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MANUFACTURE OF CHROMIC ACID

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The invention is a process for the manufacture of chromic acid from ferrichrome. The chromic acid is useful in the electrodeposition of chromium metal and for other purposes, the ultimate use of the chromic acid being no part of the present invention.

In the process to be described the ferrochrome is dissolved electrolytically by connecting it as anode in a sulphuric acid electrolyte. The cell used for this purpose is equipped with a porous diaphragm designed to keep the bulk of the chromium compounds in the vicinity of the anode and in the hexavalent state. Portions of the anolyte are removed, either continuously or periodically, and worked for the recovery of chromic acid. The mother-liquor is preferably treated further for the removal of iron compounds in order that the sulphuric acid content of the anolyte, or more accurately that part of the sulphuric acid which has not combined with iron, may be restored to the process.

Sulphuric acid, part of which may be that recovered in the manner just referred to, is fed to the cathode compartment of the cell in such a way as to keep conditions in the cell reasonably constant. Because of the elevated temperature of the electrolyte, water will evaporate from both compartments. The operation of the cell results in the transfer of sulphur acid from the cathode compartment to the anode compartment but the evaporation of water from the catholyte tends to prevent the concentration of sulphuric acid in the catholyte from being diminished. The concentration of acid and metal compounds, in the anolyte tends to increase continuously.

The cathode is preferably lead. The diaphragm may be made from any porous, acid-proof material structurally adapted for the purpose, diaphragms composed of filtros or alundum having been used with good results. The ferrochrome may contain any proportion of chromium but a high content is preferred. An alloy produced by reducing a high grade ore with carbon in the electric furnace gives good results.

The recovery of chromic acid from the anolyte is conveniently accomplished by crystallization, with such concentration by evaporation as is necessary to make possible the recovery of the desired proportion of the chromium compound. A high concentration of sulphuric acid greatly facilitates the crystallization of chromic acid, and this may of course be obtained by suitable evaporation. To minimize the evaporation required, a high concentration of sulphuric acid is preferably maintained in the anolyte, though the process is operable with much less than the preferred concentration of sulphuric acid in the anolyte. The concentration of dissolved material in the anolyte should of course not be permitted to increase to the point where solid compounds begin to crystallize in the cell.

The iron can be removed from the anolyte by crystallization, best after the bulk of the chromic acid has been crystallized and removed. Thus 70% or more of the CrO_3 can be recovered in a single crystallization, and 90% or more can be recovered in two crystallizations with intervening concentration by evaporation. A recrystallization for the removal of iron will remove 85% to 90% of that present. It will be apparent that the sulphuric acid can be sufficiently separated from the metallic compounds to permit the return of the acid to the process by introducing it into the cathode compartment of the cell from which it was taken or into another similar arranged and operating cell.

I prefer to regulate the additions to the catholyte in such a way that the density of the catholyte will remain approximately 10° Bé; and I preferably withdraw anolyte having a density of about 40° Bé. to 45° Bé. Proper concentrations can be maintained in the two compartments by appropriate additions of strong or dilute sulphuric acid, mother-liquor, or water. The process as a whole produces chromic acid and ferric sulphate and consumes ferrochrome anodes, sulphuric acid equivalent to the ferric sulphate produced, and the water which is evaporated for purposes of concentration and in the cell.

By way of illustration it may be remarked that suitable conditions include an electrolyte temperature of about 85° C., a current density of about 100 amperes per square foot, and a potential of about 4.3 volts. Un-

der these conditions the anode efficiently (by which is meant the quotient of the total chromium dissolved by the electrochemical equivalent of the current passed) may be as high as 100% when ferrochrome anodes containing about 68% of chromium are used.

Throughout the process a small quantity of chromium tends to be reduced to the trivalent state. This occurs during evaporation and also in the cathode compartment because of the fact that the mother-liquor introduced into the cathode compartment still contains some chromium. The reducing chromium can be kept below any chosen maximum by using auxiliary cells with lead or other insoluble anodes to reoxidize it to the hexavalent state. Trivalent chromium is preferably eliminated as far as possible before crystallization as it interferes with the recory of the chromic acid.

I claim:

1. Process of manufacturing chromic acid which comprises electrolytically dissolving chromium from a ferrochrome anode in the anode compartment of a diaphragm cell with an anolyte strongly acid with sulphuric acid and substantially free from alkali metal and alkaline earth metal compounds; and recovering chromic acid from the anolyte.

2. Process of manufacturing chromic acid which comprises electrolytically dissolving chromium from a ferrochrome anode in the anode compartment of a diaphragm cell with an anolyte strongly acid with sulphuric acid, and recovering chromic acid from the anolyte.

3. Process of manufacturing chromic acid which comprises a electrolytically dissolving chromium from a ferrochrome anode in the anode compartment of a diaphragm cell containing sulphuric acid electrolyte; drawing off anolyte at a density of 40° Bé. to 45° Bé.; and crystallizing chromic acid therefrom.

In testimony whereof, I affix my signature.

MARVIN J. UDY.