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PURIFICATION OF COBALT SOLUTIONS CONTAINING IRON AND MANGANESE WITH OXIDATION MIXTURE OF SO2 AND OXYGEN

(57) Abstract
Disclosed herein is a process for selectively removing an iron constituent and a manganese constituent from a cobalt-bearing composition, in particular for removing iron and manganese impurities from cobalt-bearing leach solutions and electrolytes, comprising the steps of: (a) subjecting said composition to a first oxidation mixture of SO2 and oxygen, at conditions sufficient to oxidize said iron constituent; (b) hydrolyzing said iron constituent; (c) subjecting said composition to a second oxidation mixture of SO2 and oxygen at conditions sufficient to oxidize said manganese constituent; and (d) hydrolyzing said manganese constituent; (e) wherein, in steps (a) and (b), the composition is maintained at a pH sufficient to precipitate iron while minimizing precipitation of manganese or cobalt, and (f) wherein, in steps (c) and (d), the composition is maintained at a pH sufficient to precipitate manganese while minimizing precipitation of cobalt.
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BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

The present invention relates to techniques for the production of high quality cobalt-bearing materials, such as cobalt metals, salts and the like.

2. DESCRIPTION OF THE RELATED ART

The production of high quality cobalt metal or cobalt salts, such as the carbonate, chloride and sulphate forms thereof, requires the cobalt solution or electrolyte to be purified for metals such as iron, copper, aluminum, nickel, manganese and zinc. For example, in the Republic of Congo, Gecamines plants, where a large portion of the world cobalt has been produced, the feed solution for cobalt recovery goes to a series of hydrolysis steps, to remove in succession copper, then iron, aluminum, silica followed by sulphide precipitation to remove zinc and nickel. In Zambia, similar feed solutions go through a copper hydrolysis, followed by iron and aluminum/silica hydrolysis, zinc solvent extraction with DEHPA (a trademark) and nickel removal by ion exchange with DOWEX 4185 (a trademark). None of these processes remove manganese from solution. The purified solutions containing cobalt and manganese are thereafter "electrowon", a term well known in the art involving an electric potential driven cathodic and anodic reactions. Manganese is oxidized at the anode and forms MnO₂ while cobalt is deposited on the cathode in the form of cobalt metal. Some of the manganese dioxide formed at the anode peels off thereby requiring frequent clean up of the cell to minimize manganese inclusion in the cathode.

Recent progresses in solvent extraction have led to the development of extractants for cobalt. One such reagent commercially used for cobalt solvent extraction (hereinafter referred to as "Co/SX") is CYTEC's CYANEX 272 (a trademark). One of the drawbacks of CYANEX 272 is that it is not selective against manganese. Rather, any manganese present in the solution fed to
SX will be loaded together with the cobalt, decreasing the loading capacity of the solvent for cobalt. Manganese will be stripped together with cobalt and report to the electrolyte, leading to similar problems as mentioned earlier.

Iron hydrolysis is also a problem. Ferrous (Fe^{2+}) precipitation does not occur at the low pH levels (that is below 3) used in typical processing plants. Instead, iron must be oxidized to its ferric (Fe^{3+}) form to eliminate it completely prior to Co/SX or cobalt electrowinning (hereinafter referred to as “Co/EW”). Oxidation is performed by sparging air or oxygen through the solution. This process is inefficient and takes up to 10 hours to achieve satisfactory results.

In the case of Manganese, a proposed solution involves oxidizing, and then precipitating, manganese prior to Co/SX or Co/EW. Oxidants suggested to conduct this operation are expensive and usually difficult to handle, such as ozone, hydrogen peroxide and hydrogen peroxysulphate (known as Caro’s acid).

Among the literature are two processes which relate to the use of SO_{2} with air as an oxidant in processes to precipitate certain ionic species from solution. For example, US 2,816,819 to Wallis et al. discloses a system which uses SO_{2}/Air to precipitate iron from a cobalt-bearing solution. Canadian Patent 935,650 discloses a technique by which a mixture of SO_{2}/Air is used to precipitate a number of impurities from a cobalt solution. However, neither reference makes any suggestion toward the selective precipitation of iron or manganese from a cobalt solution in a manner that minimizes the precipitation of cobalt, along with the subject iron or manganese.

It is therefore an object of the present invention to obviate or mitigate these disadvantages.

SUMMARY OF THE INVENTION
Briefly stated, the present invention involves a process for selectively removing an iron constituent and a manganese constituent from a cobalt-bearing composition, comprising the steps of:

(a) subjecting the composition to a first oxidation mixture of SO₂ and oxygen, at conditions sufficient to oxidize the iron constituent;

(b) hydrolyzing the iron constituent;

(c) subjecting the composition to a second oxidation mixture of SO₂ and oxygen at conditions sufficient to oxidize the manganese constituent; and

(d) hydrolyzing the manganese constituent,

(e) wherein, in steps (a) and (b), the composition is maintained at a pH sufficient to precipitate iron and not manganese nor cobalt, and

(f) wherein, in steps (c) and (d), the composition is maintained at a pH sufficient to precipitate manganese and not cobalt.

In another aspect of the present invention, there is provided a process for selectively removing an iron constituent and a manganese constituent from a cobalt-bearing composition, comprising the steps of:

(a) subjecting said composition to a first oxidation mixture of SO₂ and oxygen, at conditions sufficient to oxidize said iron constituent;

(b) hydrolyzing said iron constituent;
(c) subjecting said composition to a second oxidation mixture of SO₂ and oxygen at conditions sufficient to oxidize said manganese constituent; and

(d) hydrolyzing said manganese constituent,

(e) wherein, in steps (a) and (b), the composition is maintained at a pH sufficient to precipitate iron while minimizing precipitation of manganese or cobalt, and

(f) wherein, in steps (c) and (d), the composition is maintained at a pH sufficient to precipitate manganese while minimizing precipitation of cobalt.

In another aspect of the present invention, there is provided a process for removing a manganese constituent from a cobalt-bearing composition comprising the steps of:

- subjecting the composition to an oxidation mixture of SO₂ and oxygen, at conditions sufficient to oxidize the manganese constituent and at a pH sufficient to precipitate manganese and not cobalt; and

- hydrolyzing the manganese constituent.

In still another aspect of the present invention, there is provided a process of removing iron and manganese constituents from a cobalt-bearing solution comprising the steps of:

(a) converting substantially all of the iron to an Fe³⁺ valence state;

(b) precipitating the iron from solution, while leaving substantially all of the manganese and cobalt in solution; and thereafter

(c) converting substantially all of the manganese to an Mn⁶⁺ state;
(d) precipitating the manganese from solution, while leaving substantially all of the cobalt in solution.

In yet another aspect of the present invention, there is provided a process of removing iron and manganese impurities from a cobalt solution, comprising the steps of:

(a) reacting the solution with an oxidation mixture of $SO_2$ and oxygen at a pH sufficient to oxidize the iron impurity, while leaving the manganese impurity and the cobalt in a substantially unreacted state;

(b) precipitating the iron impurity from solution, and thereafter

(c) reacting the solution with an oxidation mixture of $SO_2$ and oxygen at a pH sufficient to oxidize the manganese impurity, while leaving the cobalt in a substantially unreacted state;

(d) precipitating the manganese impurity from solution, wherein substantially all of the cobalt remains in solution.

BRIEF DESCRIPTION OF THE DRAWINGS

Several preferred embodiments of the present invention will now be described, by way of example only, with reference to the appended drawings in which:

Figure 1 is a schematic view of a process to purify cobalt;

Figure 2 is a schematic view of another process to purify cobalt;

Figure 3 is a plot of iron removal versus retention time;
Figure 4 is another plot of iron removal versus retention time;

Figure 5 is a schematic view of still another process to purify cobalt;

Figure 6 is another plot of iron removal versus retention time for the process of figure 5; and

Figure 7 is a plot of manganese removal versus retention time for the process of figure 5.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As will be described, the present invention, in one of its aspects, involves a process for selectively removing an iron constituent and a manganese constituent from a cobalt-bearing composition, comprising the steps of:

(a) subjecting the composition to a first oxidation mixture of SO₂ and oxygen, at conditions sufficient to oxidize the iron constituent;

(b) hydrolyzing the iron constituent;

(c) subjecting the composition to a second oxidation mixture of SO₂ and oxygen at conditions sufficient to oxidize the manganese constituent; and

(d) hydrolyzing the manganese constituent,

(e) wherein, in steps (a) and (b), the composition is maintained at a pH sufficient to precipitate iron and not manganese nor cobalt, and

(f) wherein, in steps (c) and (d), the composition is maintained at a pH sufficient to
precipitate manganese and not cobalt.

Preferably, the pH is maintained between 2.5 and 3.5, more preferably 2.8 and 3.3 and still more preferably 3.

In one embodiment, the oxygen is in the form of \( O_2 \). Preferably, the oxidation mixture includes Air, with \( O_2 \) being a constituent thereof. In this embodiment, the \( SO_2 \) is at a concentration from 0.1 percent to 2 percent, with the balance being Air. More preferably, the \( SO_2 \) is at a concentration from 0.2 to 1.4 percent, still more preferably from 0.4 to 0.6 percent.

Preferably, steps (a) and (c) occur at a temperature ranging from 40 to 90\(^\circ\)C, more preferably, at a temperature ranging from 50 to 75\(^\circ\)C and still more preferably at a temperature ranging from 58 to 64\(^\circ\)C. Most preferably, steps (a) and (c) occur at 60\(^\circ\)C.

In another embodiment, the oxygen is in the form of substantially pure \( O_2 \). In this embodiment, the \( SO_2 \) is at a concentration from 0.5 percent to 10 percent, with the balance being \( O_2 \). More preferably, the \( SO_2 \) is at a concentration from 1 to 8 percent, still more preferably from 2 to 3 percent.

In another aspect of the present invention, there is provided a process for removing a manganese constituent from a cobalt-bearing composition comprising the steps of:

- subjecting the composition to an oxidation mixture of \( SO_2 \) and oxygen, at conditions sufficient to oxidize the manganese constituent and at a pH sufficient to precipitate manganese and not cobalt; and

- hydrolyzing the manganese constituent.

In still another aspect of the present invention, there is provided a process of removing
iron and manganese constituents from a cobalt-bearing solution comprising the steps of:

(a) converting substantially all of the iron to an Fe$^{3+}$ valence state;

(b) precipitating the iron from solution, while leaving substantially all of the manganese and cobalt in solution; and thereafter

(c) converting substantially all of the manganese to an Mn$^{4+}$ state;

(d) precipitating the manganese from solution, while leaving substantially all of the cobalt in solution.

In yet another aspect of the present invention, there is provided a process of removing iron and manganese impurities from a cobalt solution, comprising the steps of:

(a) reacting the solution with an oxidation mixture of SO$_2$ and oxygen at a pH sufficient to oxidize the iron impurity, while leaving the manganese impurity and the cobalt in a substantially unreacted state;

(b) precipitating the iron impurity from solution, and thereafter

(c) reacting the solution with an oxidation mixture of SO$_2$ and oxygen at a pH sufficient to oxidize the manganese impurity, while leaving the cobalt in a substantially unreacted state;

(d) precipitating the manganese impurity from solution, wherein substantially all of the cobalt remains in solution.

As will be described herein below, the present invention provides an improved process to purify cobalt, particularly from solutions containing such impurities as iron and manganese. This
is achieved, for example, by improving the efficiency by which iron as well as manganese are isolated from the solution, along with other impurities therein, leaving the cobalt constituent for a final isolation step thereof.

Furthermore, the present process isolates, in one embodiment manganese selectively from cobalt compositions, and in another embodiment both iron and manganese selectively, that is substantially one at a time, for example with only trace amounts of manganese or cobalt, if any, precipitated with the iron, and trace amounts cobalt, if any, precipitated with the manganese. Trace amounts in this case would vary from 0 to 4 percent of the total cobalt present in the initial solution.

In one example, a gas mixture of SO₂ and oxygen are applied to the solution first to oxidize the iron into its ferric form. Thereafter, the iron is hydrolyzed with an hydroxide bearing agent such as lime, to yield an easily removed iron-bearing precipitate. Thereafter, manganese is removed in a similar manner. In this case, both steps involve a relatively inexpensive and plentiful oxidant, a gas mixture of O₂/SO₂, or alternatively Air/SO₂, or still alternatively 100% pure Air can be used together with equivalent amounts of SO₂, preferably added as SO₂ in a gaseous or liquid form, or added as a constituent in a solution containing, for example, sodium metabisulphite, ammonium metabisulphite, potassium metabisulphite or other suitable forms of metabisulphite.

The oxidant can be a 0.1-5% SO₂, 99.9-95% O₂ mixture, a 0.02-1% SO₂, 99-99.98% Air mixture. Alternatively, 100% pure Air can be used together with equivalent amounts of SO₂, preferably added as SO₂ in a gaseous or liquid form, or added as a constituent in a solution containing, for example, sodium metabisulphite, ammonium metabisulphite, potassium metabisulphite or other suitable forms of metabisulphite.

Iron Oxidation/Hydrolysis

The oxidation reaction of ferrous can be conducted at temperatures ranging from 30 to
95°C, but better results are obtained between 50 and 60°C. The oxidation of ferrous occurs via the reaction:

$$2\text{FeSO}_4 + \text{SO}_2 + \text{O}_2 \rightarrow \text{Fe}_2\text{(SO}_4)_3$$

The oxidation occurs even at high acid content, but is more efficient at pH's above pH 2.0 to minimize the effects of an unwanted side reaction as shown in (2) which consumes SO₂.

$$\text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SO}_4$$

Once oxidized, the iron can then be eliminated from solution by hydrolysis as per reaction (3):

$$\text{Fe}_2\text{(SO}_4)_3 + 4\text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 3\text{H}_2\text{SO}_4$$

In reaction (3), iron is shown to be hydrolyzed as goethite. To maintain the efficiency of the process, the acid generated in (2) and (3) can be neutralized, for example with lime, limestone, or any other material consuming acid.

The oxidation and the hydrolysis operations can be practiced one step after the other, or together. In the latter case, the overall reaction of the oxidation/hydrolysis of ferrous when using this oxidation process can be written as reaction (4):

$$2\text{FeSO}_4 + \text{SO}_2 + \text{O}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{FeOOH} + 3\text{H}_2\text{SO}_4$$

Another way to enhance the oxidation reaction is to add small quantities of ferric ion to the solution being purified. Either fresh ferric sulphite solution can be added or better, some bleed of the oxidized solution as shown in Figure 2. This occurs because the ferric ion tends to act as a catalyst for further oxidation.
This process is particularly interesting if the oxidation has to be operated in batch mode or at the start up of a continuous operation. Under the conditions described above and at a temperature greater than 60°C, the iron precipitate formed is mostly goethite and is relatively easy to settle and filter.

Manganese Oxidation/Hydrolysis

Another feature of the present invention is the removal of manganese prior to the cobalt recovery system (precipitation, cobalt SX, cobalt EW) using oxidation/hydrolysis. The oxidant used is advantageously the same as the one used for iron oxidation, namely SO₂/Air or SO₂/O₂ or metabisulphite/Air.

Similar to the oxidation of iron, the proportion of SO₂ in the gas mixture is 0.1 to 5% SO₂, 95-99.9% O₂ (preferably 2% SO₂, 98% O₂) or equivalent proportions when using SO₂/O₂/Air or metabisulphite/Air. Temperature ranges between 30-90°C preferably between 50 and 60°C. The oxidation occur, even at high acidities but efficiency increases with increasing pH. Optimum pH is around pH = 2.5. Here too, it is preferable to neutralize acid generated (during oxidation).

The oxidation reaction for manganese can be written as shown in reaction (5).

\[ \text{MnSO}_4 + \text{SO}_2 + \text{O}_2 \rightarrow \text{Mn}^{4+} + 2\text{SO}_4^{2-} \]  

(5)

The oxidized manganic ion is hydrolyzed as MnO₂ (reaction 6). The resulting MnO₂ is easy to settle and to filter.

\[ \text{MnSO}_4 + \text{SO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}_2\text{SO}_4 \]  

(6)
It is critical that the mixture of gas be well mixed to maintain efficiency. The gas mixture may be introduced under the impeller, or using a porous gas sparger, or any other device providing good gas-mixing.

Embodiments of the present invention will be described with reference to the following Examples which are presented for illustrative purposes only and are not intended to limit the scope of the invention.

EXAMPLES

Example 1 - PRIOR ART

A sample of cobalt solution produced during the acid leaching of a copper-cobalt ore from Africa contained 7 g/L Co, 0.7 g/L Al, 2.5 g/L Fe, 0.6 g/L Si and 0.7 g/L Mn. The iron was batch oxidized by blowing pure oxygen through the liquid. The oxidized iron was hydrolyzed with lime. The graph in Figure 3 shows the kinetics of iron oxidation/hydrolysis using oxygen. After 10 hours oxidation with pure oxygen, there was still 1.2 g/L Fe left in solution. This amount of iron is not compatible with downstream processing to recover pure cobalt.

Example 2

The same solution as described in Example 1 was batch oxidized using the present process. A mixture of 99.6% Air, 0.4% SO₂ (vol) was sparged through the liquid at 60°C. All other conditions were similar to those of Example 1. The kinetics of iron removal are shown in Figure 4. In 3 hours, all the iron was removed.

Example 3

A sample of cobalt solution produced during the acid leach of a copper-cobalt ore sample
from Africa was treated to remove iron, aluminum and silica. After treatment, the cobalt solution assayed: 3.1 g/L Co, 0.226 g/L Mn, 1.4 mg/L Fe, 11 mg/L Al. The solution sample, still containing manganese, was batch oxidized/hydrolyzed using SO₂/Air. The solution temperature was held at 60°C. The proportion in the gas mixture was 0.4% SO₂, 99.6% Air. The kinetics of manganese removal are illustrated in Table 1. Further removal of manganese occurs with longer retention times. Results indicate a very selective process and minor cobalt losses, that is in the order of 0.5 to 1% of the total cobalt in the initial solution.

Example 4

A large sample of the same cobalt solution as described in Examples 1 and 2 was continuously treated during a pilot plant at a feed rate of 60 L/h. The flowsheet to treat the solution included the new process of this invention, namely iron and manganese were oxidized/hydrolyzed using SO₂/Air mixtures. The overall process flowsheet is illustrated in Figure 5.

From a solution containing an average 6321 mg/L Co, 1767 mg/L Fe, 639 mg/L Al, 103 mg/L Cu and 568 mg/L Mn, the present process was used incorporating SO₂/Air oxidation/hydrolysis for both the iron and the manganese, and produced a purified cobalt solution assaying 6442 mg/L Co, 1.2 mg/L Fe, 5.4 mg/L Al, 8.4 mg/L Cu and 11.5 mg/L Mn. Overall cobalt losses throughout the purification circuit were limited to between 2 and 4% of the total cobalt.

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**TABLE 1:**
CLAIMS

1. A process for selectively removing an iron constituent and a manganese constituent from a cobalt-bearing composition, comprising the steps of:

(a) subjecting said composition to a first oxidation mixture of $\text{SO}_2$ and oxygen, at conditions sufficient to oxidize said iron constituent;

(b) hydrolyzing said iron constituent;

(c) subjecting said composition to a second oxidation mixture of $\text{SO}_2$ and oxygen at conditions sufficient to oxidize said manganese constituent; and

(d) hydrolyzing said manganese constituent,

(e) wherein, in steps (a) and (b), the composition is maintained at a pH sufficient to precipitate iron while minimizing precipitation of manganese or cobalt, and

(f) wherein, in steps (c) and (d), the composition is maintained at a pH sufficient to precipitate manganese while minimizing precipitation of cobalt.

2. A process as defined in claim 1 wherein said pH is between 2.5 and 3.5.

3. A process as defined in claim 2 wherein said pH is between 2.8 and 3.3.

4. A process as defined in claim 3 wherein said pH is 3.

5. A process as defined in claim 1 wherein said oxygen is in the form of $\text{O}_2$. 
6. A process as defined in claim 5 wherein said oxidation mixture includes Air.

7. A process as defined in claim 6 wherein steps (a) and (c) occur at a temperature ranging from 40 to 90°C.

8. A process as defined in claim 7 wherein steps (a) and (c) occur at a temperature ranging from 50 to 75°C.

9. A process as defined in claim 8 wherein steps (a) and (c) occur at a temperature ranging from 58 to 64°C.

10. A process as defined in claim 9 wherein steps (a) and (c) occur at 60°C.

11. A process as defined in claim 5 wherein said SO₂ is at a concentration from 0.5 percent to 10 percent, with the balance O₂ gas.

12. A process as defined in claim 11 wherein said SO₂ is at a concentration from 1 to 8 percent.

13. A process as defined in claim 12 wherein SO₂ is at a concentration from 2 to 3 percent.

14. A process as defined in claim 5 wherein SO₂ is at a concentration from 0.1 percent to 2 percent, with the balance being Air.

15. A process as defined in claim 14 wherein said SO₂ is at a concentration from 0.2 to 1.4 percent.

16. A process as defined in claim 15 wherein SO₂ is at a concentration from 0.4 to 0.6 percent.
17. A process for removing a manganese constituent from a cobalt-bearing composition comprising the steps of:

- subjecting said composition to an oxidation mixture of SO₂ and oxygen, at conditions sufficient to oxidize said manganese constituent and at a pH sufficient to precipitate manganese while minimizing precipitation of cobalt; and

- hydrolyzing said manganese constituent.

18. A process as defined in claim 17 wherein said pH is between 2 and 3.5

19. A process as defined in claim 18 wherein said pH is between 2.8 and 3.3.

20. A process as defined in claim 19 wherein said pH is 3.

21. A process of removing iron and manganese constituents from a cobalt-bearing solution comprising the steps of:

(a) converting substantially all of said iron to an Fe³⁺ valence state;

(b) precipitating said iron from solution, while leaving substantially all of said manganese and cobalt in solution; and thereafter

(c) converting substantially all of said manganese to an Mn⁺⁺ state;

(d) precipitating said manganese from solution, while leaving substantially all of said cobalt in solution.

22. A process as defined in claim 21 wherein step (a) includes subjecting said solution to an
oxidation mixture of SO₂ and oxygen at conditions sufficient to oxidize said iron constituent.

23. A process as defined in claim 22 wherein step (a) includes maintaining the pH between 2.0 and 3.5.

24. A process as defined in claim 23 wherein the pH is between 2.8 and 3.3

25. A process as defined in claim 24 wherein said pH is 3.

26. A process as defined in claim 21 wherein step (c) includes subjecting said solution to an oxidation mixture of SO₂ and oxygen at conditions sufficient to oxidize said iron constituent.

27. A process as defined in claim 26 wherein step (c) includes maintaining the pH between 2.0 and 3.5.

28. A process as defined in claim 27 wherein the pH is between 2.8 and 3.3

29. A process as defined in claim 28 wherein said pH is 3.

30. A process of removing iron and manganese impurities from a cobalt solution, comprising the steps of:

(a) reacting the solution with an oxidation mixture of SO₂ and oxygen at a pH sufficient to oxidize the iron impurity, while leaving the manganese impurity and the cobalt in a substantially unreacted state;

(b) precipitating the iron impurity from solution, and thereafter
(c) reacting the solution with an oxidation mixture of SO₂ and oxygen at a pH sufficient to oxidize the manganese impurity, while leaving the cobalt in a substantially unreacted state;

(d) precipitating said iron impurity from solution, wherein substantially all of said cobalt remains in solution.

31. A process as defined in claim 20 wherein the pH of step (a) is between 2.0 and 3.5.

32. A process as defined in claim 31 wherein the pH is between 2.8 and 3.3.

33. A process as defined in claim 32 wherein said pH is 3.

34. A process as defined in claim 30 wherein steps (a) and (c) include the step of establishing SO₂ in solution by sparging SO₂ gas there through.

35. A process as defined in claim 30 wherein steps (a) and (c) include the step of establishing SO₂ in solution by mixing a metabisulphite therewith.

36. A process as defined in claim 30 wherein steps (a) and (c) include the step of establishing SO₂ in solution by mixing H₂SO₃ therewith.
**FIG. 1**

DECOPPERIZED Co SOLUTION

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PURIFIED Co SOLUTION (TO SX OR EW)

**FIG. 2**

Co SOLUTION (IMPURE)

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<th>Fe HYDROLYSIS</th>
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Co SOLUTION

**SUBSTITUTE SHEET (RULE 26)**
Co SOLUTION (pH = 2.8) 60 L/h

Fe OXIDATION

SO₂/AIR
CaCO₃

65°C
pH = 2.8
TOTAL 2 HOURS

Fe / Al
PRECIPITATION

CaCO₃

65°C
2 HOURS

Cu PRECIPITATION

NaSH

65°C
5 MIN

RESIDUE (DISPOSAL)

L S

Mn OXIDATION

SO₂/AIR
CaCO₃

60°C
2 HOURS
pH = 2.2

NEUTRALIZATION

CaCO₃

pH = 3.8
0.5 HOUR

L S

Mn CAKE

PURIFIED Co SOLUTION

FIG. 5

SUBSTITUTE SHEET (RULE 26)
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
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<td>Y</td>
<td>US 2 816 819 A (A.E. WALLIS ET AL.) 17 December 1957 (1957-12-17) cited in the application the whole document</td>
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<td>US 3 685 965 A (KNIPRATH ELMAR) 22 August 1972 (1972-08-22) column 1, line 15 - line 36; claims 1,2,4; examples 3,4</td>
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Further documents are listed in the continuation of box C.

Special categories of cited documents:

*A* document defining the general state of the art which is not considered to be of particular relevance

*E* earlier document but published on or after the international filing date

*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

*O* document referring to an oral disclosure, use, exhibition or other means

*P* document published prior to the international filing date but later than the priority date claimed

*Y* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

*H* document member of the same patent family

Date of the actual completion of the international search: 11 August 2000

Date of mailing of the international search report: 22/08/2000

Name and mailing address of the ISA

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Tel. (+31-70) 940-2040, Tx. 31 851 epo nl
Fax: (+31-70) 340-3016

Authorized officer

Bombeke, M
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