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ELECTROCHEMICAL PROCESS OF TREATING
CHROMITE ORE

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13 Claims. (Cl. 204—89)

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This invention relates to the conversion of chromium containing ores to soluble chromium compounds and insoluble non-chromium compounds.

The present application is a continuation-in-part of my copending application, Serial No. 317,970, filed February 8, 1940.

In accordance with the present invention, I have provided a process whereby chromium compounds can be economically produced from chromium ores. If desired, the metal chromium can be easily obtained from such chromium compounds by known commercial processes. Chromite ore is a complex combination of chromium, iron and oxygen, together with certain other impurities. For the purposes of illustration pure chromite may be represented by the empirical formula $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The ore is substantially insoluble in acid and alkalies at normal temperature. I have discovered that if an electric current is passed through a body of chromite ore placed adjacent an anode and in an electrolyte containing a halate salt, the ore may be rapidly converted into soluble chromium compounds with a low consumption of power and the non-chromium compounds in the ore will for the most part remain as or be converted into insoluble compounds permitting their separation.

I have found that changes in the concentration of the halate compound in the electrolyte varies the rate of conversion of the ore. It is preferred to maintain the concentration of the halate in the electrolyte between 100 grams per liter of water and saturation. My process may be operated at normal room temperatures although higher or lower temperatures may be used if found desirable to further the operation under certain conditions.

Metal halates, preferably the alkali metal halates such as the chlorates, bromates, and iodates, may be used either separately or in combination. The halates used may be added, of course, to the bath as such or formed therein during the electrolysis, the controlling factor being that they be present during electrolysis so as to be effective for the practice of my invention as described. The term "halate" as used herein refers to chlorates, bromates and iodates.

I have found that the reduction of the ore is improved when I use anode material of a relatively high oxygen over-voltage. The reason for this may be that an anode of high oxygen over-voltage maintains the halates in a more strongly oxidized state at which condition they appear to give the most effective action.

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I also prefer to use ore in a relatively fine state of sub-division. A fineness of between about 20 and 100 mesh or more has been used successfully.

It is not fully understood how the halogen compounds enter into the process except that they appear to perform a catalytic action. Without the presence of a halate, no effective reduction of the chromite ore is obtained. While I do not wish to impose any limitations on my invention by way of theorizing as to the explanation of its operation, my present understanding is that the electrolytic process may have two actions, that is, a primary and a secondary action. The primary action may comprise an exchange of electrons closely adjacent the anode, while the secondary action appears to involve an interaction between the ions of the electrolyte and the ions or charged particles of the ore. These actions may produce two separate compounds, a chromate on the one hand and an iron hydroxide on the other. The chromate being soluble in an alkaline electrolyte is held in solution in the electrolyte while the iron hydroxide which is insoluble in such electrolytes forms a precipitate.

The chromates formed in or passing into the electrolyte may be converted into chromium trioxide by any one of several well known commercial methods which in turn can be converted into substantially pure metallic chromium by any suitable method, such as the method disclosed in my U. S. Patent No. 2,063,760. The insoluble iron compounds and other impurities may be removed by settling or filtration.

The anode used in the present process preferably should be insoluble in the electrolyte and the electrolytic action of the process. Such materials as platinum and graphite suitably may be used for this purpose.

Since the halates usually include alkaline impurities, an aqueous solution of the salt in the electrolyte will usually be slightly alkaline. The alkalinity may be increased or at least maintained substantially uniform during the process by adding sodium hydroxide or other alkaline agents.

To further theorize, it is believed that the electrolyte during electrolysis becomes acid in the vicinity of the anode and remains alkaline in the vicinity of the cathode. The ore in the vicinity of the anode therefore is believed to be attacked by an acid medium even though the electrolyte as a body will test alkaline. During prolonged processing the alkalinity of the electrolyte weakens, the ore giving off acid radicals which neutralize some of the hydroxide ions. To maintain the

electrolyte as a whole at a substantially uniform alkalinity, I find it desirable to add an alkaline agent, such as sodium hydroxide, to neutralize the acid radicals picked up from the ore. These additions of sodium hydroxide maintain the electrolyte preponderantly alkaline so that the iron in the ore will precipitate when it is converted into compounds such as ferric hydroxide.

For purposes of illustration, one embodiment of the invention comprises the use of an insoluble anode of high oxygen over-voltage, such as platinum, an electrolyte consisting in the proportions of 550 grams of sodium chlorate, 5 grams of sodium hydroxide and 1 liter of water. The chromite ore is crushed to about 20 to 40 mesh and placed in the electrolyte and on or adjacent to the anode. The term "adjacent the anode" is used herein to mean that portion of the cell which is closer to the anode than it is to the cathode, i. e., the anolyte portion of the cell. The ore adjacent the anode actually may be in contact with the anode or may be spaced therefrom, or portions of the ore body may be in contact with and portions spaced from the anode. A current of electricity is then passed between the anode and the electrolyte at about two amperes per square inch of the submerged anode with the electrolyte at a temperature of about 45° C. The conversion of the chromite ore to soluble chromium compounds and insoluble iron compounds results according to this embodiment at the rate of 10.2 ampere hours per gram of chromium. It will be understood, of course, that this result can be varied considerably by varying the current density and the temperature and ingredients of the electrolyte.

Another embodiment of the invention using a bromate salt in aqueous solution comprises an electrolyte in the proportions of 350 grams of sodium bromate, 3.50 grams of sodium hydroxide and 1 liter of water. Chromite ore is crushed to about 100 mesh and placed in the electrolyte on or adjacent a platinum or other suitable anode. With a current density of 1 ampere per square inch of submerged anode and the electrolyte at a temperature of about 70° C. the conversion of the chromite to soluble chromium compounds and insoluble iron compounds takes place at the rate of about 2.56 ampere hours per gram of chromium.

To illustrate the effect of different temperatures on the process, the above described embodiment was run at a temperature of about 40° C. with the same current density and the conversion of the ore was found to take place at the rate of approximately 5.54 ampere hours per gram of chromium. These and additional runs taken at different temperatures showed that the current consumption per gram of chromium varied considerably. The higher temperatures require less current and are therefore preferred, the selection of operating temperature, depending, however, on other conditions such as the ingredients of the electrolyte.

The degree of concentration of the halate also varies the results of the process, the other variables remaining the same. The nearer to saturation the halates are used, the better the results. This can be illustrated with a run using sodium chlorate at a lower concentration and at a higher temperature than used in the first embodiment described above. Taking, for example, a solution consisting of 300 grams of sodium chlorate and 3.5 grams of sodium hydroxide per liter of water at 70° C., a current density of 2 amperes per

square inch of submerged anode gave a conversion of chromite crushed to 100 mesh at the rate of about 10.0 ampere hours per gram of chromium. Thus by decreasing the concentration of the halate and increasing the temperature, substantially the same results were obtained.

From the foregoing, it will be clear that I have discovered a new process for economically producing from chromium ore, particularly chromite, chromium compounds from which substantially pure chromium can be easily obtained by known commercial processes. I am aware that the process herein disclosed is capable of modification for example, as to the contents and concentrations of the electrolyte, that a wide selection of temperatures may be made and that the density of the current applied may be considerably varied as well as the anode material without departing from the spirit of this invention. It is to be understood, therefore, that the embodiments of the process disclosed are to be regarded as illustrative of the invention only and not in restriction thereof.

I claim:

1. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell having an aqueous alkaline solution of an alkali metal halate and passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in the solution and non-chromium compounds which are insoluble in the solution.
2. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of sodium chlorate, and passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in the solution and non-chromium compounds which are insoluble in the solution.
3. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution containing a relatively strong concentration of sodium chlorate, and passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in the solution and non-chromium compounds which are insoluble in the solution.
4. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of an alkali metal halate, and passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in alkaline solution and non-chromium compounds which are insoluble in alkaline solution, and maintaining the catholyte portion of the solution sufficiently alkaline during the treatment to prevent the solution of the non-chromium compounds.
5. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of sodium

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chlorate, passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in the alkaline solution and non-chromium compounds which are insoluble in the alkaline solution, and adding the alkaline agent to the solution during the treatment to maintain the catholyte portion of the solution alkaline.

6. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous solution of an alkali metal halate and sodium hydroxide, passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in alkaline solution and non-chromium compounds which are insoluble in alkaline solution, and adding sodium hydroxide to the solution during the treatment to maintain the catholyte portion of the solution alkaline.

7. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of sodium bromate, and passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in the solution and non-chromium compounds which are insoluble in the solution.

8. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of an alkali metal bromate, passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in alkaline solution and non-chromium compounds which are insoluble in alkaline solution, and adding sufficient alkaline agent to the solution during the treatment to maintain the catholyte portion of the solution alkaline.

9. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of an alkali metal halate, said anode being composed of a material of relatively high oxygen over-voltage, and passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in the solution and non-chromium compounds which are insoluble in the solution.

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10. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of an alkali metal chlorate, and passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in the solution and non-chromium compounds which are insoluble in the solution.

11. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in finely divided form adjacent the anode of an electrolytic cell having therein an alkaline aqueous solution of an alkali metal halate in the concentration of between about 100 grams and saturation, said anode being insoluble in the solution during the treatment and being composed of material of relatively high oxygen overvoltage, passing a direct current of electricity through the cell to oxidize the ore adjacent the anode into chromium compounds which are soluble in alkaline solution and non-chromium compounds which are insoluble in alkaline solution, and adding an alkaline agent to the solution during the treatment to maintain the catholyte portion of the solution alkaline.

12. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in a finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of an alkali metal halate, and passing a direct current of electricity through the cell to transform the ore adjacent the anode into chromium compounds which are soluble in the solution and non-chromium compounds which are insoluble in the solution, said treatment of the ore causing the release of acid radicals adjacent the anode, and adding an alkaline substance to said solution during the said treatment to neutralize said acid radicals.

13. A method of treating chromite ore to facilitate the recovery of chromium therefrom which comprises placing the ore in a finely divided form adjacent the anode of an electrolytic cell containing an aqueous alkaline solution of an alkali metal halate, and passing a direct current of electricity through the cell to convert the halate to a strongly oxidized state and to transform the ore adjacent the anode into chromium compounds which are soluble in the solution and non-chromium compounds which are insoluble in the solution.

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