are based on the same reactions and hence are both generally applicable to the recovery of the same metals and metalloids. The processes are particularly suited to the recovery of the halides of metals which cannot be recovered from aqueous solutions by ordinary methods. For example, when aqueous solutions containing zirconium chloride are evaporated to recover the chloride, the product obtained is largely an oxychloride. By the practice of my invention, the desired chlorides are obtained, dissolved in an anhydrous fused salt menstruum, from which many of the halides may be recovered by heating the fused bath to a temperature sufficient to volatilize the metal halide.

The elements which form chlorides may be considered as falling into three more or less clearly defined groups. A first group composed of the elements which are highly metallic is characterized by the formation of chlorides which are completely or substantially completely stable in water solutions and which can therefore be recovered substantially undecomposed from an aqueous medium. Exemplary of this group are the alkali metals, the alkaline earth metals, and such metals as silver, lead and copper. A second grouping of the elements comprises those which are considered completely or partially nonmetallic, such as sulphur, phosphorus, boron and silicon. On contact with water, the chlorides of these elements hydrolize completely and therefore cannot be recovered from aqueous solutions. Furthermore, the chlorides of this second group of elements when formed in nonaqueous systems are substantially insoluble in and/or immiscible with fused melts of alkali metal or alkaline earth metal halides. The remaining elements which form chlorides constitute a transition group. These elements form chlorides which unlike the first group cannot be recovered from aqueous solutions without complete or at least substantial decomposition. Unlike the second group, these elements form chlorides which will dissolve or which will react with alkali metal or alkaline earth metals fused halide melts to form at elevated temperatures a continuous phase of electricity-conducting properties.

It will be seen that some metals form chlorides which place them on the border line of more than one of the above groups. For example, by the use of specialized techniques involving hydrogen chloride gas or ammonium chloride, the chlorides of magnesium and cerium may be recovered from aqueous solutions and hence these elements are properly classifiable either in the first or third group. As a practical matter, they should be treated as belonging to the transition group. Other metals such as titanium will fall in more than one group depending upon the valence state of the chloride. Thus tetravalent titanium would be classed in the non-metallic group since titanium tetrachloride is substantially insoluble in fused halide melts, while as a trivalent element it would fall in the transition group.

The reactions previously set forth are applicable to the production of a wide variety of halides, particularly the chlorides, including the chlorides of the elements falling in the third group above described. These comprise aluminum, beryllium, cerium, chromium, hafnium, molybdenum, zirconium, tantalum, titanium (as a chloride lower in valence than 4), thorium, tungsten, uranium, vanadium, and the other rare earth (atomic number 57–71) or refractory metals. The chlorides so produced may be electrolyzed in a manner well known in the art to obtain the desired metal.

The following example will serve to further illustrate the practice of my invention.

Example I

An intimate mixture of carbon, sodium chloride and basic zirconium carbonate was formed by grinding the three ingredients together in the proportion of about 4 parts by weight of lampblack, 13 parts by weight of sodium chloride and 40 parts by weight of basic zirconium carbonate, containing about 23.4% ZrO_2. The mixture was formed into small briquettes about one-half inch in diameter and one-half inch in length by means of a hand arbor press.

A reaction chamber was constructed in accordance with the drawing by providing a graphite tube **20** about 18 inches long, 2 inches external diameter, and 1⅜ inches internal diameter. One end of tube **20** was plugged with a rubber stopper **24** having a connection **26** for admitting chlorine and the other end was provided with a porous carbon plug **22**. Plug **22** was about 4 inches in length. A hole ⅝ inch in diameter was drilled through about 3½ inches of the plug so that the end of the hole inside was about flush with the end of the graphite tube. The graphite tube **20** was partially filled with briquettes **30** and then was placed in a fused salt bath **12** formed of sodium chloride, in a vertical electrically heated furnace.

Chlorine gas was admitted through the inlet and the entire assembly was heated (by means not shown) gradually to the melting point of sodium chloride and, as chlorination proceeded, to a temperature of almost 900° C. Thereafter the assembly was cooled and the salt bath surrounding the tube was an analyzed for zirconium. It was found that about 6.4% $ZrCl_4$ was present in the sodium chloride.

The complex fused salt was melted in a conventional electrolytic cell and electrolyzed therein under a controlled atmosphere at about 750° C. with a cell voltage of between about 2.2 and 2.4 volts and a current density of about 100 amps./square decimeter, whereby the zirconium was recovered as a cathode deposit on a steel cathode.

Instead of permitting the fused bath to solidify, and transferring the salt to an electrolytic cell, for remelting, it will be obvious that the electrolysis could have been conducted in the original cell by providing a cathode and impressing a potential across the hollow anode and the cathode. Indeed the crucible itself may serve as the cathode in many cases.

While I have disclosed the process as applied to the recovery of zirconium, it will be appreciated by those skilled in the art that it is equally applicable to many other oxidic metal compounds, and even to oxygen-contaminated metal scrap which may be thereby converted to a chloride in an anhydrous fused salt bath and subsequently recovered therefrom by known electrolytic procedures.

In the following claims I have employed the term "transition group element" to include the elements characterized as neither highly metallic nor completely non-metallic on the basis of the manner in which the chlorides behave in aqueous and fused media.

I claim:

1. A process of preparing a fused salt composition adapted to be electrolyzed which comprises: providing a refractory vessel; establishing a fused salt bath consisting essentially of at least one halide from the group consisting of alkali metal halides and alkaline earth metal halides; providing a container adapted to contain material to be chlorinated and consisting of a tubular element confining the material to be chlorinated within a solid tubular upper portion and a porous lower portion; charging into said container an oxygen-containing compound of an element other than the alkali metals and alkaline earth metals and selected from the group of elements forming chlorides which cannot be recovered from aqueous solutions in substantially undecomposed and unhydrolyzed form and whose chlorides are miscible in fused alkali halide melts, alkaline earth halide melts and molten mixtures of alkali halide and alkaline earth halides; immersing said container in said fused salt bath so that the porous portion of the container is beneath the surface of the bath; passing a chlorinating gas into the upper portion of said charge-filled container, thereby forming a chloride of the element whose oxygen-containing compound constituted the charge; and recovering said chloride in said molten bath by passage of said chloride through the pores of said porous portion of the charge-confining container and directly into the surrounding molten bath.

2. An electrolytic apparatus comprising a refractory vessel adapted to contain a molten salt electrolyte and having a cover to enclose the contents of the vessel; means for heating the contents so as to maintain it in molten form; a hollow tubular anode element adapted to contain solid material to be chlorinated, said element being mounted so as to pass through said cover and having an upper end extending above said cover and a lower end adapted to extend into the molten contents of the vessel; a plug in the upper end of said tube; a first means extending through said plug for admitting a chlorinating gas into said tubular element; a second means extending through said plug for introducing a charge of solid material to be chlorinated into said tubular element; a porous plug disposed within the lower end of said tubular element so as to support a charge of material to be chlorinated in said tubular element and to permit the egress of chlorinated reaction products from said tubular element directly into the molten contents of the vessel; whereby a fused salt composition may be formed from which the element which is chlorinated may be recovered by a fused salt electrolysis.

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