METHOD FOR DISSOLUTION OF CHROMIUM FROM CHROMITE ORES

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This invention relates to a method for the dissolution of chromium bearing ores, and particularly relates to the dissolution of ores of the chromite series, chromium spinel ores, and similar difficulty soluble chrome ores. Still more particularly the invention relates to a method for the dissolution of such chromium ores using the spent anolyte from a process for the electrowinning of chromium.

Chromium ores such as those of the chromite series (Dana's "The System of Mineralogy," 7th edition, vol. I, page 709), spinel series (page 689 of the aforementioned reference) and like ores can be dissolved only with great difficulty. It has been found possible to digest such ores in concentrated sulfuric acid (i.e., greater than 65% by weight H₂SO₄), and it is also necessary to employ strong oxidizing agents such as hexavalent chromium compounds, lead peroxide, manganese dioxide or the like in order to effect complete dissolution of the chromium values thereof. Whenever a solution containing ammonium ions is employed for dissolving the chrome ore, as in the case where the spent anolyte from processes for the electrowinning of chromium is so used, a highly insoluble iron ammonium complex, probably a ferric ammonium complex, is formed during the digestion. This complex appears to contain or occlude a considerable portion of chromium and also causes chromium losses due to its tendency to form on and coat the ore particles, thereby preventing dissolution.

Accordingly, it is an object of this invention to provide a simple and economical method for the dissolution of certain difficulty soluble chromium ores.

It is another object of the invention to provide a method for the dissolution of chromite ores when the solution contains ammonium ions, without concurrently forming insoluble metallic ammonium complexes.

Other objects and advantages will be apparent or will appear hereinafter.

These objects and advantages are accomplished in accordance with this invention wherein the chromite ore is digested in a solvent comprising a dilute sulfuric acid solution containing an oxidizing agent at superatmospheric pressures.

Suitable chrome ores for treatment in accordance with this invention include those of the aforementioned chromite series such as magnetitechromite, chromite, and the like; those of the spinel series such as chromium spinel, chro-
if necessary, sufficient chromic acid is added to bring the total chromic acid to about 2 to 7 per cent of the weight of the total sulfuric acid concentration. Batches of low grade chromic concentrates are wet ground to about minus 270 mesh and dried in any suitable manner. The ore is digested in batches using a stoichiometric quantity of the fortified anolyte. Such digestion has been carried out conveniently in a stainless steel lined reactor capable of withstanding pressures as great as 100 p. s. i. The temperature during digestion is maintained at between about 130 to 150 degrees centigrade, and this control was achieved by maintaining the pressure in the digester at about 40 p. s. i. gage; as has been mentioned before the reaction is exothermic, therefore, it is unnecessary to have an external heat supply. At the completion of the digestion period, or when the heat of reaction is insufficient to maintain the elevated temperature and pressure within the digestor, the raw digest liquor is removed as a normal metal sulfate solution and containing practically no excess sulfate radical.

The raw digest liquor contains various ionic constituents in addition to the chromium and sulfate; e.g., iron, aluminum, etc. The term normal metal sulfate solution is used to indicate that the amount of sulfate present is that stoichiometrically necessary to form normal sulfates of the various metals present in the raw digest liquor.

When it is desired to recrystallize this regenerated solution through the electrolytic cells, it is necessary to purify the raw digest liquor. This can be accomplished by diluting the raw digest liquor with spent mother liquor obtained in a subsequent crystallization process described hereafter to produce a solution containing about 42 grams of chromium (calculated as elemental chromium) and 150 grams of ammonium sulfate per liter, appreciable quantities of iron, aluminum, magnesium, and sodium, and small quantities of several other metals. This diluted solution is filtered at 65 degrees centigrade to remove silicious gangue and heated to 80 degrees centigrade for one hour. The liquor is sent immediately to a vacuum crystallizer, where all of the aluminum and most of the iron and magnesium are removed at 4 degrees centigrade. These ammonium sulfate complex crystals contain most of the leached impurities. Chromium remains in solution because of the above-mentioned prolonged heat treatment. These "impurity" crystals are removed in a rubber-lined basket centrifuge, and the purified mother liquor is clarified in a wooden filter press and sent to aging.

Aging takes place in a Koroseal-lined thickener at 30 degrees centigrade. Chromium reverts from the green to the violet modification and crystallizes as chromium ammonium sulfate containing some ferric iron and small quantities of many other impurities. The chrome alum is removed by centrifuging; and the spent mother liquor containing about 22 grams chromium (calculated as elemental chromium) per liter, can be used to dilute the raw digest liquor as aforementioned.

One more crystallization of the chrome alum in a thickener at 30 degrees centigrade, using spent catholyte from the electrowinning cells as recrystallizing liquor, reduces iron and other impurities below the critical concentrations. The iron in the crude alum is reduced to the ferrous state by the divalent chromium in the spent catholyte and does not recrystallize with the chromium. The pure chrome alum is mixed with glubers salts, recovered from the impurity alums, and dissolved to produce cell feed containing 85 grams of chromium (calculated as elemental chromium), 115 grams of ammonium sulfate, and 60 grams of sodium sulfate per liter.

The following process may be carried out, but the invention is not limited thereto.

Example I

A sample of 500 grams of chrome ore was charged into a jacketed stainless steel autoclave and a solution was added which contained 1,250 grams of sulfuric acid, 2,326 grams of water, 45 grams of hexavalent chromium, and 34 grams of ammonia as ammonium sulfate. The chrome was digested in this 35 per cent acid for 6 1/2 hours at 80 pounds pressure and 165-175 degrees centigrade. At the end of this period 33 per cent of the chromium in the ore was rendered water soluble and no dehydrated alum was produced. When this process was repeated, using a 65 per cent sulfuric acid solution, a large quantity of insoluble alum was produced which contained substantially all of the chromium.

Example II

A brick-lined digestor was constructed with a pressure cover but without any means of applying external heat. This digestor was charged with 450 pounds of chrome ground to 98 per cent minus 325 mesh along with a solution containing 39.5 pounds of hexavalent chromium, 12.5 pounds of ammonia as ammonium sulfate and 210 pounds of sulfuric acid. The digestor was heated and an additional 960 pounds of acid was pumped in, making a 45 per cent sulfuric acid solution. The temperature began to rise and at the end of 30 minutes was 145 degrees centigrade, and the pressure was 38 pounds gage. Steam, and some inert gas, was bled off gradually to keep the temperature at 130 to 145 degrees centigrade. After 10 hours, the temperature dropped to 100 degrees centigrade, the digestor was opened and the solution tested. Analysis showed that 23 pounds of acid remained and 99 per cent of the chromium in the ore was water soluble. No dehydrated alums were present.

From the foregoing description and examples it is apparent that a simple process for the dissolution of chromite in the spent anolyte from electrolytic cells for the electrowinning of chromium has been developed.

While the invention has been particularly described for the digestion of chrome ores, it is not limited thereto; other chrome ores exhibiting solubility characteristics in sulfuric acid can also be dissolved by this process.

While the invention has been particularly described as employing hexavalent chromium as the oxidizing agent, it is not limited thereto and other oxidizing agents can be substituted therefor.

Since many widely differing embodiments of the invention will occur to one skilled in the art, the invention is not limited to the specific details illustrated and described, and various changes can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A method for the dissolution of chrome ores in a solution containing ammonium ions
without the formation of chrome ammonium alum which comprises dissolving said ores in a solution containing ammonium sulfate, chromic acid, and 30 to 50 per cent sulfuric acid by weight, said solution having a temperature within the range of 165° C. to 125° C., the temperature decreasing with the increase in percentage of sulfuric acid.

2. In a process for the electrowinning of chromium from an electrolyte which contains trivalent chromium in the presence of sulfate ion and ammonium ion, the improvement which comprises regenerating the chromium concentration of the spent electrolyte which contains chromic ion, ammonium ion and sulfate ion by increasing the sulfuric acid concentration to from 30 to 50 per cent by weight, and dissolving chrome ore in the thus formed solution at a temperature within the range of 165° C. to 125° C., the temperature decreasing with the increase in percentage of sulfuric acid.

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