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Evaluation of cobalt from zinc and cadmium electrolysis by-products

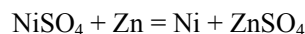
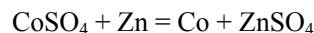
This work deals with testing the possibilities for enriching with cobalt the waste sludge from the production of electrolytic zinc and cadmium. Cobalt is present in zinc concentrates, as accompanying metal, in low concentrations (0,001-0,005%). During certain stages of hydrometallurgical zinc and cadmium production, cobalt is, however, concentrated up to commercially important values. In the cadmium production process, which is technologically connected with zinc production, the so called "cobalt purification cake" precipitate presents such a resource of cobalt. This precipitate contains 0,6-1% Co, 2-6% Cd, 40-55% Zn, 0,1-0,6% Ni, 0,1-0,7% Cu, 30-35% H₂O, etc. The metals present are leached from the fresh cobalt purification cake by a sulphuric acid solution (150g/dm³), with strict pH control of the reaction pulp, and as a result of this, a precipitate with a cobalt concentration of 6-12%, is obtained. Sulphates of the leached metals go back to the process, while precipitate with higher cobalt content ("cobalt-concentrate") can be used for various purposes. Starting from cobalt concentrate, CoO(OH), Co₂O₃, CoSO₄·7H₂O, ceramic pigments, etc, have been obtained.

Key words: production of electrolytic zinc and cadmium, cadmium production, zinc production, „cobalt purification cake“

INTRODUCTION

The raw material for cadmium production in most of Hydrometallurgical Zinc and Cadmium Plants is a zinc-sulphate solution purification cake. Purification of the zinc sulphate solution is done by zinc powder, whereby the metals that are electrically more positive than zinc fell as cement cake. The average composition of that cake is as follows: Zn - 40-60%, Cu - 10-16%, Cd - 2-10%, Co - 0,1%, H₂O - 30-35%. Apart from these elements, Pb, Fe, Ni, Sb, As, Ge, In, and others are presented in considerably lower amounts.

Obtaining cadmium from zinc-sulphate purification cake is a complex process consisting of many chemical, electrochemical and metallurgical operations [1, 2]. As a result of these processes, metal cadmium of high quality is obtained, and additionally, solution contains cobalt, nickel and other metal cations. Cobalt, besides many other metals, as it is already known, shows harmful effect on zinc electrolysis. All these metals (Cu, Co, Ni, Sb, etc.) have to be eliminated carefully from electrolyte solution by zinc powder cementation:



In order to recovery zinc, the solution released from cobalt and nickel sponges is included in Zinc Calcine Leaching Plant. The cake that consists of Co, Ni and following metals represents, so called, "cobalt purification cake".

The use of zinc concentrates of various origins and chemical compositions for zinc and cadmium production results in variable compositions of the by-products obtained in the process. That is why the raw material for cobalt concentrate production (cobalt purification cake) contains different quantities of cobalt and accompanying metals. The most frequent composition of cobalt purification cake is as follows: Co - 0,6-1%, Cd - 2-6%, Zn - 40-55%, Ni - 0,1-0,6%, Cu - 0,1-0,7%, H₂O - 30-35%, whereas antimony content are much lower and varies depending on type of zinc concentrate and, consequently, Zinc Calcine Leaching Plant operation.

According to mass balance studies in an average zinc factory (100.000t zinc annually), the cobalt purification cake accumulates annually between 6 and 8t of cobalt which means both considerable and cheap resource of cobalt [3]. Because

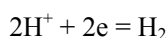
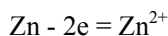
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of the high quantity of zinc in the cobalt purification cake, it has a remarkable commercial value, so some zinc producers return that cake in the process through Zinc Concentrate Roasting Plant, by mixing with zinc concentrate. Such a practice is, however, harmful because it leads to copper, cobalt and nickel revolving in the process.

This paper shows a different method of cobalt valuation from cobalt purification cake where cobalt is extracted from the process through commercially valuable enriched cobalt cake - cobalt concentrate, while considerable parts of present zinc and cadmium are returned in the process. The cobalt concentrate chemical treatment can obtain a large scale of useful products based on cobalt [4-6].

The principle of obtaining cobalt concentrate from cobalt purification cake is based on selective dissolution of accompanying metals from this cake by sulphuric acid, the tendency being, as little dissolved cobalt as possible. For this reason, fresh cobalt purification cake is used for the cobalt concentrate production in order to prevent cobalt oxidation by air. (Cobalt oxide is much easier dissolved by sulphuric acid solution than metal cobalt is [2, 6, 7]). Should a substantial oxidation of the cake occur, which is possible with air exposure, the process of accompanying metal selective dissolution induces an intensive, undesirable cobalt dissolution [8]. In that case, cobalt, as CoSO_4 , is converted into liquid phase, which leads to obtaining poorer cobalt concentrate.

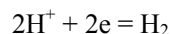
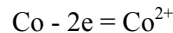
Sulphuric acid solution, in the leaching process, reacts upon cobalt purification cake. In that process, present metals are leached in different ways. In cobalt purification cake present metals are sponges, which originate from cementation reaction between corresponding ions and zinc powder [1,2,9]. In sulphuric acid solution, the mixture of different metal sponges leads to form plenty of galvanic cells. For example, a direct contact between zinc and copper sponge, presented in cake, in the sulphuric acid solution makes corrosion cell in which zinc is dissolved and hydrogen evolves on copper surface [10].



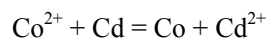
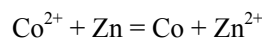
Similarly, some other galvanic cells are possible: $\text{Zn}|\text{H}_2\text{SO}_4|\text{Cd}$; $\text{Zn}|\text{H}_2\text{SO}_4|\text{Co}$; $\text{Cd}|\text{H}_2\text{SO}_4|\text{Cu}$; $\text{Co}|\text{H}_2\text{SO}_4|\text{Cu}$, etc. Only copper can not be

considerable oxidized in all the possible combinations: in cobalt purification cake, among all present cations, copper shows the most positive normal electrode potential [7,10].

The reactions:



describe work of the galvanic cell of $\text{Co}|\text{H}_2\text{SO}_4|\text{Cu}$ and represent an undesirable cobalt dissolution process. Because of the normal electrode potential of the reaction, ($E^0_{\text{Co}^{2+}/\text{Co}} = -0.288\text{V}$), and hydrogen overpotential on cobalt surface, the possibility of their carrying out is considerable. However, as long as the content of Zn and Cd in leaching cake are high enough, dissolved cobalt could be cemented spontaneously and returned to precipitate. These processes are represented by the following reactions:



Which of the present metal sponges should be much oxidized (dissolved), additionally depends on leading process conditions: acidity, duration of leaching, mass relationship solid-liquid in reaction slurry, temperature, mixing intensity, etc.

Zinc and cadmium have the highest contents (40-50% Zn and 2-6% Cd), as well as, the most negative electrode potentials, respectively (-0.76V/SHE, and -0.44V/SHE) in the cobalt purification cake. Because of that, the reaction of sulphuric acid solution upon cobalt purification cake, could make Zn and Cd most intensively dissolved. At the same time, the reduction of hydrogen ions will take place on the sponge metal surface where the hydrogen overpotential is the least (Cu and Co) [6,7,10].

According to the above showed reactions, it follows that during the leaching process, low acidity and a low temperature should be maintained, as well as achieving an intensive mixing, limiting the process duration and preserving an aeration of the suspension.

Generally, the reaction of sulphuric acid upon fresh cobalt purification cake, (previously unoxidized), results in remarkable zinc and cadmium dissolution from the cake, followed by less Co dissolution, according to the main idea that cobalt is concentrated in the leaching cake [2,6,8].

EXPERIMENTAL PART, RESULTS AND DISCUSSION

Experimental work under the laboratory conditions is conducted in the following way: sulphuric acid solution is added in the controlled way into the suspension (slurry) prepared of the weighed quantities of the cake and water, without additional heating. During the experiment, pH value of the reaction slurry is monitored while the speed of adding acid solution is adjusted so that constant slurry acidity is maintained. Having the process finished, liquid phase containing sulphates of accom-

panying metals is separated from the solid phase representing cobalt concentrate by filtration. In order to optimize the process, diversified parameters have been varied, such as: duration of air influence upon fresh cobalt purification cake, the cake composition, solid phase share in the initial suspension, experiment duration, temperature, mixing intensity, pH value. These parameters have different, above discussed, influences on the process of metal dissolution from the purification cake. Results of several characteristic laboratory experiments are given in the Table I.

Table I - Survey selected results from laboratory experiments for obtaining Co concentrate

Exp. number	pH	Experiment duration, h	Cobalt purification cake, %						Cobalt concentrate, %					
			Co	Ni	Zn	Cd	Fe	Cu	Co	Ni	Zn	Cd	Fe	Cu
1	2,5	12	0,46	0,5	43,5	23,2	0,3	0,2	3,9	2,6	7,7	9,7	1	3,3
2	2,5	8	1	0,5	54,9	7,6	0,5	0,5	9,5	3,6	25	3,9	0,7	7,2
3	≥ 3	5	0,56	0,2	45,7	2,3	0,3	0,24	10,4	4,8	11,3	4,4	2	5,4
4	≥ 3	5	1,4	0,3	44,3	2,9	0,3	0,37	11,1	2,7	21	3,4	1,1	3,1
5	≥ 3	4	1,28	0,9	54,9	5,6	0,5	0,6	12	10	47	4,4	1,3	68

In experiments showed in Table I, an optimal solid phase share in initial suspension was applied, as well as an intensive mixing. During the experiments, the harmful suspension aeration was suppressed.

According to the Table I, it can be noticed that composition of cobalt purification cake is very changeable, and it depends on composition of calcine and Zinc Calcine Leaching Plant operations and experiment carrying on conditions. In the first experiment, cobalt purification cake of unique composition is used with relatively poor cobalt content (0,46%), and high cadmium content (23,2%). Enriching of Co in the first two experiments is low, because of low cobalt inlet, and additionally, in these experiments pH value is maintained at 2,5. In the next experiments, pH value was ≥ 3, resulting in lower Co leaching, and consequently in higher Co content in cobalt concentrate. It was emphasized, that when leaching of a good cobalt purification cake was prolonged above optimal duration, in the condition of optimal acidity, the leaching of cobalt was increased (exp. 4 and 5), decreasing cobalt content in the product.

A much better cobalt concentrate quality (with higher Co content), could be achieved if the raw material with more cobalt content is used. (In order

to obtain a Co pigment, starting from the chosen raw material, according to the presented process, Co concentrate with 19% of Co was produced by the industrial method based on described laboratory procedure. [7,8]

Results of selected laboratory experiments, given in Table I indicate that it is possible to obtain cobalt concentrate of a satisfactory composition (with 4 to 12% Co) according to the optimized procedure. To end this, it is required: to use fresh (unoxidized) cobalt purification cake - to prepare reaction slurry respecting mass share: cobalt purification cake : water = 1 : 0,5; to maintain optimal acidity of reaction slurry, (pH ≥ 3); not to heat the reaction slurry additionally; to use 150 g/dm³ concentration sulphuric acid as a medium for preparation of leaching medium from cobalt purification cake; to limit leaching duration to 4 hours.

Based on the parameters determined in laboratory tests, an investigation of obtaining cobalt concentrate in Pilot Plant conditions was conducted, whereby all preciously established parameters were confirmed.

CONCLUSION

Based on laboratory studies, Pilot-Plant studies and industrial experiments, the procedure of cobalt

valuation is defined from cobalt purification cake by selective leaching of presented metals giving enriched cake by cobalt (cobalt concentrate).

Industrial production of cobalt concentrate with cobalt contents ranging from 4% to 12% is possible by employing described procedure.

Economic effects of cobalt extraction from zinc and cadmium hydrometallurgical production process enable reaching optimum technical and economical parameters in zinc and cadmium production, having in mind that, the well-known adverse effect of cobalt, nickel and copper, on electrolysis process is avoided; respectively, there are no harmful metals revolving in the process.

Cobalt concentrate may be further processed into other cobalt compounds such as: CoO(OH) , Co_2O_3 , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, pigments, etc

REFERENCES

- [1] L. Baimakov, A. Zurin: Electrolysis in hydrometallurgy, Moskva, (1977), 210-214
- [2] B. Nikolić: Metallurgy of Zinc, Beograd, (1996), 173-184
- [3] L. Šaljić, V. Matković: Significance of valorization of non-ferrous and rare metals from secondary raw materials of metallurgy, Special Publications Series: Recycling of wastes and secondary raw materials - Metallurgy, Beograd (1995), 153-165
- [4] L.J. Kostić-Gvozdrenović, M. Penić-Mandić, B. Ivanović, S. Erić: Synthesis of Three-component Pigments Based on Waste Mud Concentrate from Cadmium Metal Electrolysis, Material science Monographs 66A, P. Vincenzini, Elsevier Science Publishers B.V. Amsterdam, (1991), 245-251
- [5] S. Erić, L.J. Kostić-Gvozdrenović, M. Miladinović, L.J. Pavlović: Synthesis of Ceramic Pigments Based on Cobalt from Industrial Waste Matter, Silicati, 34, (1990), 61-66
- [6] Project Z.6.0448, financed 1991-1992 by Ministry of Science and Technology of Serbia, Beograd (1992), Annual report 132-137
- [7] A. Despić, D. Dražić, O. Tatić-Janjić: Basic Electrochemistry, Beograd, (1970), 164-165, 303-304 (in Serbian)
- [8] M. Todorović, D. Stanojević: Valuation of cobaltic waste products, VI Yugoslav symposium on metallurgy, V. Banja, (1996), Book of Abstract, 217-220
- [9] D. Stanojević, B. Krstić: Intensifying of the process zinc dissolution in sulphuric acid using copper cathode, "Material Protection" (1), Beograd (1997), 1-6
- [10] D.D. Stanojević, M.B. Rajković, D. Tošković, Hydrometallurgical treatment of copper sludge from blue vitriol production, The Sixth European Meeting on Environmental Chemistry, Belgrade, Serbia and Montenegro, Decembar 6-10, 2005, Book of Abstracts and CD, 263

IZVOD

DOBIJANJE KOBALTA IZ MEĐUPRODUKATA PROIZVODNJE ELEKTROLITIČKOG CINKA I KADMIJUMA

Predmet ovog rada je ispitivanje mogućnosti za obogaćivanje kobaltom otpadnog mulja iz proizvodnje elektrolitnog cinka i kadmijuma. Kobalt je u koncentratima cinka, kao prateći metal, prisutan u malim količinama (0.001 - 0.005%). U pojedinim fazama hidrometalurške proizvodnje cinka i kadmijuma, kobalt se, međutim, koncentriše do komercijalno značajnih vrednosti. U procesu proizvodnje kadmijuma, koja je tehnološki vezana za proizvodnju cinka, tzv. "talog od prečišćavanja kobalta" predstavlja takav resurs kobalta. Ovaj talog sadrži 0.6-1% Co, 2-6% Cd, 40-50% Zn, 0.1-0.6 % Ni, 0.1-0.7% Cu i td. Iz svežeg taloga od prečišćavanja kobalta rastvorom sumporne kiseline (150 g/dm^3), uz striktnu kontrolu pH vrednosti reakcione pulpe, izlužuju se prisutni metali, a kao rezultat luženja dobija se isprani talog u kome se koncentriše kobalt (6-11%). Sulfati izluženih metala se vraćaju u proces, dok se talog sa povišenim sadržajem kobalta može koristiti u različite svrhe. Polazeći od ovog taloga u laboratoriji su dobijeni: Co_3O_4 , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, keramički pigmenti i td.

Ključne reči: *elektrolitička proizvodnja cinka i kadmijuma, proizvodnja kadmijuma, proizvodnja cinka, „talog od prečišćavanja kobalta“*