PROCESS FOR THE PURIFICATION OF NICKEL CONTAINING SOLUTIONS

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ABSTRACT

Aqueous solutions containing nickel can be purified of metals capable of forming anionic complex chlorides, particularly, iron and cobalt, by raising the chloride content of the solution to from 2N to 6N by adding a completely dissociated salt of hydrochloric acid followed by contacting the solution with an anion exchange resin at a temperature above 20°C. The process is particularly suitable for purifying the anolyte from an electrolytic process for the purification of ferro-nickel or nickel matte, the purified nickel containing solution being recycled to form the catholyte.

6 Claims, No Drawings
PROCESS FOR THE PURIFICATION OF NICKEL CONTAINING SOLUTIONS

This invention relates to a hydrometallurgical process for the separation of metals and more particularly to a process for purifying nickel solutions containing in admixture small quantities of metals such as cobalt, iron, and, optionally, molybdenum, copper, aluminum, manganese, and zinc.

The nickeliferous ores generally contain relatively large quantities of iron and cobalt, and for industrial applications it is desirable to carry out treatments with a view to separately obtaining high-purity nickel and, where appropriate, high-purity cobalt.

It is relatively easy by metallurgical processes to eliminate most of the iron, although it is not possible efficiently and economically to obtain complete separation of the iron and even less of the cobalt. This is because nickel and cobalt are very similar to one another in most of their physical and chemical properties and in addition frequently incorporate such impurities as arsenic and sulphur which cannot readily be eliminated.

Thus in order to obtain nickel of high purity chemical and/or electrochemical methods have generally been employed. Electrochemical processes are most commonly employed because they enable a pure metal to be obtained in a compact homogeneous form. The impure anolyte is usually cast from an iron/nickel/cobalt alloy or from matte, i.e., sub-sulphides of these metals. The anodic corrosion of these cast ingots in anode compartments containing an aqueous electrolyte based on nickel chloride, forms on the one hand an impure anolyte rich in nickel and containing iron, cobalt and optionally other metals, and on the other hand an insoluble anodic sludge consisting mainly of metallicoids, sulphur and arsenic or certain metal compounds thereof.

Generally, the impure anolyte has to be subjected to a chemical treatment in order to completely remove the iron and cobalt present therein and thus provide a purified electrolyte which can be used as a catholyte. From the purified catholyte, the nickel is electrodeposited on metal plates, for example consisting of stainless steel or nickel, in cathode compartments. The catholyte poor in nickel is then transferred to the anode compartments by diffusion through porous fabric partitions which limit the cathode compartment.

Several methods have been used for chemically treating the impure anolyte with a view to separating the metals other than nickel. Most of these well-known processes are based on the fact that iron and cobalt are more readily oxidised from the divalent state to the trivalent state than nickel. Using oxidizing agents such as peroxides, chlorine, hypochlorites, or perchlorates, the iron and cobalt are precipitated in the form of hydroxides. Separation is possible by virtue of the fact that the hydroxides thus obtained are relatively less soluble at certain pH values than the nickel hydroxide.

Unfortunately, the operations involved in completely purifying the anolyte and quantitatively recovering an average-purity cobalt oxide are complicated and require filtering systems that are very difficult to handle in so far as they require considerable labor.

In addition, the most inexpensive oxidizing agents, chlorine for example, involve the use of apparatus which is both expensive and laborious to maintain by virtue of the corrosive action of the chemical agents. Finally, it is known that these somewhat outdated processes involve excessive consumption of chemicals which cannot be recovered and considerable losses of nickel.

Iron hydroxide for example entrains a fairly large quantity of cobalt and nickel through absorption, whilst the cobalt hydroxides emanating from selective precipitations never reach the level of purity required because they always contain substantial quantities of nickel.

Although it has been recently proposed to employ different methods for separating iron, nickel and cobalt, including for example selectively reducing the nickel from a solution containing cobalt and nickel, it is obvious that a process such as this cannot be applied in an electrolysis circuit. The same applies as regards the preferential sulphurisation of cobalt, a process whose selectivity is by no means certain.

It has also been proposed to separate these metals in the form of their chlorides by preferential extraction in solvents. The transition metals form more or less strong hydrochloric complexes which can be extracted under certain conditions of hydrochloric acidity. Thus, in a very strong hydrochloric medium, there is no difficulty in separating the chlorides of cobalt and nickel by means of ether oxides. In order to obtain satisfactory results, it is necessary to operate at an acid concentration with a normality in excess of 6.

Similarly, the chlorides of cobalt and nickel could be separated by equivalent means, such as for example by means of certain amines or carboxylic acids. Unfortunately, these processes cannot be applied to purification by electrolysis because they involve conditions of acidity that are incompatible with the process of electro-deposition.

In addition, it has been proposed to use ion-exchange resins for the purposes of separation by virtue of the fact that the hydrochloric complexes of transition metals show different levels of affinity for such resins. The methods described in the literature which are applicable to analysis in particular, comprise preferential elution with highly concentrated hydrochloric solutions which is comparable with the extraction by solvents referred to above.

It has recently been found that absorption of cobalt by an anion-exchange resin could be effected from a solution containing cobalt and nickel if a highly concentrated solution of ammonium chloride is used.

In the practical application of this process, the nickel-cobaltiferous material has to be dissolved in a solution of ammonium chloride to obtain solutions containing nickel cations and complex cobalt chloride anions. Ammonia is given off during this reaction, with the result that the technique is not suited to the conditions under which electrolytic purification is carried out, i.e., generally in an acid medium and in the presence of completely dissociated salts such as sodium chloride. In addition, the quantities of ammonium salts required for the treatment are prohibitive because they lie between concentrations of 4N and 10N, usually at six to eight times final.

The present invention provides an efficient process which is easy to carry out in that it involves very few manual operations whilst at the same time enabling a certain number of metals, in particular nickel, iron and cobalt, to be almost completely separated from mixtures containing them.

Thus the present invention relates to a process for purifying solutions containing nickel in admixture with metals capable of forming anionic complex chlorides, wherein the anionic complex chlorides of these metals are formed by addition to the solution of an alkaline or alkali earth metal chloride, the chloride concentration of the solution being from 2 to 6N and the temperature above 20 °C, after which the solution is contacted with an anion exchange resin to adsorb the complex anions of the metals capable of forming anionic complex chlorides and the nickel solution thus treated is removed.

The solution will generally then be treated to remove from it all metals other than those emanating from the supply of the dissociated chloride.

The metals capable of forming complex chlorides include in particular cobalt and iron and also molybdenum, manganese, aluminum, and zinc.

The process according to the invention is particularly applicable to the treatment of anolytes such as those emanating from the electrolytic refinement of ferro-nickel or mattes. However, it may also be used for separating cobalt, iron and nickel from mixtures emanating from the direct dissolution of materials containing them. Thus, the process may be used with particular advantages for the purification of nickel salts obtained by the action of hydrochloric acid on such substances as industrial waste, spent catalysts and carbonates and hydroxides emanating from the precipitation of spent nickel-plating baths with soda.
In the case of impure anolytes emanating from the attack of ferro-nickel anodes, these anolytes generally have a pH value of around 4 and contain from 70 to 85 g/liter of nickel, from 0.5 to 1 g/liter of iron and from 0.10 to 0.20 g/liter of cobalt, and also quantities of sodium chloride of the order of 60 g/liter and more generally between 60 and 180 g/liter.

In the electrolysis of a matte currently being produced in the factories of LE NICKEL at Noumea, it has been found that the optimum efficiency in terms of current utilization was obtained for the following anolyte concentrations:

<table>
<thead>
<tr>
<th>Anolyte</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>75 g/liter</td>
</tr>
<tr>
<td>Cobalt</td>
<td>2 g/liter</td>
</tr>
<tr>
<td>Iron</td>
<td>2 g/liter</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>150 to 300 g</td>
</tr>
</tbody>
</table>

and that the best deposition was obtained by operating at elevated temperatures, the most favourable temperatures being around 80°C.

The dissociated hydrochloric acid salts are preferably alkali metal chlorides and more particularly sodium chloride and potassium chloride.

The chloride concentration of the solution, amounting to between 2 and 6N, is preferably 3N to 4N. The temperature employed, in excess of 20°C, is preferably in a range from about 60°C to about 80°C, these being the temperatures at which the anionic exchange resin has a maximum effect and does not undergo any deterioration.

In the practical application of the process, it is preferred to use resins that are known to have strongly basic outline groups, such as quaternary amines. A preferred resin is polystyrene with active groups of the quaternary ammonium type, this resin working in the form of its chloride which is its most stable form. One example of such a resin is commercially available under the name IMAC S 540.

Other basic anionic resins that are commercially available may also be used, such as for example AMBERLITE IRA 400 which is a polystyrene resin containing

\[ \text{Na}^+ (\text{CH}_3)_2\text{CH}_2\text{Cl} \]

and DOWEX 1 which is a polystyrene resin containing

\[ \text{Na}^+ (\text{CH}_3)_2\text{CH}_2\text{Cl} \]

groups.

Finally, weakly basic resins such as that commercially available under the name IMAC A 20 P, of which the active groups consist of primary, secondary and tertiary amines, may be satisfactorily used in the specific case of anolytes with the concentration indicated previously, because the pH and temperature conditions correspond ideally to the range of activity of these types of base.

In one embodiment of the invention, the process comprises anodically attacking nickeliferous, cobaltiferous and ferruginous substances in a hot concentrated solution of a nickel chloride and sodium chloride and continuously treating this solution be percolation on an anion-exchange resin in the form of its chloride, so as to absorb the iron and the cobalt and give a solution of nickel chloride and sodium chloride which is directly recycled to the cathode compartment for the electro-deposition of the nickel in a pure form. In practice, the impure solution issuing from the anode compartment passes at a predetermined rate through an anion-exchange resin column (such as the resin IMAC S 540).

Thus, during the treatment which is carried out by percolating the anolyte through the column containing the resin kept at a temperature around 80°C, the nickel cations pass through the column without being retained whilst the complex cobalt/iron anions are adsorbed by the resin. This results in a complete separation of all the iron and cobalt from the nickel.

The invention also relates to a process for recovering metals other than nickel retained in complex anionic form by the iron exchanger, comprising desorbing the aforementioned exchanger with optionally acidulated water or even with an aqueous solution of dissociated salts at such a concentration that the aforementioned complex is destroyed.

The cobalt is preferably extracted with a semi-normal solution of dissociated chlorides, the iron, aluminum, zinc and so on preferably being eliminated with a deionized to normal hydrochloric acid solution. Thus, the desorbed metals are directly recovered in the form of chlorides. Eulon with the chlorides simultaneously regenerates the resin which is re-available for continuing the purification cycle.

The invention is illustrated by the following examples.

### EXAMPLE 1

An impure anolyte emanating from the anodic corrosion of a New Caledonian nickel matte which had been subjected to intense metallurgical purification to eliminate the iron present in it, is represented by a solution of the following composition:

<table>
<thead>
<tr>
<th>Anolyte</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>76.0 g/liter</td>
</tr>
<tr>
<td>Co</td>
<td>1.84 g/liter</td>
</tr>
<tr>
<td>Iron + copper</td>
<td>0.1 g/liter</td>
</tr>
<tr>
<td>Na⁺</td>
<td>115 g/liter</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>520 g/liter</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>30 g/liter</td>
</tr>
<tr>
<td>pH</td>
<td>4</td>
</tr>
</tbody>
</table>

Six liters of this solution taken from the anode compartment of a test electrolytic purification cell is passed through a 1,500 cc ion exchange resin column (IMAC S 540 in the form of its chloride).

The column has a double jacket enabling a temperature of 85°C ± 5°C to be maintained during the experiment. Percolation is carried out at an average speed of 4,500 liters per hour.

Five liters of the effluent solution are recovered before the appearance of insignificant traces of cobalt. A total absence of iron and copper is noticeable even after the passage of the sixth liter of effluent solution.

On completion of the cycle, the resin is washed with 3 liters of saturated sodium chloride solution in order to entrain the nickel retained, and the cobalt is eluted by percolating hot water through the resin.

The following table confirms the path along which the various operations progress.

<table>
<thead>
<tr>
<th>Volume recovered (in ml)</th>
<th>Analysis at fractionation</th>
<th>Ni (g/l)</th>
<th>Co (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percolation of anolyte</td>
<td></td>
<td>1,500</td>
<td>50.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3,000</td>
<td>70.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4,500</td>
<td>78.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6,000</td>
<td>80.89</td>
</tr>
<tr>
<td>Percolation of brine</td>
<td></td>
<td>6,500</td>
<td>56.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7,750</td>
<td>1.49</td>
</tr>
<tr>
<td>Percolation of water</td>
<td></td>
<td>9,750</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10,000</td>
<td>0</td>
</tr>
</tbody>
</table>

A solution of 457.5 g of nickeliferous material containing 11 g of cobalt in a weight ratio of Co: Ni of 25:1000 was treated on the resin.

333 g of nickel were recovered in completely pure form, free from cobalt, iron and copper.

108.7 g of nickel were recovered in a semi-pure form admixed with 1.2 g of cobalt (Ni/Co weight ratio = 11:1000).

7.34 g of cobalt were recovered in perfectly pure form, whilst a mixture of 1.9 g. nickel and 3 g cobalt (substantially representing the residue to complete the material balance), was recovered in the form of a mixture which, as will readily be appreciated, can be recovered and separated during the following cycle.

### EXAMPLE 2

Six liters of an anolyte which is produced by the electrolytic purification of a nondeferritized matte and having the following composition:

<table>
<thead>
<tr>
<th>Anolyte</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
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</tr>
<tr>
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<td>520 g/liter</td>
</tr>
<tr>
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<td>pH</td>
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Five liters of the effluent solution are recovered before the appearance of insignificant traces of cobalt. A total absence of iron and copper is noticeable even after the passage of the sixth liter of effluent solution.

On completion of the cycle, the resin is washed with 3 liters of saturated sodium chloride solution in order to entrain the nickel retained, and the cobalt is eluted by percolating hot water through the resin.

The following table confirms the path along which the various operations progress.
are brought into contact in a manner substantially similar to that described in Example 1 in the same ion-exchange column which was used for treating the anolyte containing only very small quantities of impurities other than cobalt.

The first 6 liters of effluent contained less than 50 mg per liter of cobalt and less than 20 mg per liter of nickel. In addition, almost all the cobalt, i.e., 11.27 g, is recovered in pure form, the iron being desorbed from the resin on completion of the cycle by washing with water at a high rate, i.e., at a rate of four times the volume of resin per hour.

It should be noted that these outstanding results were obtained despite the fact that the ion-exchange resin column had not been heated at the beginning of operation, with the result that the temperature of the effluent never rose above 80°C.

EXAMPLE 3

On this occasion, an anolyte solution of the following composition is used:

\[
\begin{align*}
\text{Ni}^{2+} & \quad 86.7 \text{ g/l.} \\
\text{Co}^{2+} & \quad 1.4 \text{ g/l.} \\
\text{Fe}^{3+} & \quad 1.0 \text{ g/l.}
\end{align*}
\]

in chloride form

The apparatus used consists of a double-jacket column 1 meter high with an internal diameter of 2 cm, being filled to 60 cm. The volume occupied by the resin, IMAC S 540, is 150 cc.

The hot solution is percolated so that it issues from the anode compartment at 80°C through the bed, the double jacket enabling this temperature gradient to be maintained through the circulation of hot water.

A solution of the following composition is recovered:

\[
\begin{align*}
\text{Ni} & \quad 71.4 \text{ g/l.} \\
\text{Co} & \quad 0.023 \text{ g/l.} \\
\text{Fe} & \quad 0.010 \text{ g/l.}
\end{align*}
\]

corresponding to a recovery of 99 percent of the nickel introduced.

Following the starting solution, a small quantity of aqueous NaCl solution (35 percent of NaCl) was percolated. This solution entrained the nickel retained which had impregnated the resin. The operation by which the cobalt is recovered comprises percolating with water. The aqueous eluate thus entrains 89 percent of the cobalt introduced. This metal is recovered in the form of its chloride free from nickel.

The iron which is still retained at this stage is eluted with a normal aqueous HCl solution. In this last phase, 95 percent of the quantity of iron originally present are recovered.

EXAMPLE 4

Following the same procedure as in Example 2, an aqueous solution with the following composition:

\[
\begin{align*}
\text{NaCl} \cdot 6\text{H}_2\text{O} & \quad 61 \text{ g/l.} \\
\text{CoSO}_4 \cdot 7\text{H}_2\text{O} & \quad 13.80 \text{ g/l.} \\
\text{NaCl} & \quad 338 \text{ g/l.}
\end{align*}
\]

passes at 75°C through an ion-exchange resin column (Amberlite IRA 400).

The initial Ni:Ni+Co weight ratio is 83.8%. After treatment, it reaches 99.1 percent. The cobalt complex is released during desorption in the form of a solution of cobalt chloride in which the weight ratio of Ni:Co is lower than 2 percent.

EXAMPLE 5

A nickeliferous dross emanating from a slag obtained during the pyrometallurgical treatment of a matte of the following weight composition:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td>42.3%</td>
</tr>
<tr>
<td>NiCl₂</td>
<td>11.1%</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>4.3%</td>
</tr>
<tr>
<td>MnCl₂</td>
<td>2.6%</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>1.1%</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>17.8%</td>
</tr>
<tr>
<td>Insolubles</td>
<td>20.8%</td>
</tr>
<tr>
<td>SiO₂ in particular</td>
<td>20.8%</td>
</tr>
</tbody>
</table>

This residue is dissolved in water by an appropriate means. The liquid resulting from this treatment, following filtration of its insoluble components, is percolated at 100°C through an ion-exchange resin column (Dowex 1 chloride form). A solution of nickel chloride free from every metal other than potassium, issues from the column. By progressive washing, the cobalt, iron, manganese and zinc are successively desorbed. The cobalt is recovered in the form of a solution of highly pure chloride which merely has to be concentrated in order to convert into one of its hydrates in a form suitable for sale.

We claim:

1. A process for the purification of an aqueous solution containing nickel and at least one impurity selected from the group consisting of cobalt, iron, copper, manganese and zinc, said process comprising:
   a. adding to said aqueous solution at least one chloride solution comprising the alkali and alkali earth metal chlorides in an amount such that said aqueous solution has a chloride concentration in the range from 2N to 6N;
   b. contacting said aqueous solution with an anion exchange resin at a temperature between about 60° and 110°C;
   c. recovering from said anion exchange resin an aqueous solution containing nickel and free from said at least one impurity.

2. A process as claimed in claim 1 wherein said at least one impurity is subsequently eluted from said anion exchange resin with an eluant selected from the group consisting of water, acidulated water and aqueous solutions of alkali and alkali earth metal chlorides at such a concentration that the said metal is removed from said anion exchange resin.

3. A process as claimed in claim 1 wherein said anion exchange resin has active groups of the quaternary ammonium type.

4. A process as claimed in claim 1, wherein said chloride is sodium chloride.

5. A process as claimed in claim 1, wherein said chloride is potassium chloride.

6. A process as claimed in claim 1, wherein said chloride concentration is in the range from about 3 to 4N.