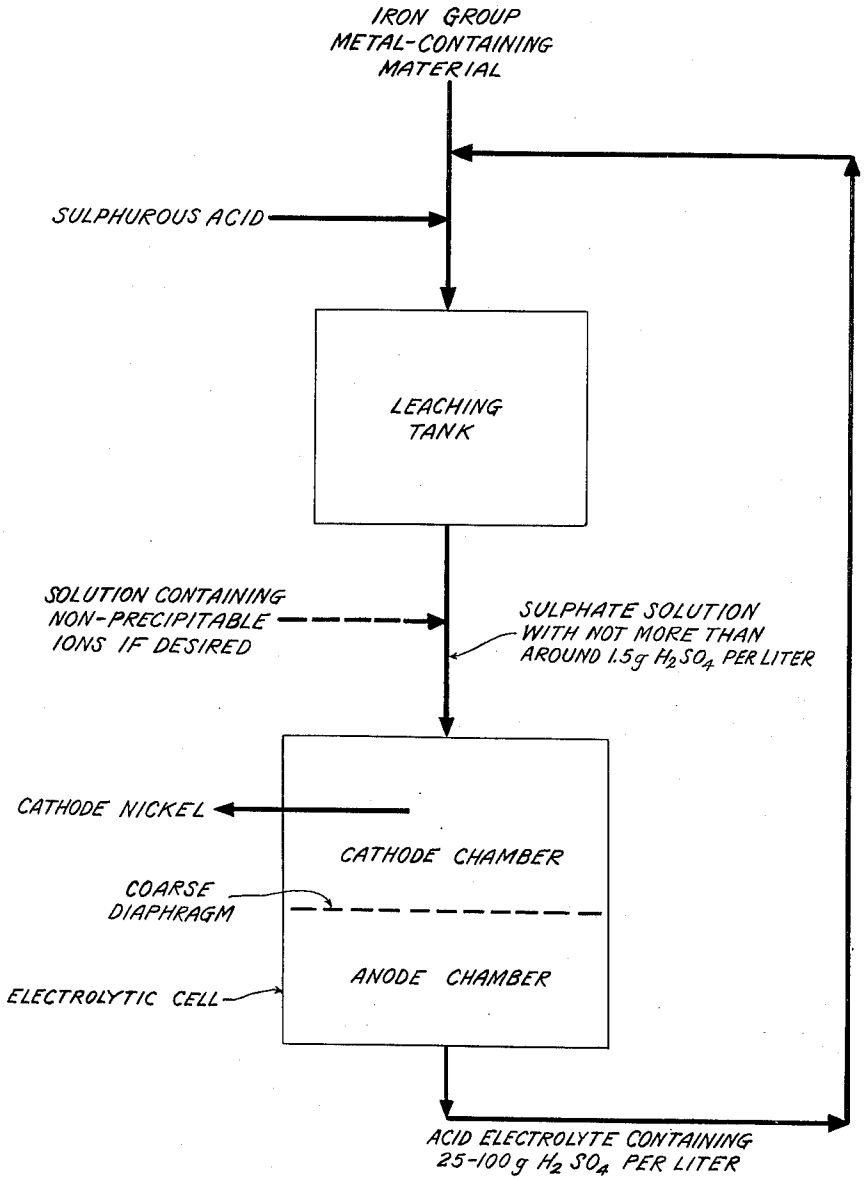
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METHOD OF ELECTROLYTICALLY RECOVERING NICKEL

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METHOD OF ELECTROLYTICALLY RECOVERING NICKEL

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1

The present invention relates to a method for recovering the metals of the iron group particularly nickel and cobalt or salts of these metals from materials containing said metals, by leaching with acid solutions and electrolysis of said solutions. The leaching is preferably performed by using sulphurous acid solutions and the electrolysis is carried out under such conditions that the anolyte may be used for leaching said material containing said metals.

The leaching method or the electrolytic method may of course be used in any suitable or known metal recovering process without using the other method.

A great number of methods for recovering especially nickel by means of electrolysis in a cell with insoluble anode has hitherto been proposed but never obtained any greater technical importance due to the fact that the solution adjacent to the cathode must be substantially neutral. On account hereof neutralizing agents such as nickel hydrate must be added during the electrolysis if a diaphragm cell be not used. On the other hand an employment of an ordinary diaphragm cell with a compact diaphragm involves the usual difficulties in filling up the pores of the diaphragm. According to this invention a comparatively coarse porous diaphragm is used which readily can be cleaned in case that the pores would be filled up. As great an obstacle for the technical use of the electrolytic process with insoluble anode has been the great difficulties to dissolve the metal by means of the slightly acid electrolytes from basic materials of average content or metallurgical intermediate products. Thus it has for instance been necessary to leach the basic material with strong acids and precipitate metal hydrate from the solution by neutralizing agents and use metal hydrate as neutralizing agents for the exit electrolyte. According to our invention we obtain in the electrolysis a comparatively strong acid exit electrolyte which after sulphurous anhydride being added to it is an excellent solvent for metal in the basic material. Thus a rational leaching and electrolytic process is possible in which the consumption of chemical agents is very low. Necessary sulphurous anhydride may usually be available in the form of fluegas containing sulphurous anhydride. The combined leaching and electrolytic process according

2

to the invention give over the processes in which the electrolysis is performed with a soluble anode consisting in raw metal among others the great advantage that any impurities do not enter the electrolytic cell whereby an unlimitedly pure metal may be produced.

The leaching according to the invention is substantially characterized in that materials containing metallic nickel and/or cobalt are leached with a solution of sulphurous acid or a solution containing sulphurous acid, for instance in such a manner that sulphurous anhydride is allowed to bubble through the leaching liquor. The metal is dissolved considerably more rapidly and more completely in sulphurous anhydride containing solutions than in for instance sulphuric acid, which involves an essentially increased production by the leaching apparatus. Thus it is possible to obtain leaching yields which cannot be attained in a reasonable time in leaching with other liquors. A suitable basic material for the production of nickel is e. g. nickel copper sponge, produced from nickel copper concentration matte. On account of the reducing effect of the sulphurous anhydride oxidation and dissolving of copper from the sponge are prevented. As leaching liquor in the production of nickel one ordinarily uses the exit electrolyte from the subsequent nickel electrolysis, containing for instance 25 grams sulphuric acid per liter. To said electrolyte is added as great an amount of sulphurous anhydride as is necessary to make up the loss of acid in the process. Nickel sulphite and excess of sulphurous anhydride are oxidized by air into sulphate and sulphuric acid.

The invention is not limited to the leaching of reduced metal sponge, but comprises leaching nickel and cobalt containing products generally by the addition of sulphurous anhydride.

Thus nickel may be recovered directly from nickel copper concentration matte of low sulphur content (ratio Cu:S about 4:1) by means of leaching with a sulphurous acid solution. A great part (about 70%) of the nickel content of the matte—not completely corresponding to the nickel which is present in metallic form—is leached comparatively rapidly. The leaching then takes place essentially slower. If the concentration matte converting is controlled so that all the nickel may be considered to be present in

metallic form the yield during the first rapid leaching step may be increased in a corresponding degree. In this case, however, the amount of nickel which is scorified in the concentration matte converting and which must be returned to the matte furnace will be considerable. The leaching is facilitated if the concentration matte is present in granulated form.

Dissolving pure metallic nickel and cobalt or leaching other products containing said metals is also advantageously carried out by means of solutions containing sulphurous acid.

The electrolysis according to the invention is carried out by means of an insoluble anode in a diaphragm cell. The electrolyte is introduced into the cathode chamber as a neutral or slightly acid salt solution for instance a sulphate solution and is allowed to flow through the diaphragm into the anode chamber at such a velocity that the catholyte remains slightly acid and the anolyte so highly acid that it may be used for leaching purposes. The acid liquor is purified after the leaching and returned to the cathode chamber.

An insoluble anode is used for the electrolysis of a solution, which, by a separate operation, has been completely freed from impurities. As the catholyte and the anolyte both are pure a cathode metal of unlimited degree of purity can be produced independent of the velocity of flow being correctly controlled or of possibly occurring damages of the diaphragm. If the velocity of flow is too low or if the diaphragm is damaged the development of hydrogen gas will increase and the defect may be easily observed and repaired. Even under such abnormal conditions a good cathode metal is obtained but the current yield is not optimal. In case of too high a velocity of flow the acid content of the anolyte will decrease so that metalliferous material cannot be satisfactorily leached by the exit electrolyte and if no special steps be taken, the catholyte may be neutral, whereby basic salts deposit on the cathode. If a moderate average current yield will satisfy, the velocity of flow may be allowed to vary in a comparatively wide range. As no precipitations or solids occur in the electrolyte the permeability of the diaphragm will be constant, and therefore the velocity of flow may be easily controlled by arranging the level of the liquid in the cathode chamber somewhat higher than that in the anode chamber. The cheapest acid for the process is normally sulphuric acid. In the electrolysis of for instance a pure nickel sulphate solution containing 50 grams nickel per liter at a temperature of 60° C. the content of acid in the cathode chamber is maintained at 0.5 to 1.5 grams per liter, whereby the content of acid in the anode chamber will amount to 25 to 100 grams per liter depending on the quality of the diaphragm. Thus the current yield will range from 70% to 90%. If a salt solution, containing nonprecipitable metal ions, preferably alkaline ions, is added to a nickel sulphate solution the pH of the catholyte may be allowed to rise above 6 without any risk for basic precipitations in the bordering layer at the cathode surface. With such an admixture the admitted range of acidity will increase, and the control of the velocity of flow will be facilitated. Besides, it will be possible to essentially increase the average current yield. At a pH about 6 a current yield of 95%–100% will be obtained. Sodium or ammonium sulphates are suitable alkaline salts. Also salts of magnesium and aluminium may be used.

In the electrolysis of a pure cobalt sulphate solution one may allow the pH to rise very much, for instance to pH 6 without running any risk of basic precipitations in the bordering layer of the cathode. The current yield may easily be raised to 95%–100%.

The most suitable material for the diaphragm is nitrated fabric of cellulose fibre, for instance cotton, cellulose or staple fibre. Fabric of silicate fibre, for instance glass wool fabric or stone wool fabric may also be used. The diaphragm may consist also of ceramic plates.

According to the present invention the exit anolyte may contain a sufficiently great amount of acid, as to admit of a rational leaching process such as leaching metal sponge in counter current or leaching other soluble forms of metals or metal compounds.

Primarily the electrolysis according to the invention relates to the recovery of the metals of the iron group from their ores, but, of course, it may be applied also in the recovery of other basic materials and in surface treatment in an electrolytic way.

As mentioned above and as will appear from the detailed description above of the leaching and electrolytic processes said processes may be used in combination with each other constituting a complete metal recovering process. The scope of the invention is, however, not limited to this combination but the improved leaching and the electrolytic methods may also be used separately or combined with any known or suitable method or methods for recovering metals or metal salts.

Having thus described our invention we declare that what we claim is:

1. A method of recovering nickel from materials containing said nickel in its metallic state that comprises leaching said materials with a leaching liquor containing sulphuric acid and sulphurous anhydride, electrolyzing the resulting nickel-containing leaching liquor by passing it into the cathode chamber of an electrolytic cell in the form of a sulphate solution containing no more than about 1.5 grams of sulphuric acid per liter, the electrolytic cell containing an insoluble anode and a coarse, porous diaphragm that will permit the flow of electrolyte between the cathode and anode compartments, causing the leaching liquor to flow from the cathode to the anode compartment of the cell at a velocity such as will maintain the liquor in the cathode compartment at not more than around 1.5 grams of sulphuric acid per liter but will raise the acidity of the leaching liquor in the anode compartment to around 25 to 100 grams of sulphuric acid per liter, withdrawing leaching liquor from the anode compartment and returning it to the leaching step of the process.

2. A method as defined in claim 1 further characterized in that the material to be leached is a nickel concentration matte having a low sulphur content.

3. A method as defined in claim 1 further characterized in that the material to be leached is a nickel concentration matte containing about four times as much copper as sulphur.

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