

COBALT SALTS PRODUCTION BY USING SOLVENT EXTRACTION

Liudmila V. Dyakova*, Aleksander G. Kasikov, Elena S. Kshumaneva,
Svetlana V. Drogobuzhskaya

*I.V. Tananaev Institute of Chemistry and Technology of Rare Elements and Mineral Raw Materials of Kola Science
Centre of Russian Academy of Science, 26a, Fersman str., Apatity, Murmansk reg., 184209, Russia
e-mail: dyakova@chemy.kolasc.net.ru, phone: +7(81555)79160, fax: +7(81555)79653

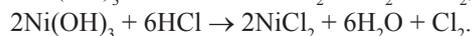
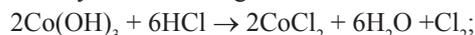
Abstract: The paper deals with the extracting cobalt salts by using mixtures on the basis of tertiary amine from multicomponent solutions from the process of hydrochloride leaching of cobalt concentrate. The optimal composition for the extraction mixture, the relationship between the cobalt distribution coefficients and modifier's nature and concentration, and the salting-out agent type have been determined. A hydrochloride extraction technology of cobalt concentrate yielding a purified concentrated cobalt solution for the production of pure cobalt salts has been developed and introduced at Severonikel combine.

Keywords: cobalt, solvent extraction, tertiary amines, salting-out, octanoic acid.

Introduction

Cobalt is a strategic element widely applied both in the form of a high-quality metal and pure salts. In Russia, cobalt is produced from cobalt concentrates resulting from the copper-nickel ore processing [1]. One of the major producers of cobalt in Russia is Severonikel combine of the Kola Mining and Metallurgical Company, where the cobalt concentrates contain, w/o: Co – 45-46; Ni – 2-4; Fe – 3.5-5; Cu – 0.1-1.0; Mn – 0.1-0.3; Pb – 0.1-0.5; SO₄ – 5-10, and also trace amounts of As, Pb, Zn, SiO₂.

Separating cobalt from impurities involves preliminary dissolution of cobalt concentrate in, for instance, hydrochloric acid. The peculiar feature of this reaction is that dissolving of Co(III) and Ni(III) hydrate concentrates is accompanied by evolution of gaseous chlorine:



Since the reactive gaseous chlorine has to be utilized, this complicates the process.

The solvent extraction hydrochloride technology of cobalt concentrates developed and introduced at the Institute of Chemistry KSC RAS and introduced at Severonikel Combine, incorporates digestion of the concentrate in the presence of a solid-phase reducer, preventing chlorine evolution at the leaching stage and providing a fast and safe transition of cobalt and impurity elements to solution [2]. The resulting concentrated multicomponent chloride solutions can be effectively processed by an advanced, easily controllable and automated method, i.e. solvent extraction. The non-ferrous metals and iron, contained in solution, form complex MeCl_2^- , MeCl_3^- , MeCl_4^{2-} anions of varying stability and, consequently, can be extracted by anion-exchanging extracting agents, for instance, by tertiary amines Fig.1 [3].

This work discusses cobalt extraction by mixtures based on tertiary amine from multicomponent solutions resulting from hydrochloride leaching of cobalt concentrate of a quality sufficient for producing pure cobalt salts.

Result and discussion

Creating of an efficient pattern enabling to process multicomponent solutions after cobalt concentrate digesting has involved a quest for the optimal composition of the extraction mixture and studying of the effect of the salt background nature and concentration on cobalt extraction.

In many cases, extracting elements with tertiary amines makes one resort to modifiers enhancing the solubility of extracted components in the extracting phase, facilitating phase stratification, and reducing the amine viscosity (spirits, ketones, tributylphosphate, etc.) [4].

In practice, the easiest commercial available modifiers are synthetic fatty alcohols. It is known, however, that alongside with increasing the metal complex solubility in the organic phase, alcohols inhibit extraction due to the process of salvation. Quite the reverse with ketones, which facilitate the extracting agent interaction with the metal anion complex, thus increasing the extraction degree. Notwithstanding the fact that ketone modifiers contribute to achieving higher cobalt distributions coefficients, their application is limited due to their high solubility in solution. Therefore we recommend octyl alcohol as modifier for the organic mixture based on tertiary amine.

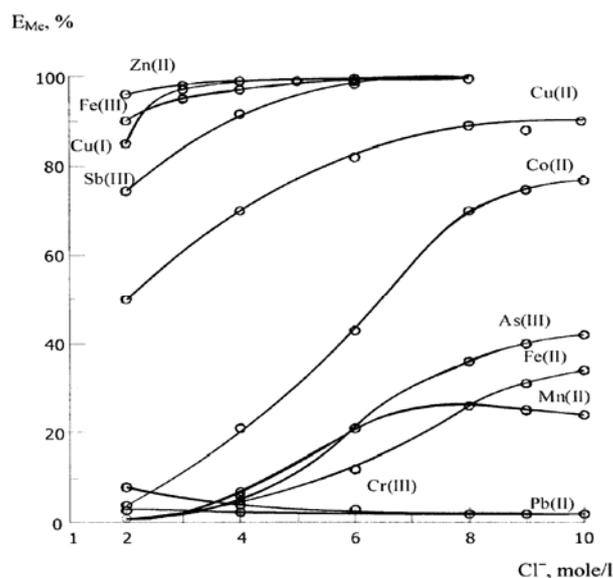


Fig. 1. Plots of metals recovery level vs. $[Cl^-]$ concentration.

Our experiments, taking into account the time of phases mixing and separation, and distribution coefficients, have led us to propose an organic mixture of the following composition, % v/v: (30-35) TAA + (10-20) long-chain aliphatic alcohol, the rest being a diluent.

During the solvent extraction from multi-component solutions of the target component (cobalt in our case) its extraction may be affected by different metal salts. Sometimes the components proper of the salt background are not extracted but, nevertheless, seriously affect the extraction of other elements. This is due to the fact that the activity of both water and other solution components may be changing due to the nature and concentration of the salting-out agent. The process may be occurring either way: increasing of the element distribution coefficient (salting-out) or decreasing one (salting-in) [5, 6]. In this connection, we have studied the impact of the nature and concentration of a large number of metal chlorides on cobalt extraction by organic mixtures based on tertiary amines.

It has been found that the cobalt distribution coefficient is affected both by salting-out agent concentration and nature or, to be more exact, the cation radius and its charge [7]. This is due to the cation ability to bind various water quantities in their hydrate shells, which changes the share of water able to solvate the metal compound being extracted.

The desalinating action of cations can be formulated thus: the lower the level of salting-out agent hydration, the greater the water activity and the lower the active concentration of dissolved substance. So, hydrating of salting-out agent ions will be diminishing the quantity of free water and increasing the activity of $CoCl_2$ ions. To put it differently, the diminishing free water concentration will promote the growth of chlorine ions concentration, facilitating the formation of an anion, readily extractable complex, $CoCl_4^{2-}$. Comparing the chlorides investigated according to their salting-out ability, it is evident that they can be arranged in the following series:



Notwithstanding the fact that H^+ is also highly hydrated in aqueous solutions, the degree of cobalt extraction from HCl is considerably lower than from most of the salt solutions. The reason for it is that the tertiary amine chlorides can additionally extract hydrochloric acid inhibiting the $CoCl_4^{2-}$ extraction. At a later stage, the nickel-containing cobalt solutions were processed using nickel chloride, in which case no extra reagents are needed.

The research has resulted in developing, large-scale testing and introducing of a solvent extraction hydrochloride technology of cobalt concentrate at Severonikel Combine Fig.2.

After starting the plant, we solved the problem of separating cobalt from the bulk of impurities and produce fairly pure chloride solutions from which cobalt carbonate was further precipitated.

At the first stage, by precipitating cobalt carbonate from re-extracts, products containing less than 0.1% of impurity non-ferrous metals and iron were obtained. However, their quality was inferior because of the presence of 0.5% residual sodium and chlorine, unremovable by washing with water. Therefore we looked into the impact exerted by the nature of precipitator and precipitation conditions on the level of sodium and chlorine ions' entering into the structure of carbonate precipitates.

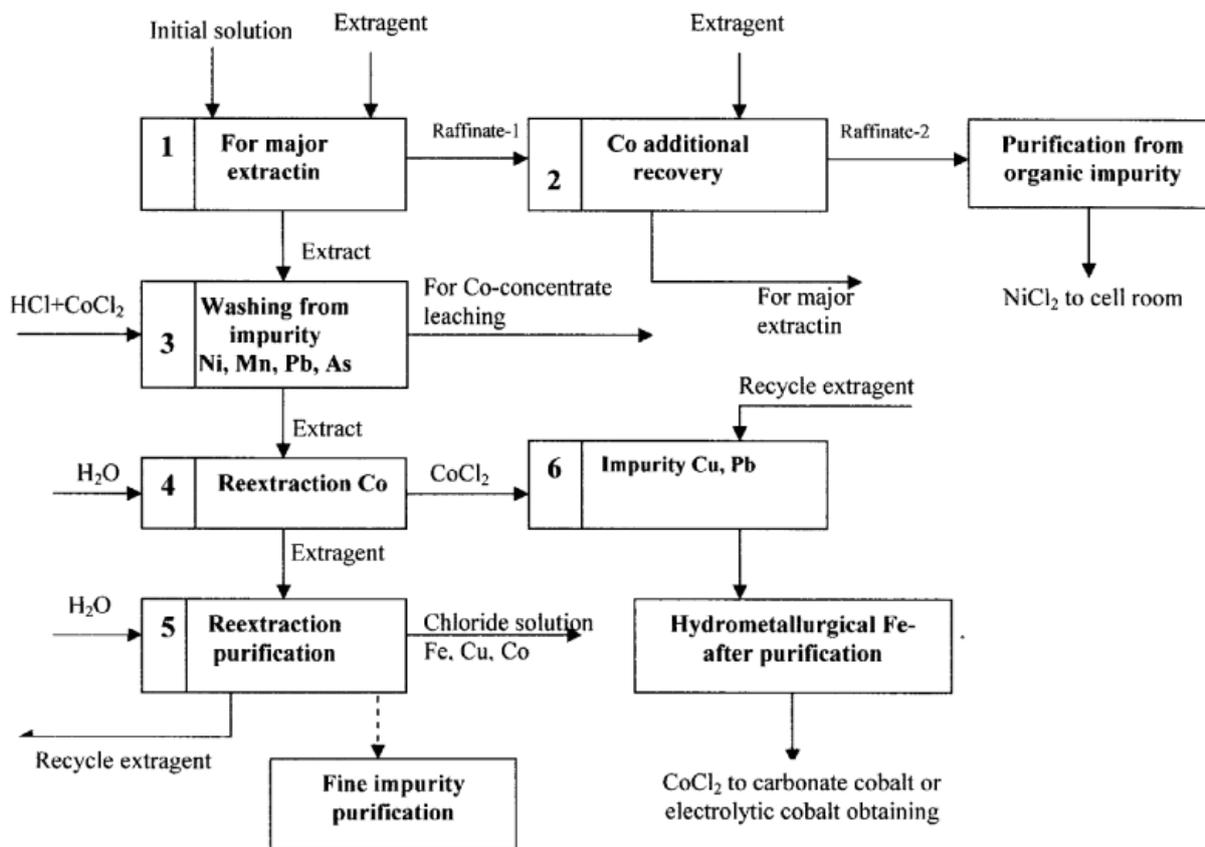


Fig. 2. Principle diagram of Co extraction at Severonikel combine.

In particular, the first parameters to be investigated were the effect of the ratio between the precipitator (Na_2CO_3 , NaHCO_3 and CoCl_2), initial CoCl_2 concentration, temperature, duration and order of reagent feeding, and also exposure of the precipitate formed in the mother liquor, and the structure and composition of forming precipitates. It was discovered that the main prerequisite for minimizing the chlorine content in precipitates (0.01% w/o) is duration and order of reagent feeding.

Slow feeding of soda solution to cobalt chloride solution creates a stable deficit of CO_3^{2-} ions with resulting precipitates containing up to 4.6% of structural chlorine unremovable by water. In the case of reverse slow adding of cobalt chloride solution to a vigorously stirred Na_2CO_3 solution, the process occurs under an excess of carbonate ions preventing the chlorine from entering into the structure.

At the same time, the excess of carbonate ions in solutions should not be too high, since it may promote the formation of $[\text{Co}(\text{CO}_3)]^{2-}$ anion complexes interacting with sodium cations to form a hardly soluble salt, $\text{Na}_2[\text{Co}(\text{CO}_3)]$, which explains why a part of sodium can be removed from cobalt carbonate.

Based on these studies, we developed a method [8] for the production of basic cobalt carbonate, yielding a salt containing not less than 0.05% of sodium and chlorine. Currently the Severonikel Combine has manufactured several thousand tons of paste and dry cobalt carbonate.

Besides the basic cobalt concentrate, the chloride solutions with limited impurity contents can be used in the production of other cobalt salts such as acetate, nitrate and sulphate. From the viewpoint of economic and technological efficiency, an attractive method is that of extraction conversion, which consists in extracting of cobalt from chloride solution using a cation-exchange extracting agent followed by re-extracting with respective acids to target salts.

Table 1

Composition of high-purity cobalt salts obtained from cobalt chloride solutions

Element	Content, ppm			
	hydroxide	dichloride	acetate	carbonate
Co	base	base	base	Base
Ni	20	20	30	30
Cu	0.6	0.9	1	0.8
Fe	10	10	10	20
Mn	0.5	2	1	0.9
Si	<7	5	<2	5
Bi	<0.1	<0.1	<0.1	<0.1
Sb	<0.5	<0.5	<0.5	1
Sn	<0.1	<0.1	<0.1	0.5
Pb	0.2	0.1	0.1	0.1
Zn	1	0.5	0.2	2
P	<0.5	<0.5	<0.5	-
Mg	2	1	0.5	5
Te	<0.1	<0.1	<0.1	<0.1
Tl	<0.01	<0.01	<0.01	<0.01
Na	15	10	2	100
Ca	15	10	2	200

The possibility of carrying out the method of cation-exchange solvent extraction conversion in continuous regime was tested at a laboratory cascade, when cobalt was extracted from a chloride solution of the following composition, g/l: Co – 112; Ni – 0.01; Fe, Mn, Cu <0.005 with ammonium form of n-octanoic acid in Escaid 100 at four stages followed by a two-stage re-extraction with a 2 mole/l vinegar acid solution. The pattern of the experiment on the production of cobalt acetate solution at an extractor cascade with ammonium form of n-octanoic acid is presented in Fig. 3.

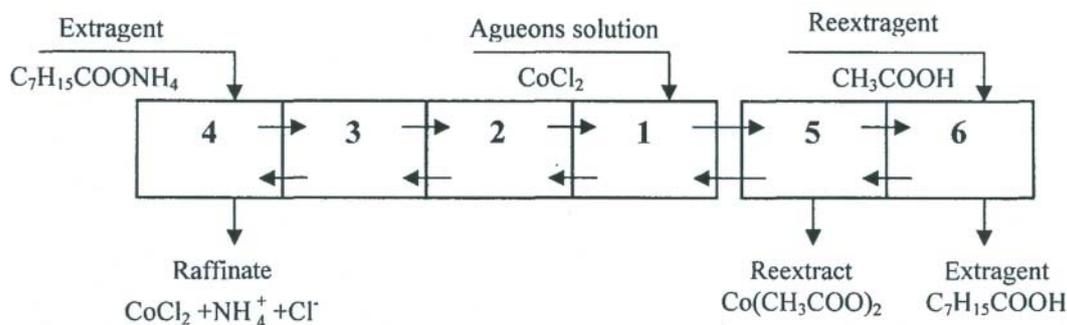


Fig. 3. Pattern of cobalt chloride extraction conversion to acetate at an extractor cascade.

The obtained cobalt acetate solution was filtered and evaporated. After cooling, the crystals were separated at a nutsch filter and dried under vacuum by gradually increasing the temperature to 100°C. The content of impurities in the salt is given in Table 1.

The impurity elements were determined by mass spectrometry in induction-bound argon plasma (MS IBP) on ELAN 9000 DRG-e (Perkin Elmer, USA). The method was developed at the Institute of Chemistry Laboratory of chemical and optic methods of analysis.

The same method is applied to cation-exchange extraction conversion of cobalt chloride to nitrate, sulphate and other cobalt salts, which are important intermediate products for the synthesis of highly effective catalysts, solid electrolytes and capacitors. So, the method allows expanding the range of cobalt products.

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