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PROCESS FOR SEPARATING NICKEL CONTAINED IN SOLUTIONS OF MIXED COBALT AND NICKEL SALTS

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The present invention involves a process for separating nickel from cobalt contained in a solution of mixed salts of cobalt and nickel which consists essentially in separating the nickel by using, jointly with a metal more electronegative than nickel, iron for example, a metalloid compound formed from two or more of the following elements: sulphur, selenium, tellurium, antimony and arsenic. A second step of the process involves redissolving the separated nickel and then purifying the resulting nickel solution to ultimately obtain the nickel in a commercial metallic form.

The present invention is specifically directed to an economical process of separating nickel from cobalt and ultimately obtaining a cobalt salt solution substantially free from nickel, and a nickel salt solution substantially free from cobalt. These solutions may be electrolyzed to obtain the corresponding metals.

It is well known that a metal may be displaced from solutions containing it by another metal having a greater electromotive force than the metal in solution. The metal which performs the displacement of the metal from the solution is more electronegative than the metal in solution.

It is also known that displacement of a metal from a solution containing it may be promoted by the presence of another metal which has a lower electromotive force than the metal to be displaced from the solution. This metal having a lower electromotive force is more electropositive than the metal in solution. For example, in U.S. Patent No. 2,509,918 various impurities such as cobalt, nickel, cadmium and antimony are eliminated from a concentrated solution of zinc sulphate by precipitating the impurities with zinc powder mixed with small quantities of copper, arsenic and silver.

It is also well known, as evidenced by U.S. Patent No. 2,671,712, that the separation of nickel from a solution containing salts of cobalt and nickel can be promoted by adding various elements such as sulphur, arsenic antimony, selenium and tellurium. However, this patent does not recognize that compounds of sulphur, arsenic, antimony, selenium and tellurium are more active in promoting the separation of the nickel than the elements are when individually used.

It is also well known, as evidenced by U.S. Patent No. 2,829,965, that sulpharsenide and arsenide ores of cobalt and nickel are effective in promoting the separation of nickel from a solution containing salts of cobalt and nickel. However, this patent does not recognize that metalloid compounds consisting solely of sulphur, arsenic, antimony, selenium and tellurium are also active in promoting the separation of the nickel. The metalloid compounds of the present invention contain only metalloidic elements while the compounds of the last mentioned patent contains a metal in combination with metalloidic elements.

It is an extremely difficult problem to separate nickel from a nickel-cobalt solution when the nickel is contained therein in very small quantities in proportion to the cobalt. This difficulty is due particularly to the fact that electromotive force of cobalt and nickel are very close to each other in the electromotive force series: —0.24 for nickel, and —0.277 for cobalt (Latimer scale). We have discovered that some metalloid compounds such as arsenic and antimony sulphides, together with a metal more electronegative than nickel, for example iron, are particularly advantageous in promoting the selective separation of nickel from nickel-cobalt solutions. Normally, copper is also added to the solution to aid in the separation. The metalloid compound to be employed in the present invention consists of a compound formed entirely from two or more of the following metalloid elements: sulphur, selenium, tellurium, antimony and arsenic. These metalloid compounds are available in the natural state or may be chemically prepared. Examples of natural metalloid compounds are the realgars, orpiments and stibnites. These and other metalloid compounds may also be obtained by chemical synthesis thereof.

The metalloid compounds have a very noteworthy power for promoting the separation of nickel from a mixed nickel-cobalt salt solution which appears to be directly correlated to the molecular composition of the compounds. For example, a mere mixture of the constituents of the compounds, even in proportions equal to those that exist in the compound, results in inferior results in the process. The following examples clearly illustrate this fact: 1,000 cc. of a nickel-cobalt salt solution containing 70 grams cobalt and 7 grams nickel per litre were treated at 60° C., pH=2.5, reaction lasting 10 minutes in the presence of 9 grams of iron and 0.2 gram of copper, by the following materials:

(*a*) 7 grams metallic arsenic alone,
(*b*) 7 grams of sulphur flower alone,
(*c*) 7 grams of an intimate mixture of arsenic and sulphur
  (4.3 grams arsenic+2.7 grams sulphur corresponding to As_2S_3)
(*d*) 7 grams of the arsenic-sulphur compound As_2S_3

The quantity of nickel precipitated compared with the initial quantity thereof present in the solution was as follows in each of the four cases:

(*a*) 21.5%
(*b*) 9.3%
(*c*) 13.0%
(*d*) 98.0%

The above examples show that the arsenic sulphide compound was the most effective in promoting the separation of the nickel from the solution while the arsenic sulphur mixture, even though it contained amounts of arsenic and sulphur strictly adhering to the proportions in the compound As_2S_3, produced the yield of nickel grossly inferior to that produced by the arsenic sulphide compound. A method of carrying out the present invention is as follows:

A mixed saline solution of sulphates or chlorides of cobalt and nickel is heated to a temperature between 50–100° C. and thoroughly mixed. Copper is then added to the solution in the form of a soluble salt or in the form of a sulphide mixed with the metalloid compound. Then the metalloid compound is added, possibly simultaneously with the copper and the metal more electronegative than nickel. The metalloid compound is, for example, arsenic sulphide, and can be mixed with the copper sulphide as indicated above. The metal more electronegative than nickel can be iron in a finely divided form. Acid is then added to bring the pH of the solution to about 2.5 as rapidly as possible, and thereafter acid additions are made to maintain the pH close to 2.5 throughout the operation. The temperature is maintained between 50–100° C. until the nickel contained in the original solution has almost completely disappeared. The disappearance of the nickel from the solution can be determined in any known manner.

The solids in the solution are composed essentially of the metalloid compound, copper, nickel (completely or partially combined with the metalloid compounds), a small amount of cobalt which has been precipitated along with the nickel, and any excess portion of the metal more electronegative than nickel, such as iron. The solids are separated from the solution by filtration, the residue on the filter is washed and the wash liquid added to the filtrate from the filtration step.

The filtrate contains substantially pure cobalt, practically free from nickel. The filtrate can be treated in any well-known manner to eliminate small impurities such as iron, and is finally electrolyzed to extract the metallic cobalt therefrom.

The second step of the process is directed toward a solubilization of the nickel in the residue from the above filtration step, and may be performed in any known manner and in particular by the steps described hereinafter.

The above residue is suspended in an aqueous medium and gaseous chlorine is bubbled through until the nickel, and possibly any included cobalt, is totally dissolved. The other metals contained in the solids are at least partly dissolved during the chlorination. The suspension is then filtered to remove any remaining residue, which residue is normally sulphur, when the starting metalloid compound is a sulphide. This filtrate is then strongly acidified and a metallic sulphide, for example iron sulphide, or hydrogen sulphide, is added to precipitate the arsenic and copper in the form of sulphides if the metalloid compound is As_2S_3. The solution is again filtered to remove the arsenic and copper sulphides which are returned to the first step of the process to be reused. As the metalloid compound (arsenic sulphide) is repeatedly reused, the copper progressively becomes interspersed through the compound. Therefore, it is advisable to periodically remove the metalloid compound and copper from the process and separate the copper by any known method before reintroducing the materials into the process. This results in a separation of the copper from the metalloid compound.

The filtrate from the last mentioned filtration step, to which any wash liquid used in washing the obtained residue has been added, contains the remaining metals including the nickel and possibly small amounts of cobalt. This solution is then treated to precipitate the cobalt and iron as hydroxides in a well-known manner. The cobalt is obtained in the form of solid cobalt hydroxide and includes a small amount of nickel. After filtration of the solution, the residue is recycled to the first step of the process and thereby reprocessed. The filtrate is now a solution of substantially pure nickel which is electrolyzed to obtain metallic nickel.

A good separation of the nickel is effected by maintaining the pH constant throughout the whole process. The pH may vary between 1 and 5, but preferably its value is maintained at about 2.5. As the pH is increased from 2.5 to 5, the amount of cobalt precipitated along with the nickel, increases. As the pH is reduced from 2.5 to 1, the yield of nickel decreases progressively. The regulation of the pH at the desired value and the use of only the exact amount of metal more electronegative than nickel necessary to precipitate the nickel tends to limit the amount of cobalt coprecipitated with the nickel.

The amount of metal more electronegative than nickel which is added to the solution can be in an amount ranging from 1 to 5 times the amount of nickel present, on an atomic basis, but preferably the amount of metal added is maintained between 1.1 and 1.3 of the amount of nickel present, on an atomic basis.

The reaction rate depends upon the amount of the metalloid compound added in proportion to the amount of nickel present. Preferably the metalloid compound is added in an amount ranging from 1 to 2 times the amount of nickel present in the solution, on a weight basis. For example, with all other operating conditions being constant, 98% of the nickel was precipitated at a temperature of about 85° C. in one minute when the weight ratio of arsenic sulphide to nickel present was equal to about 2; and in ten minutes when the ratio of arsenic sulphide to nickel present was equal to about 1.

The effect of the presence of the addition of copper to the solution to be treated is to increase the speed of the precipitation of the nickel. Thus, if all other operating conditions are the same, a precipitation of 98% of the nickel in the solution was obtained in ten minutes when no copper was present in the solution; but, with the addition of copper to the solution in a form of soluble salt equal to 100 milligrams for each 7 grams of nickel present, the 98% precipitation of nickel was obtained under the same operating conditions in five minutes.

If the solution of mixed cobalt and nickel salts does not contain any copper initially, the copper may be added in the form of a soluble salt. The copper present, or to be added to the solution, must be in the range of 0.3–2% by weight of the nickel present in the solution. The copper may also be added in the form of copper sulphide simultaneously with the metalloid compound addition; however, when this copper compound is used, the proportion of copper sulphide which must be added, compared to the nickel present, is about 10–25%.

The reaction rate also depends upon the temperature used in the process. The rate increases as the temperature increases, and to render the operation economically interesting and feasible, the temperature must be maintained between 50°–100° C. and is preferably maintained at about 60° C.

The reaction speed also increases as the metal more electronegative than nickel is more finely divided.

Example

100 litres of a solution of mixed cobalt and nickel chlorides containing 65 grams of cobalt and 7.3 grams of nickel per litre were combined with 116 grams of cobalt and 7 grams of nickel in the chloride form coming from the hydrochloric dissolution of a nickel-cobalt hydroxide obtained during the second step of a previous run of the process.

14 grams of copper in chloride form were introduced into the solution. The solution was then heated to 60° C., and 810 grams of arsenic trisulphide and 940 grams of iron powder, passing through a 100 sieve, were added to the solution. Hydrochloric acid was then progressively added to maintain a pH of 2.5 in the solution and additional hydrochloric acid was periodically added to maintain this pH throughout the whole operation.

The temperature was maintained at about 60° C. and after about ten minutes most of the nickel had precipitated, partly in a form combined with the arsenic sulphide, and partly in a form of metallic nickel.

The solid residue was filtered from the solution and washed with 15 litres of cold water until only traces of the cobalt were determinable in the wash water. The filtrate and wash water were combined and contained 11 grams of nickel and 6.499 grams of cobalt. Therefore, 98.5% of the nickel had been extracted, and 1.76% of the cobalt had been coprecipitated with the nickel.

The filtrate was then further treated in a well-known manner to remove any impurities and electrolyzed to obtain metallic cobalt.

The washed solid residues from the filtration were then suspended in water and chlorine gas bubbled through until the nickel and cobalt contained in the residues were completely dissolved. After filtration, hydrogen sulphide was then bubbled through the suspension to precipitate the arsenic and copper in the form of sulphides. This suspension was then filtered to remove the arsenic and copper sulphides, which were washed and recycled to the beginning of the process.

The filtrate, containing nickel and cobalt chloride, was then treated in a well-known manner to precipitate the iron. After this treatment, the solution contained 725.9 grams of nickel and 116 grams of cobalt. The cobalt was then separated in the form of a hydroxide which carried along 7 grams of nickel. The cobalt hydroxide and nickel were filtered from the solution and returned to the first step of the process to be reprocessed. The filtrate was substantially pure nickel containing only a few traces of cobalt. This filtrate was electrolyzed to obtain metallic nickel.

The invention is not limited to the preferred embodiment but might be otherwise embodied or practiced within the scope of the following claims.

We claim:

1. A process for separating nickel from cobalt contained in a solution of mixed salts of cobalt and nickel which comprises adding to said solution a solid metal more electronegative than nickel and a solid metalloid compound consisting essentially of at least two of the members from the group consisting of sulphur, selenium, tellurium, antimony and arsenic, maintaining the pH of the solution between 1–5; the nickel separating from the solution as a solid material; and separating the solids containing the nickel from the solution containing substantially only cobalt.

2. A process according to claim 1 wherein said solid metal is added in an amount ranging about 1 to 5 times the amount of nickel present, on an atomic basis.

3. A process according to claim 1 wherein said solid metal is added in an amount ranging about 1.1 to 1.3 times the amount of nickel present, on an atomic basis.

4. A process according to claim 1 wherein said solid metalloidal compound is added in an amount ranging about 1 to 2 times the amount of nickel present, on a weight basis.

5. A process according to claim 1 wherein said solid metalloidal compound is added in an amount ranging about 1 to 2 times the amount of nickel present, on a weight basis; and said solid metal is added in an amount ranging about 1.1 to 1.3 times the amount of nickel present, on an atomic basis.

6. A process according to claim 1 wherein copper is added to the solution.

7. A process according to claim 1 wherein said solid metalloidal compound is added in an amount ranging about 1 to 2 times the amount of nickel present, on a weight basis; and said solid metal is added in an amount ranging about 1.1 to 1.3 times the amount of nickel present, on an atomic basis; and copper is added to the solution in an amount ranging about 0.3 to 2.0% of the amount of nickel present, on a weight basis.

8. A process for separating nickel from cobalt contained in a mixed solution of the salts of cobalt and nickel which comprises adding to said solution a solid metal more electronegative than nickel and a solid compound consisting essentially of arsenic and sulphur, maintaining the pH of the solution between about 1 to 5 and the temperature of the solution sufficiently high to separate the nickel from the solution as a solid; separating the solids containing the nickel from the solution containing substantially only cobalt.

9. A process according to claim 8 wherein the solution is maintained at a temperature between 50–100° C.

10. A process according to claim 8 wherein the pH is maintained at about 2.5.

11. A process for separating nickel from cobalt contained in a mixed solution of the salts of cobalt and nickel which comprises adding to said solution a solid metal more electronegative than nickel and a compound consisting essentially of As_2S_3; maintaining the pH of the solution between about 1 to 5 and the temperature of the solution sufficiently high to separate the nickel from the solution as a solid; separating the solids containing the nickel from the solution containing substantially only cobalt.

12. A process according to claim 11 wherein said solid metal is iron.

13. A process according to claim 11 wherein the solution is maintained above 50° C. during the process and the pH is maintained at about 2.5.

14. A process according to claim 11 wherein said solid metal is added to the solution in an amount ranging about 1.1 to 1.3 times the amount of nickel present, on an atomic basis; and the As_2S_3 is added to the solution in an amount ranging about 1 to 2 times the amount of nickel present, on a weight basis.

15. A process according to claim 11 including forming an aqueous suspension of the solids containing the nickel, chlorinating the suspension to dissolve the nickel, adding a sulphide compound to the suspension to convert any arsenic and copper in the suspension into sulphides, removing the arsenic and copper sulphides from the suspension, and removing any cobalt from the suspension in the form of a hydroxide to produce a solution of substantially pure nickel.

16. A process for separating nickel from cobalt contained in a solution of mixed salts of cobalt and nickel which process consists essentially of adding to said solution a solid metal more electronegative than nickel and a solid metalloid compound formed solely from at least two members from the group consisting of sulphur, selenium, tellurium, antimony and arsenic; said compound being substantially free of nickel and cobalt; maintaining the pH between about 1–5; the nickel in the solution separating as a solid material; and separating the solids containing the nickel from the solution containing substantially only cobalt.

17. In the removal of nickel from aqueous solutions containing nickel and cobalt in the form of their soluble salts; the process which comprises heating such a solution to a temperature between about 50–100° C. and at a pH between about 1–5; said solution containing a solid metal more electronegative than nickel and a solid metalloidal compound consisting essentially of at least two members from the group consisting of sulphur, selenium, tellurium, antimony and arsenic, in amounts sufficient to separate substantially all of the nickel from the solution as a solid material, and separating the solids containing the nickel from the solution containing substantially only cobalt.

18. The process according to claim 17 wherein said solid metal is present in the solution in a quantity 1 to 5 times the quantity of nickel present in the solution, on an atomic basis; and the solid metalloid compound is present in the solution in a quantity 1 to 2 times the quantity of nickel present in the solution, on a weight basis.

19. In the removal of nickel from aqueous solutions containing nickel and cobalt in the form of their soluble salts; the process which comprises heating such a solution to a temperature above 50° C. and at a pH between about 1–5; said solution containing a solid metal more electronegative than nickel and a solid metalloid material, in amounts sufficient to separate substantially all of the nickel from the solution as a solid material, and separating the solids containing the nickel from the solution containing substantially only cobalt; the improvement which consists in using as said solid metalloid material a solid metalloid compound consisting essentially of at least two members from the group consisting of sulphur, selenium, tellurium, antimony and arsenic.

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