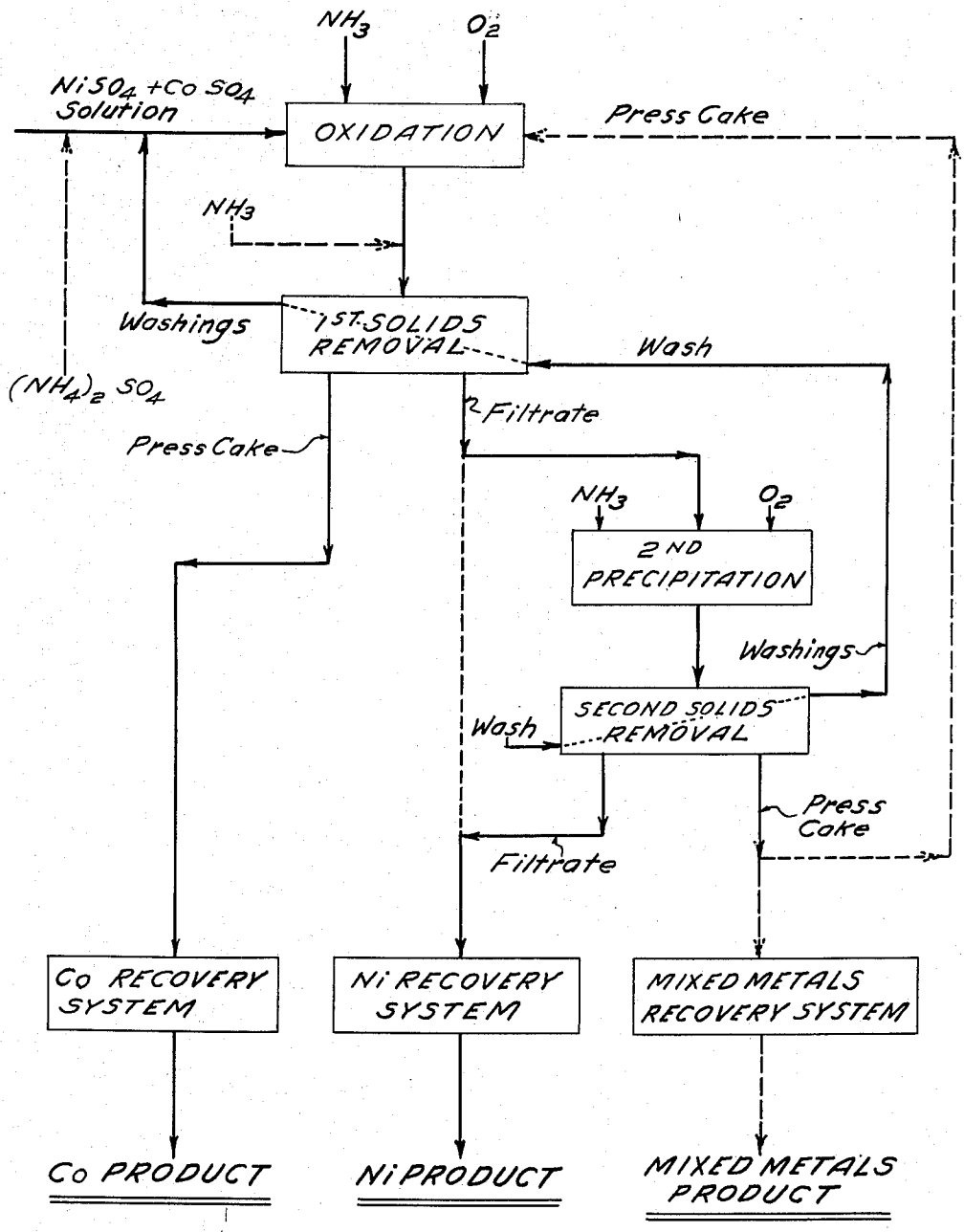
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SEPARATION OF NICKEL AND COBALT

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SEPARATION OF NICKEL AND COBALT

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This invention relates to the hydrometallurgy of nickel and cobalt. More specifically, it is concerned with the separation of these metals from one another when both are contained in the same solution. Still more specifically, it involves a new method of precipitating a substantially nickel-free cobalt product from solutions containing the mixed soluble salts of both metals in any reasonable proportion.

Nickel and cobalt metals, and their naturally occurring minerals, are very similar to one another in both physical and chemical properties. Moreover, both metals generally occur together in their natural deposits and cannot be separated by ore dressing methods. For these reasons, both metals are generally present, in varying amounts, in all solutions that result from any type of leaching of either nickel or cobalt natural or intermediate products.

In the conventional metallurgy of either nickel or cobalt, the presence of relatively large quantities of the minor metal in the ores and concentrates of the major one has always been a serious and difficult problem. This problem has never heretofore been solved in a satisfactory manner whereby the bulk of each metal may be recovered in a separate, relatively pure product. In present practice, when small amounts of cobalt are present in nickel concentrates, most of that cobalt is discarded in the slag from nickel smelting. The remainder is sold in the nickel bullion or cathodes as nickel metal. Very little is recovered and sold as cobalt metal, primarily because the cost of separation, by present methods, is at least as great as the additional value of the cobalt metal.

When small amounts of nickel are present in cobalt concentrates, and, therefore, in the cobalt solutions, this nickel is generally either discarded at considerable cost, or is recovered with the cobalt. In the latter case, the nickel becomes an impurity in the cobalt metal, and the producer is generally not paid for it. In some cases, certain nickel and cobalt mixed metals are marketable as such, but usually at a price below the value of the pure metals in separate products.

It is, therefore, apparent that a process for the efficient separation of cobalt and nickel into separate products would be very useful in both nickel and cobalt conventional metallurgy.

A large number of such processes have been either proposed or used for the treatment of cobalt and nickel electrolytes. Most of these processes involve the simultaneous or successive selective oxidation of cobalt to cobaltic hydroxide, while the electrolyte is being partially neutralized with an alkali. Cobalt is slightly easier to oxidize to the trivalent state than nickel under certain conditions, and the resulting cobaltic salt will hydrolyze and precipitate from a slightly more acidic solution than will the parallel nickel hydroxide.

One process which uses this principle employs sodium or potassium perchlorate as an oxidizing agent, and lime plus soda ash to neutralize the solution. The resulting

precipitate is a mixture of gypsum, limerock, and a cobalt-enriched hydroxide solid which may be treated for the removal of cobalt and nickel. The liquid is then generally suitable for electrolytic precipitation of at least part of the contained nickel. It may have to be recycled for a second or third cobalt removal before all of the nickel can be stripped from it.

Another variation of the above type of process involves the oxidation of cobalt with chlorine gas, which forms HCl plus HOCl in solution, and the neutralization of the solution with soda ash. This process results in the precipitation of a mixture of cobalt and nickel hydroxides, and the liquor may be made free of cobalt. The liquor is then ready for electrolysis or any other type of nickel recovery. The residue must be retreated. Various recycling systems have been worked out to improve the separation of nickel and cobalt in each of the above processes.

An additional acid liquor separation process involves the electrolytic oxidation of cobalt to the higher state. This is followed by a chemical precipitation of the cobalt as a mixed hydroxide with nickel. The mixed hydroxide is removed by filtration, and then a second electrolysis is conducted for the recovery of electrolytic nickel. When the cobalt ratio again becomes high, the solution is either returned to the leaching or to the cobalt oxidation steps of the process.

There are several methods of separating nickel and cobalt from ammonium carbonate leach liquors. Most of these involve fractional distillation of the ammonium carbonate. The mother liquor, at different stages in the process, thereby becomes concentrated with either nickel or cobalt. This liquor may then be removed and treated separately. The residue may be redissolved and retreated separately.

Conventional processes for the production of nickel or cobalt result in products containing relatively large amounts of the other metal respectively. This relatively poor separation is probably due, in part at least, to the fact that the separations are made by the precipitation of hydroxide or basic carbonate solids. These solids always occlude or adsorb large quantities of the solution from which they are precipitated. This adsorption or occlusion effect also generally makes the filtration of hydroxides difficult to perform efficiently.

Most of the conventional acid separation processes require the use of large quantities of chemical reagents, many of which are non-regenerative. This creates a disposal problem. Those processes which do not require large quantities of chemical reagents either result in high metal losses or are extremely complicated in the amount of processing that is required to achieve minimum metallurgical results.

It is, therefore, an object of this invention to provide an improved method for the separation of cobalt from nickel. It is a further object of this invention to provide a method of processing cobalt and nickel containing ores or minerals concentrates, whereby these metals may be recovered in a percentagewise amount and at an economy both heretofore unrealized. Such a process should involve the use of only commonly available chemical reagents. The process should also involve the use of only those chemical reagents which may be either regenerated or sold as a valuable by-product of the process.

Surprisingly, the desired objects of this invention have been achieved in an amazingly effective manner. In general, the over-all process is surprisingly simple. It requires, first adjusting the anion ratio of the solution of the metals so as to provide a concentration of the anion sufficient to form a cobaltic salt from the cobalt present in the solution.

This solution is then saturated with ammonia, to form

complex amine salts of the metals. It is pressurized, heated to about 250° F. and subjected to oxidation with a substantially sulfur-free, oxidizing gas. Under the proper conditions a yellow-orange crystalline cobaltic ammine salt virtually free of nickel will be precipitated, while the nickel will remain in the solution, presumably in its original form.

The resulting slurry is filtered and the presscake washed. The presscake, comprising the cobaltic ammine as a crystalline salt which is virtually non-soluble in cold water, may be easily washed substantially free of nickel salts, It may be further processed by known methods to recover pure cobalt metal. The filtrate is not necessarily cobalt-free, but may have to be subjected to a second treatment with ammonia. This second treatment will remove the remaining cobalt as an intermediate cobalt product, and will purify the nickel solution so that it can be used for the direct production of pure nickel. The intermediate cobalt product can be recycled to the first step of the process or can be used to make a mixed metal product if desired.

This invention provides an effective separation of nickel and cobalt, irrespective of the original ratio of either metal in the solution. It will also be noted that this invention enables the almost complete recovery of both metals from virtually any type of salt solution.

Although the description of the flow diagram will be applied to a sulfate solution of cobalt and nickel, it should be understood that the invention is just as applicable to other salt solutions of the metals.

The general procedure of this invention may be more fully described in conjunction with the accompanying drawing. This latter constitutes a simplified flow diagram illustrating the principal steps of the present process.

With reference to the flow diagram it will be seen that the first step of the process involves the optional addition of ammonium sulfate to the solution comprising Ni and Co salts. This permits adjustment of the anion ratio, if it does not already exist, so as to provide at least sufficient anions, in this case $SO_4^=$, to satisfy each mol of cobalt in its trivalent state, and each mol of nickel in its bivalent state. Ammonia is then added to saturate the solution. The solution is then pressurized and heated, and subjected to oxidation. Heating is conducted so as to raise the temperature of the solution to about 150°–450° F., preferably about 200°–350° F. At lower temperatures the reaction is too slow, at higher temperatures the total pressure becomes too great to be handled in conventional equipment. Moreover, at too high temperatures the nickel is also oxidized. Sufficient pressure should be used to keep the major portion of the ammonia in solution. A substantially sulfur-free, oxygen-bearing, oxidizing gas is injected into the vessel to oxidize the cobalt from the cobaltous to the cobaltic state.

The above procedure results in the oxidation of the cobalt to the trivalent state and the formation of a cobaltic ammine sulfate which precipitates as an orange colored crystalline product. Under the proper operating conditions, nickel is not believed to be oxidized. If it is, however, it remains in solution. The precipitate will contain up to about 85% or more of the cobalt originally in the solution, depending upon the cobalt to nickel concentration, and practically none of the nickel. This salt has a dry analysis which corresponds approximately to the formula $[Co(NH_3)_6]_2(SO_4)_3 \cdot 2H_2O$. It is only slightly soluble in the strongly ammoniacal treating solution, but more soluble in hot water, dilute ammonium hydroxide and dilute acids. It is easily filterable and has no tendency to adsorb solutions.

After oxidation, the resultant slurry is cooled and the solids collected, usually by filtration as shown in the drawing. If the process has been properly conducted, the resulting presscake, as indicated above, will contain as the cobaltic ammine sulfate up to at least about 85% of the cobalt originally in solution, but practically none of the nickel. The collected solids are washed, washings being recycled as shown, and then sent to a recovery system for recovery of the pure metal cobalt. This recovery system may involve any suitable method, the exact nature of which forms no part of this invention.

The residual liquor contains substantially all of the nickel and the residue of the original cobalt. If so desired, this liquor may be sent directly, as shown by the alternative flow line, to a nickel recovery system. Recovery per se of the nickel metal forms no part of this invention. Accordingly, any suitable method for the recovery thereof may be employed.

As shown in the drawing, rather than being sent directly to a nickel recovery system, the filtrate may be further treated to remove the remaining cobalt, thus leaving a substantially cobalt free nickel filtrate. This treatment of the filtrate comprises another addition of ammonia to further decrease the solubility of the cobaltic salt. Treatment is continued until all remaining cobalt is precipitated as the cobaltic ammine. Included in this precipitate will be a part of the nickel, probably as the nickelic ammine.

As shown, the mixed metal precipitate resulting from the second treatment with ammonia is collected as before by being washed and filtered. Washings may be recycled, usually to the first solids removal step. The substantially cobalt free nickel filtrate is sent to the nickel recovery system.

Two flows exist for disposing of the mixed metals presscake. One of these, as shown, involves the recycling thereof to the oxidation step for a further separation. Alternatively, the presscake may be sent to a mixed metals recovery system for recovery of a mixed metals product. As with the nickel and cobalt recovery systems, the exact nature of the mixed metals recovery system forms no part of this invention.

Shown on the flow diagram are two other alternative flows. Immediately following the oxidation step is shown the addition of ammonia. Partial addition, at this point, of the required amount of ammonia allows the addition of less in the oxidation step. This permits the use of lower total pressures during oxidation. Moreover, it constitutes a more accurate control of the ammonia addition.

The other alternative flow is an oxidation treatment at the second solids precipitation. Such a step may be necessary to insure complete oxidation of the cobalt to the trivalent state. Whether this step is warranted will depend upon the extent of the original oxidation. Moreover, this step may be employed alone to complete the precipitation of the cobalt provided sufficient ammonia was initially added. Generally, however, initial ammonia addition will be such that the second oxidation step, if required, will not be used alone but in combination with a further treatment with ammonia.

Concerning the operation of the process, certain factors should be considered. The preferred operating temperature range is between about 200° to 350° F. Much higher operating temperatures may be employed but the use of such will necessitate the use of equipment adapted to withstand the correspondingly higher pressure. Moreover, at these higher temperatures, oxidation of the nickel increases. For these reasons, it is desirable, although not essential, to operate within the preferred range mentioned.

There is no specific range of total operating pressure conditions. However, a total pressure should be maintained at least equivalent to the vapor pressure of the solution. Likewise, there is no specific range of O_2 partial pressure. The partial pressure of O_2, however, should be such as to at least insure oxidation of the equivalent amount of cobalt from the cobaltous to the cobaltic stage.

The oxidizing agent may be any oxygen containing oxidizing gas. Air, oxygen enriched air, or oxygen may be satisfactorily employed. It is essential, however, that

the gas employed be a substantially sulfur-free gas so as to prevent the formation of the metal sulfides.

Sufficient salt-forming anions must be present in the solution to precipitate the cobaltic ammine complex in the form of a salt. The anion concentration, therefore, must be at least sufficient to permit formation of the cobaltic ammine salt as well as the nickelous ammine salt. Accordingly, the anion ratio should be at least equivalent to the sum of three chemical equivalents for each mol of cobalt and two chemical equivalents for each mol of nickel. Presence of sufficient salt-forming anions also functions as a buffer with respect to the precipitation of the cobalt as a hydroxide.

Since cobalt in the present invention is precipitated as a cobaltic ammine salt, it is essential that the ammonia concentration be such as to permit formation of the ammine. Any ammonia in excess to this serves to saturate the water and decrease the solubility of the cobaltic ammine. The total concentration of ammonia necessary is a function of the water present and will increase as the dilution increases. In all cases, however, the ammonia to water ratio required will be substantially constant.

The following examples further illustrate the invention:

Example I

A leach liquor is prepared by dissolving approximately equal quantities of reagent grade nickel and cobalt sulfates in water and adjusting with ammonium sulfate and aqua ammonia until a solution of the following composition is obtained:

Solution Composition	Concentration	Mole Ratio
$NiSO_4$	92.0 gm./l.=0.597 mol/l.	Ni/Co=1.003
$CoSO_4$	92.0 gm./l.=0.595 mol/l.	$\frac{SO_4}{Ni+Co}=1.26$
$(NH_4)_2SO_4$	40.3 gm./l.=0.305 mol/l.	$\frac{NH_3}{Ni+Co}=13.7$

The ratio

$$\frac{SO_4}{Ni+Co}=1.26$$

is necessary to provide enough sulfate ions for the cobaltic salt, as well as for the soluble nickelous salt.

The solution is charged to an agitated pressure vessel and heated to approximately 250° F., at which temperature compressed oxygen is forced into the body of the liquid until the total pressure reaches approximately 250 p. s. i. g.

These conditions of temperature, pressure and agitation are held constant for approximately one hour. The contents are then removed, filtered and the residue washed. The orange colored crystalline residue obtained analyzes approximately 85.6% of the cobalt in the feed solution but only 0.6% of the nickel. This precipitate, although produced from a solution containing equal quantities of each metal, contains a ratio of cobalt to nickel in excess of 142 to 1. The filtrate containing the remaining cobalt plus most of the original nickel is further oxidized under conditions as above but for a shorter period of time. The resulting precipitate contains virtually all of the remaining cobalt in the solution plus about 12.4% of the nickel. The second filtrate now contains approximately 86.4% of the nickel and virtually none of the cobalt.

Example II

The feed liquor of this example is obtained from a leaching treatment of a Missouri nickel-cobalt ore concentrate containing a mole ratio of approximately 5 Ni to 4 Co. Since excess sulfuric acid is also present in the leach liquor, the adjustment thereof requires only the addition of ammonia in the proper ratio, producing a solution of the following composition:

Solution Composition	Concentration	Mole Ratio
$NiSO_4$	121.5 gm./l.=0.786 mol/l.	Ni/Co=1.265
$CoSO_4$	96.4 gm./l.=0.622 mol/l.	$\frac{SO_4}{Ni+Co}=1.362$
$(NH_4)_2SO_4$	67.2 gm./l.=0.510 mol/l.	$\frac{NH_3}{Ni+Co}=9.4$

The ratio

$$\frac{SO^4}{Ni+Co}=1.115$$

is required to provide enough sulfate ions for the cobaltic salt, as well as for the soluble nickelous salt.

Oxidation, conducted similarly to that in Example I, produces an orange crystalline residue which contains 82.4% of the cobalt in the original solution and only 0.1% of the nickel. Ratio of cobalt to nickel in this residue is approximately 380 to 1. The filtrate is treated with NH_3 gas which precipitates virtually all of the remaining cobalt as well as about 8.9% of the nickel. The second filtrate contains about 90% of the nickel originally in solution but none of the cobalt. The mixed residue is recycled to the adjustment operation.

Example III

The feed liquor of this example is obtained from a leaching treatment of an Idaho cobalt-nickel ore concentrate, which contains a mole ratio of approximately 20 Co to 1 Ni. Excessive acid in the leach liquor requires the addition of lime slurry as well as aqua ammonia. The calcium sulfate precipitated is removed by filtration.

The adjusted solution has the following composition:

Solution Composition	Concentration	Mole Ratio
$CoSO_4$	126.0 gm./l.=0.815 mol/l.	$SO_4/Ni+Co=1.48$
$NiSO_4$	6.7 gm./l.=0.043 mol/l.	Co/Ni=19.0
$(NH_4)_2SO_4$	54.4 gm./l.=0.412 mol/l.	$NH_3/Ni+Co=14.4$
NH_3	210.0 gm./l.=12.35 mol/l.	

The ratio $SO_4/Ni+Co=1.47$ is required to provide enough sulfate ions for the cobaltic salt, as well as for the soluble nickelous salt.

Oxidation is identical to that of Example I and results in an orange colored precipitate. The cobalt content thereof is 95.3% of the cobalt in the feed solution, while the nickel content is only 0.1%. Cobalt to nickel ratio in this precipitate is approximately 450 to 1. The filtrate from the separation of the cobaltic salt is treated with NH_3 gas. Virtually all of the remaining cobalt is precipitated as well as about 7.5% of the nickel. The exit liquor contains about 90% of the nickel in solution and none of the cobalt. The mixed salt is recycled to the adjustment operation.

We claim:

1. A hydrometallurgical process for recovering a substantially nickel-free cobalt product in the form of cobaltic hexammine sulfate from a solution comprising dissolved cobalt and nickel sulfates which comprises: saturating said solution with ammonia so as to insure formation of the cobalt hexammine complex cation; adjusting the sulfate ion concentration so as to satisfy the dissolved cobalt content in its trivalent state and the dissolved nickel in its bivalent state; subjecting said solution at a temperature greater than about 150° F. and a pressure at least equivalent to the vapor pressure of the solution to oxidation with a sulfur-free, oxygen-bearing oxidizing gas selected from the group consisting of oxygen, oxygen-enriched air and air, whereby dissolved cobalt is oxidized and a substantially nickel-free precipitate of cobaltic hexammine sulfate is obtained; and separating said cobaltic hexammine sulfate precipitate.

2. A hydrometallurgical process for recovering a substantially nickel-free cobalt product in the form of cobaltic hexammine sulfate and a substantially cobalt-free, nickel-bearing solution from a solution comprising dissolved cobalt and nickel sulfates which comprises: saturating the solution with ammonia to insure an ammonia to dissolved nickel plus cobalt mol ratio of from about 9:1 to about 15:1; adjusting the sulfate ion concentration to satisfy the cobalt in its trivalent state and the nickel in its bivalent state; subjecting the adjusted solution at a temperature of 200–350° F. and a pressure at least equivalent to the vapor pressure of the solution to oxidation with a sulfur-free, oxygen-bearing oxidizing gas selected from the group consisting of oxygen, oxygen-enriched air and air whereby dissolved cobalt is oxidized and a substantially nickel-free precipitate of cobaltic hexammine sulfate is obtained; separating and collecting said precipitate; saturating residual liquor with ammonia; subjecting said liquor at a temperature of 200–350° F. and a pressure at least equivalent to the vapor pressure of the solution to oxidation with a sulfur-free, oxygen-bearing oxidizing gas selected from the group consisting of oxygen, oxygen-enriched air and air whereby remaining cobalt is precipitated as a mixed cobalt-nickel product; and separating said mixed metal precipitate leaving a substantially cobalt-free, nickel-bearing solution.

References Cited in the file of this patent

UNITED STATES PATENTS

2,506,159	Mantell	May 2, 1950
2,647,820	Forward	Aug. 4, 1953

FOREIGN PATENTS

609,807	Great Britain	Oct. 7, 1948

OTHER REFERENCES

Mellor: "Comprehensive Treatise on Inorganic and Theoretical Chemistry," published by Longmans, Green and Co., New York, 1935, vol. 14, page 790.

Grothe: Article on the separation of cobalt and nickel in the German publication "Metall und Erz," Number 22, Nov. 2, 1933, pages 449 to 455.