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(54) **PROCESS FOR THE RECOVERY OF METALS FROM COBALT-BEARING MATERIALS**

VERFAHREN ZUR RÜCKGEWINNUNG VON METALLEN AUS KOBALTHALTIGEN MATERIALIEN  
PROCÉDÉ DE RÉCUPÉRATION DE MÉTAUX À PARTIR DE MATÉRIAUX CONTENANT DU  
COBALT

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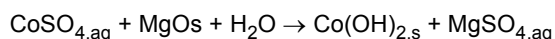
## Description

[0001] The present disclosure concerns a process for the recovery of cobalt from cobalt-bearing materials.

[0002] The rising demand for electric vehicles has initiated the booming of the lithium ion battery market. Cobalt and nickel are some of the most important metals that are used for the production of these rechargeable batteries, and the demand for these metals is therefore also growing fast.

[0003] Approximately half of the world's cobalt reserves are located in the African Copper belt which straddles the border of Zambia and the Democratic Republic of Congo. In this region, cobalt is made available as a by-product of the copper industry: the ore deposits typically contain 4-5% copper, while only 0.2-0.4% cobalt is present. The cobalt recovery plants usually get their feed from a bleed of the copper refining circuits. Bleed streams typically contain a few grams per liter of cobalt, and some nickel, together with a number of impurities that are, to a certain extent, removed on-site by means of a neutralization step. The resulting cobalt-bearing products are the so-called Mixed Hydroxide Precipitates (MHP).

[0004] The production of MHP is state of the art throughout the African Copper belt. In most cases, milk of magnesia (MgO) is used for the precipitation of cobalt hydroxide, according to the reaction:



[0005] In practice, MHP obtained according to the above reaction typically also contain basic sulfates and partially oxidized species, such as oxy-hydroxides, of the precipitated metals. Aside from cobalt, they may contain appreciable quantities of nickel, copper, or of other valuable metals.

[0006] The MHP are usually transported to specialized plants for the purification and recovery of the contained valuable metals.

[0007] In rare occasions, lime (CaO) precipitation is used instead of magnesia. The MHP are then however diluted with gypsum, which in turn leads to higher transportation and treatment costs, and additional purification requirements.

[0008] The precipitation with magnesia is however not without disadvantages. The obtained MHP are usually contaminated with a significant amount of magnesium. The presence of magnesium in the precipitate has a deleterious effect on the downstream refining flowsheet, in particular with respect to the production of high-purity cobalt salts, hydroxides or metal.

[0009] In most cases, critical purity requirements are dictated by the battery industry, which is absorbing a growing percentage of the global cobalt production. Because of these purity requirements, intricate processing routes have been developed, involving for example selective precipitation, solvent extraction and ion exchange. Most of these routes are rendered even more complex and expensive when they have to cope with the interference of magnesium.

[0010] Nevertheless, a few processes are known wherein magnesia is separated upfront of the refining steps. This approach avoids the interference of magnesium during the cobalt refining.

[0011] US2009249921A1 teaches slagging of magnesia in cobalt-nickel compounds using slag compositions based on silica/lime or silica/alumina. The process is limited to the solid state reduction of metals, a process also known as direct reduction. A subsequent melting operation is optionally performed for the purpose of separating the alloy from the slag.

[0012] WO2009100495 teaches a bath smelting process for nickel products, producing molten nickel, by controlling the chemistry of the slag so as to have a high solubility for contaminants present in the nickel product. Contaminants are defined as magnesium, calcium, cobalt, copper, manganese, silicon, sulfur, phosphorus, and aluminum in elemental form and as compounds.

[0013] The process according to the present invention also realizes the upfront separation of magnesia. But in contrast to the prior art, the invention allows for the simultaneous valorization of cobalt, and of nickel if present, in a molten metallic phase, while collecting the magnesia in a slag.

[0014] To this end, a process has been developed for the recovery of metals from a metal-bearing material containing, in oxidized form, more than 1% Co, a total of Co and Ni of more than 15%, and more than 1% Mg, comprising the steps of:

- smelting said metal-bearing material in a bath furnace together with slag formers, thereby producing an alloy phase with more than 80%, preferably more than 90% of the Co, and less than 1% of the Mg, and a slag phase, by applying reducing smelting conditions, and by selecting CaO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> as slag formers, in amounts so as to obtain a final slag composition according to the ratio's  $0.25 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 2.5$ ,  $0.5 < \text{SiO}_2/\text{CaO} < 2.5$ , and to  $\text{MgO} > 10\%$ ; and,
- separating the alloy phase from the slag phase.

[0015] All percentages are expressed by weight, after drying at 120 °C.

[0016] By "metal-bearing material in oxidized form" is meant that the metals therein are in an oxidation state higher than zero.

**[0017]** During the smelting process, Co and Ni will be collected in the alloy, while Mg will be concentrated in the slag as MgO, where after these phases are separated, e.g. by selective tapping after settling.

**[0018]** The skilled person knows how to obtain the required reducing smelting conditions, namely by the addition of a sufficient amount of reducing agents such as, but not limited to, natural gas, oil, and coal. Highly reducing conditions whereby Si starts to report to the alloy are not to be favored as the presence of Si in the alloy may complicate the Co purification process.

**[0019]** The minimum concentration of 1% Co is preferred to ensure the economical worthiness of the recovery process. Lower Co contents would render the Co-Mg interference problem less relevant as there would be insufficient economic incentive to recover and refine the Co from those materials.

**[0020]** A minimum concentration of 15% for the total of Co and Ni is preferred as this will generate a sufficient quantity of alloy during the smelting operation to allow for easy selective tapping metal-bearing material. Typical MHP contain this level of metals.

**[0021]** The process is characterized by a Co yield to the alloy of more than 80% in particular when dealing with materials with relatively low Co content, or of more than 90% in particular when dealing with materials with higher Co contents. The above-mentioned reducing conditions allow for such yields to be achieved without inducing the undesired reduction of Si. Under such conditions, less than 1% of the Mg reports to the alloy. Mg in the alloy is thus essentially avoided, as more than 99% of the Mg reports to the slag.

**[0022]** Depending on the technology used to feed the metallurgical charge to the furnace, a small fraction of the materials may be directly entrained by the off gases leaving the furnace. This fraction, if present, never reaches the molten bath, effectively bypassing the smelting step. This fraction is therefore not accounted for when considering the yields of Mg and of Co.

**[0023]** The proposed quaternary system of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ - $\text{CaO}$ - $\text{MgO}$  is selected so as to obtain a slag with a relatively low viscosity. When a slag composition is chosen in such a way that its viscosity is below 1500 cP, fragmented material can then be fed directly to the bath, as it will be readily wetted and incorporated into the slag. Charge pre-treatment steps like adding a binder to form agglomerates are then made unnecessary.

**[0024]** When using the proposed quaternary slag system, an MgO concentration in the slag of more than 10% can be reached. The higher the MgO concentration in the slag, the less amount of slag is needed to dissolve a given quantity of MgO. Metal losses in the slag are therefore lower.

**[0025]** Even more preferred slag compositions are those containing less than 35 % of CaO as this improves the kinetics of the MgO dissolution in the slag.

**[0026]** In a further embodiment, the metal-bearing material comprises MHP. The most valuable metals therein are Co and Ni. Other elements are present, but are considered as impurities.

**[0027]** In a further embodiment, the smelting step is the only smelting step of a complete Co valorization process starting from MHP.

**[0028]** Limiting the valorization process to a single smelting step is desirable for economic reasons. By smelting step is meant a pyro-metallurgical process such as calcining, roasting, smelting, and refining, performed at high temperatures. In this context, high temperatures are temperatures precluding the presence of liquid water. By complete Co valorization process is meant the process starting from MHP and ending with a Co compound having a degree of purity compatible with its intended use.

**[0029]** In a further embodiment, the process additionally comprises a step of granulation or atomization of the alloy phase.

**[0030]** Granulation, and preferably atomization, is indeed useful to enhance the kinetics of the leaching step that would typically be needed when performing the refining steps using hydrometallurgical unit operations.

**[0031]** In a further embodiment, the metal-bearing material is obtained according to a process comprising the steps of:

- feeding Co-bearing ores or concentrates to a leaching reactor;
- leaching the ores or the concentrates in acidic conditions, thereby obtaining a Co-bearing mother liquor;
- precipitating Co from the mother liquor by using MgO, thereby obtaining a metal-bearing material containing, in oxidized form more than 1% Co, and more than 1% Mg.

**[0032]** The process of the separation of the MgO from MHP is indeed most suitably combined with the upfront processes leading to such MgO-contaminated MHP.

**[0033]** In a further embodiment, the process comprises the further steps of:

- leaching the granulated or atomized alloy phase in acidic conditions, thereby obtaining a Co-bearing leach solution;
- purifying the leach solution by extracting or removing impurities from the solution, thereby obtaining a purified solution;
- recovering Co from the purified solution.

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**[0034]** The present process, when including the step of granulating or atomizing the alloy, is most suitable for the further valorization of the contained cobalt using hydrometallurgical techniques. Indeed, thanks to the absence of Mg, less impurities must be extracted or otherwise removed from the Co-bearing solution. This contrast with the situation where Mg would be present in solution, as the only practical purification scheme then involves the selective extraction of the cobalt from the solution, which is a much more complicated and expensive process.

### Example

**[0035]** Mixed hydroxide precipitates (MHP) typically contain 50% or more of free moisture. Partial drying is needed before feeding such materials to a smelting furnace. The MHP are thus first dried to a moisture content of about 20%. Drying to lower moisture levels is not recommended as this would render the product too dusty for safe handling.

**[0036]** The composition of the MHP used as a starting product is shown in Table 1. The composition is expressed w.r.t. to product dried at 120 °C.

Table 1: Composition of MHP

INPUT (wt.%)	Al	Si	Ca	Mg	Fe	Co	Cu	Ni
MHP	0,02	1,2	0,0	4,6	0,0	40,2	0,7	0,1

**[0037]** A mixture is prepared consisting of 1000 g MHP, 360 g cokes, 400 g ferro slag, and 100 g Al<sub>2</sub>O<sub>3</sub> as fluxing agent. No pretreatment such as agglomeration or the use of binders is involved. The ferro slag is of the commonly available type produced in the blast furnace of ironmaking processes.

**[0038]** The mixture is melted in a boron nitride coated alumina crucible with a volume of 1 L. A temperature of 1500 °C is maintained using an induction furnace. When melted, 4 stepwise additions of 100 g MHP are made to the crucible.

**[0039]** Once all material is added, a fixed oxygen partial pressure is enforced by blowing a mixture of 130 l/h of CO and 6 l/h for 1 h into the bath. This results in the establishment of a proper equilibrium redox potential (pO<sub>2</sub>). The skilled person will easily achieve the same redox potential at industrial scale using other commonly available reducing agents such as natural gas, oil, and coal.

**[0040]** After this, the melt is allowed to decant for 15 minutes. The good fluidity of the slag allows for an efficient decantation, i.e. without residual alloy droplets floating in the slag. After cooling, an alloy-slag phase separation is performed manually whereupon both phases are analyzed.

**[0041]** A detailed material balance is provided in Table 2.

Table 2: Detailed material balance of the smelting operation

Input (wt.%)	Mass (g)	Al	Si	Ca	Mg	Fe	Co	Cu	Ni
MHP	1400,0	0,02	1,2	0,0	4,6	0,0	40,2	0,7	0,1
Slag	400,00	3,1	16,0	24,7	3,9	2,7	0,0	0,8	0,2
Al <sub>2</sub> O <sub>3</sub>	100,00	52,9	0,0	0,0	0,0	0,0	0,0	0,0	0,0
Input (g)	Mass (g)	Al	Si	Ca	Mg	Fe	Co	Cu	Ni
MHP	1400,0	0,2	16,2	0,0	64,1	0,6	562,3	9,9	1,1
Slag	400,0	12,2	64,0	98,6	15,6	10,9	0,0	3,2	0,8
Al <sub>2</sub> O <sub>3</sub>	100,0	52,9	0,0	0,0	0,0	0,0	0,0	0,0	0,0
Total	1900,0	65,3	80,3	98,6	79,7	11,4	562,3	13,1	1,9
Output (wt.%)	Mass (g)	Al	Si	Ca	Mg	Fe	Co	Cu	Ni
Alloy	650,0	0,0	0,0	0,0	0,0	1,1	93,5	1,9	0,3
Slag	660,0	10,0	12,1	15,1	11,0	0,5	1,1	0,0	0,0
Water	590,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0

(continued)

Output (g)	Mass (g)	Al	Si	Ca	Mg	Fe	Co	Cu	Ni
Alloy	650,0	0,0	0,2	0,0	0,0	7,2	607,8	12,4	2,0
Slag	660,0	66,0	79,9	99,7	72,6	3,3	7,3	0,3	0,0
Water	590,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
Total	1900,0	66,0	80,0	99,7	72,6	10,5	615,0	12,6	2,0
Distribution (wt.%)	Mass (g)	Al	Si	Ca	Mg	Fe	Co	Cu	Ni
Alloy	34,2	0,0	0,2	0,0	0,0	68,4	98,8	97,8	99,9
Slag	34,7	100,0	99,8	100,0	100,0	31,6	1,2	2,2	0,1
Total	68,9	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0

**[0042]** The slag has a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 0.7, and a  $\text{SiO}_2/\text{CaO}$  ratio of 1.2. The Mg and Ca concentrations of respectively 11% and 15% correspond to 18.2% of MgO and 21.1% of CaO.

**[0043]** The Co yield to the alloy amounts to 98.8 %, while the Mg yield to the slag amounts to 100 %. An Mg free alloy is thus obtained.

## Claims

1. Process for the recovery of metals from a metal-bearing material containing, in oxidized form, more than 1% Co, a total of Co and Ni of more than 15%, and more than 1% Mg, comprising the steps of:

- smelting said metal-bearing material in a bath furnace together with slag formers, thereby producing an alloy phase with more than 80%, preferably more than 90% of the Co, and less than 1% of the Mg, and a slag phase, by applying reducing smelting conditions, and by selecting  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  as slag formers, in amounts so as to obtain a final slag composition according to the ratio's  $0.25 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 2.5$ ,  $0.5 < \text{SiO}_2/\text{CaO} < 2.5$ , and to  $\text{MgO} > 10\%$ ; and,
- separating the alloy phase from the slag phase.

2. Process according to claim 1, wherein the metal-bearing material comprises MHP.

3. Process according to claim 2, wherein the smelting step is the only smelting step of a complete Co valorization process starting from MHP.

4. Process for the recovery of metals from the metal-bearing material according to any one of claims 1 to 3, further comprising a step of granulation or atomization of the alloy phase.

5. Process for the recovery of metals from the metal-bearing material according to any one of claims 1 to 4, whereby the metal-bearing material is obtained according to a process comprising the steps of:

- feeding Co-bearing ores or concentrates to a leaching reactor;
- leaching the ores or the concentrates in acidic conditions, thereby obtaining a Co-bearing mother liquor;
- precipitating Co from the mother liquor by using  $\text{MgO}$ , thereby obtaining a metal-bearing material containing, in oxidized form, more than 1% Co, and more than 1% Mg.

6. Process according to any one of claims 1 or 5, comprising the further steps of:

- leaching the granulated or atomized alloy phase in acidic conditions, thereby obtaining a Co-bearing leach solution;
- purifying the leach solution by extracting or removing impurities from the solution, thereby obtaining a purified solution;

- recovering Co from the purified solution.

## Patentansprüche

1. Verfahren für die Rückgewinnung von Metallen aus einem metallhaltigen Material, das in oxidierter Form mehr als 1 % Co, insgesamt mehr als 15 % Co und Ni und mehr als 1 % Mg enthält, umfassend die Schritte:

- Einschmelzen des metallhaltigen Materials in einem Wannenofen zusammen mit Schlackenbildnern, wodurch durch Anwenden reduzierender Einschmelzbedingungen und durch Auswählen von CaO, SiO<sub>2</sub> und Al<sub>2</sub>O<sub>3</sub> als Schlackenbildner in Mengen, um eine endgültige Schlackenzusammensetzung gemäß des Verhältnisses  $0,25 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 2,5$ ,  $0,5 < \text{SiO}_2/\text{CaO} < 2,5$  und  $\text{MgO} > 10 \%$  zu erhalten, eine Legierungsphase mit mehr als 80 %, vorzugsweise mehr als 90 % des Co und weniger als 1 % des Mg, und eine Schlackenphase erzeugt wird; und

- Trennen der Legierungsphase von der Schlackenphase.

2. Verfahren nach Anspruch 1, wobei das metallhaltige Material MHP umfasst.

3. Verfahren nach Anspruch 2, wobei der Einschmelzschritt der einzige Einschmelzschritt eines vollständigen Co-Valorisierungsverfahrens ist, der von MHP ausgeht.

4. Verfahren für die Rückgewinnung von Metallen aus dem metallhaltigen Material nach einem der Ansprüche 1 bis 3, ferner umfassend einen Schritt der Granulation oder Atomisierung der Legierungsphase.

5. Verfahren für die Rückgewinnung von Metallen aus dem metallhaltigen Material nach einem der Ansprüche 1 bis 4, wobei das metallhaltige Material gemäß einem Verfahren erhalten wird, umfassend die Schritte:

- Zuführen von Co-haltigen Erzen oder Konzentraten an einen Auslaugungsreaktor;

- Auslaugen der Erze oder der Konzentrate unter sauren Bedingungen, wodurch eine Co-haltige Mutterlauge erhalten wird;

- Ausfällen von Co aus der Mutterlauge unter Verwendung von MgO, wodurch ein metallhaltiges Material erhalten wird, das in oxidierter Form mehr als 1 % Co und mehr als 1 % Mg enthält.

6. Verfahren nach einem der Ansprüche 1 bis 5, umfassend die weiteren Schritte:

- Auslaugen der granulierten oder atomisierten Legierungsphase unter sauren Bedingungen, wodurch eine Co-haltige Auslauglösung erhalten wird;

- Reinigen der Auslauglösung durch Extrahieren oder Entfernen von Verunreinigungen aus der Lösung, wodurch eine gereinigte Lösung erhalten wird;

- Rückgewinnung von Co aus der gereinigten Lösung.

## Revendications

1. Procédé de récupération de métaux à partir d'un matériau métallifère contenant, sous sa forme oxydée, plus d'1 % de Co, un total de Co et Ni de plus de 15 % et plus d'1 % Mg, comprenant les étapes suivantes :

- faire fondre ledit matériau métallifère dans un four à bain avec des formateurs de scorie, produisant ainsi une phase d'alliage avec plus de 80 %, et de préférence avec plus de 90 %, de Co, et moins d'1 % de Mg, ainsi qu'une phase de scorie, en appliquant des conditions de fusion réductrice, et en choisissant CaO, SiO<sub>2</sub> et Al<sub>2</sub>O<sub>3</sub> comme formateurs de scorie, dans des quantités permettant d'obtenir une composition finale de la scorie conformément aux ratios  $0,25 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 2,5$ ,  $0,5 < \text{SiO}_2/\text{CaO} < 2,5$ , et à  $\text{MgO} > 10 \%$  ; et

- séparer la phase d'alliage de la phase de scorie.

2. Procédé selon la revendication 1, où le matériau métallifère contient du MHP.

3. Procédé selon la revendication 2, où l'étape de fusion est la seule étape de fusion d'un procédé de valorisation complète du Co commençant par le MHP.

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4. Procédé de récupération de métaux à partir d'un matériau métallifère selon l'une des revendications 1 à 3, comprenant par ailleurs une étape de granulation ou d'atomisation de la phase d'alliage.

5. Procédé de récupération de métaux à partir d'un matériau métallifère selon l'une des revendications 1 à 4, où le matériau métallifère est obtenu conformément à un procédé comprenant les étapes :

- d'alimentation d'un réacteur de lixiviation avec des minerais ou des concentrés contenant du Co ;
- de lixiviation des minerais ou des concentrés en conditions acides, obtenant ainsi une liqueur mère contenant du Co ;
- de précipitation de Co à partir de la liqueur mère en utilisant du MgO, obtenant ainsi un matériau métallifère contenant, sous sa forme oxydée, plus de 1 % Co et plus de 1 % Mg.

6. Procédé selon l'une des revendications 1 ou 5, comprenant également les étapes :

- de lixiviation de la phase d'alliage granulée ou atomisée en conditions acides, obtenant ainsi une solution lixiviée contenant du Co ;
- de purification de la solution lixiviée en extrayant ou en éliminant les impuretés de la solution, obtenant ainsi une solution purifiée ;
- de récupération de Co à partir de la solution purifiée.

**REFERENCES CITED IN THE DESCRIPTION**

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