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SEPARATE RECOVERY OF NICKEL AND COBALT FROM MIXED COMPOUNDS CONTAINING THE SAME

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This invention relates to the separate recovery of the nickel content and the cobalt content from ores or concentrates and from any other compounds or compositions containing such metals. More particularly the invention involves a process for the separation of ions of such metals by a liquid-liquid extraction procedure in which salts of the two metals are separated and recovered in concentrated form from the resulting solutions.

Because of the very similar chemical and physical properties of nickel and cobalt and their compounds their complete separation is a problem well known in industry. Potential commercial processes for the separation are generally cumbersome and moreover none of such processes can effect a complete simultaneous separation of the two metals or their ions. In these prior methods one of the metals can be separated in purified form but the other will contain some of the first metal as an impurity.

It has heretofore been experimentally determined that the nickel and cobalt in nickel and cobalt chloride mixtures could be separated by addition of ammonium thiocyanate to an aqueous solution of the same to form a complex with the cobalt followed by extracting this cobalt complex from the resulting aqueous solution through treatment with any one of a number of water-immiscible organic solvents for said cobalt complex. This process is not suitable for or adapted to commercial operation for several reasons, including the fact that it does not recover the metal contents in the form of useful compounds and does not utilize the reagents in an economically feasible way. Furthermore the chloride-thiocyanate solution formed is corrosive.

An object of the present invention is to provide a process for the separate recovery of nickel and cobalt from mixtures of the same, which effects complete separation of the metals in an economically successful way in which the reagent consumption is small and the metals may be recovered in the form of useful compounds from substantially non-corrosive solutions.

Broadly, the invention may be considered as involving the preparation of an aqueous solution of the nickel and cobalt content of the mixed composition containing the same in the form of their thiocyanates which solution also contains calcium thiocyanate, and extracting the cobalt thiocyanate compound or complex from said aqueous solution by taking up the same in methyl isobutyl ketone or other water immiscible organic solvent for said cobalt compound. Thereupon the nickel and cobalt are recovered from the respective solutions and the thiocyanate ions converted to calcium thiocyanate. This calcium thiocyanate is recycled in the process.

The invention is particularly applicable to the separate recovery of nickel and cobalt from ore concentrates obtained from lateritic ores containing such metals. In such concentrates the amount of nickel greatly exceeds the amount of cobalt and frequently the ratio is about 10 to 1. The invention, however, is also applicable to nickel and cobalt mixtures from any source including crude salts and concentrated solutions obtained in the

recovery of nickel from scrap, and from sulfide ores such as those mined in Cobalt, Ontario.

In the treatment of ores, the nickel and cobalt may be extracted therefrom by either sulfuric acid leaching or ammonia leaching. If the latter procedure is employed, the nickel and cobalt are solubilized by the formation of an ammonium complex or complexes which are subsequently precipitated in the form of insoluble basic nickel and basic cobalt carbonates. When the free lime and magnesia content of the ores is high, ammonia leaching is preferred over sulfuric acid leaching. On the other hand, when the free lime and magnesia content is sufficiently low such that these materials do not consume large quantities of sulfuric acids, then sulfuric acid leaching is preferred. In this leaching operation the nickel and cobalt are, of course, solubilized in the form of their sulfates, and other metals in such ores such as aluminum and iron can be separated from the nickel and cobalt by known controlled precipitation techniques not constituting part of the present invention.

To prepare the thiocyanate solution of the nickel and cobalt content the raw material, if not already in the form of the required water-soluble salts, is treated with sulfuric acid or other acid, the calcium salt of which is substantially water-insoluble. If the nickel-cobalt concentrate has been obtained by sulfuric acid leaching, the composition containing the nickel and cobalt in the form of their sulfates is contacted and reacted with an excess of calcium thiocyanate solution which after the process is once started, includes the calcium thiocyanate later recovered in the process. In this reaction with calcium thiocyanate, gypsum is precipitated which upon filtration, leaves the nickel and cobalt in solution in the form of their thiocyanates in a solution substantially free of other anions. If the nickel-cobalt mixture has been obtained, instead, by ammonia leaching, then nickel and cobalt carbonates are formed therefrom and are converted to soluble thiocyanates by treatment with the calcium thiocyanate thereby forming calcium carbonate as a precipitate which on removal leaves the nickel and cobalt in the form of their thiocyanates in a solution substantially free of other anions.

In the production of aqueous solutions containing nickel and cobalt thiocyanates from the sulfates or carbonates, the amount of calcium thiocyanate added is in excess of that required to convert the nickel and cobalt content, for the free thiocyanate assists in the extraction efficiency of the step to follow. Five to seven mols of thiocyanate per mol of cobalt in excess of that necessary to convert all the nickel and cobalt to the simple $Ni(CNS)_2$ and $Co(CNS)_2$ salts gives, under most conditions, substantially complete separation of the cobalt in the extraction process. Experimentation indicates that the molar excess need never be more than about twelve. Excesses greater than this are operable but they merely increase the volume which must be handled and increase the losses of this reagent. On the other hand, if the excess is less than about five mols, then the extraction requires a greater number of theoretical stages in the extraction column and a greater volume of organic solvent must be circulated.

An alternative method for preparing the aqueous solution of nickel, cobalt and calcium thiocyanate involves the use of carbon dioxide instead of sulfuric acid. In this method the mixed nickel and cobalt compounds in the form of their hydroxides are slurried with an excess of calcium thiocyanate solution, and then carbon dioxide is introduced into the slurry in gaseous form. By this action, the nickel and cobalt are converted into their thiocyanates which are soluble and calcium carbonate is precipitated. The calcium carbonate is filtered from