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Recovery of zinc from arduous wastes using solvent extraction technique Part II. Pilot plant tests

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Abstract. Solvent extraction technique using 40 vol. % bis(2-ethylhexyl)phosphoric acid as an extractant was applied for recovery of zinc from technological solutions. Crude zinc oxides from Waelz processing of electric arc furnace dusts or ferrous waste of zinc hydrometallurgy were used for preparation of feed solutions by leaching them with diluted sulfuric acid and by pre-liminary hydrometallurgical purification. The studies were conducted step by step from laboratory to advanced pilot plant tests in continuously operating installation. Part II describes preparations and results of pilot plant counter-current experiments performed using laboratory extractive system, built from a train of mixer-settler type extractors, set in changeable counter-current manner, necessary pumps and automation systems, coupling pH measurements with neutralization agent supply. Excellent results in a form of very pure zinc sulfate solutions were obtained. ZnSO₄ concentrations are appropriate and the purity of the strip solutions very good. Comparison of natural and accelerated method of zinc extraction is done.

keywords: solvent extraction, zinc recovery, crude zinc oxide, electric arc furnace dust

1. Introduction

Background of the presented issue and a short literature survey has been presented in Part I of this paper (Gotfryd, 2011). The results of the preliminary and laboratory studies have also been presented there. These works were necessary to chose the best extractant and to establish conditions for further activities, which are described here. Part II presents the results of the pilot plant experiments of zinc recovery from preliminary purified zinc bearing technical solutions, especially prepared by leaching of industrial crude zinc oxides. Experiments, performed on pilot plant apparatus, used different solutions, prepared for this purpose from industrial crude zinc oxides by their leaching in sulfuric acid solutions. They covered also a number of extractors configurations and conditions, applied for particular series of the trials.

2. Experimental

2.1. Preparatory procedures

2.1.1. Leaching – solutions preparation

Treatment of crude zinc oxide dust consisted of the following steps:

- preparation of aqueous pulp of CZO of predetermined solid/liquid ratio, typically 250 g/dm^3 ,
- careful addition of a fixed portion of concentrated 96 % sulfuric acid,
- stirring the reacting pulp for a defined period of time, typically 1.0 hour, at 80-90 °C,
- solid/liquid separation (sedimentation and filtration).

2.1.2. Oxy-hydrolysis and cementation – preliminary solution purification

The solutions produced in the one-stage leaching process contain mainly zinc sulfate(VI) and also its typical contaminants: cations of non-ferrous (cadmium, copper, manganese, aluminum) and alkali/alkali earth (sodium, potassium, magnesium, calcium) metals, small amounts of iron and others anionic or neutral ingredients (As, Sb, chlorides, fluorides, SiO_2). Application of oxidative conditions (a batch of H_2O_2 and/or stirring with typical flotation aerator), combined with partial neutralization of the reaction environment (with milk of lime) to the level of $\text{pH} \geq 3.5$ -4.0, resulted in oxy-hydrolysis of unnecessary elements. After that operation iron was practically not observed in the solution ($< 0.001 \text{ g/dm}^3$).

Absence of arsenic in the solution after this process provided grounds for starting further activities, i.e. precipitation of such elements as Cu, Cd, Sn, Pb, (Ni, Co) by addition of zinc powder (102 % of stoichiometry). Fifteen minutes of stirring turned out to be the proper period for carrying out the process.

2.2. Continuous counter-current experiments (pilot plant test)

Experiments on that scale were performed in an installation composed of a set of extractors of mixer-settler type (each of $0.5/1.5 \text{ dm}^3$ capacity), arranged in a counter-current systems with cooperation of necessary equipment and instrumentation: membrane pumps, pH-meters, automatic systems for pH controlling, based on feedback signals to pumps providing NaOH solution and submersible ceramic heaters, coupled with automatic temperature controllers.

Media were pumped by membrane pumps at the following rates:

- organic phase: 2.75 - $3.00 \text{ dm}^3/\text{h}$,
- feed solution: 9.0 - $10.0 \text{ dm}^3/\text{h}$,
- acid for stripping: 0.45 - $0.50 \text{ dm}^3/\text{h}$,
- scrubbing solution - diluted 0.05 M ZnSO_4 : 0.40 - $0.60 \text{ dm}^3/\text{h}$.

These parameters were adjusted within given ranges according to the current needs. A more comprehensive description of the system is included in the Results and Discussion section.

A general idea of the pilot tests is depicted in Fig. 1, while the photograph in Fig. 2 presents the installation.

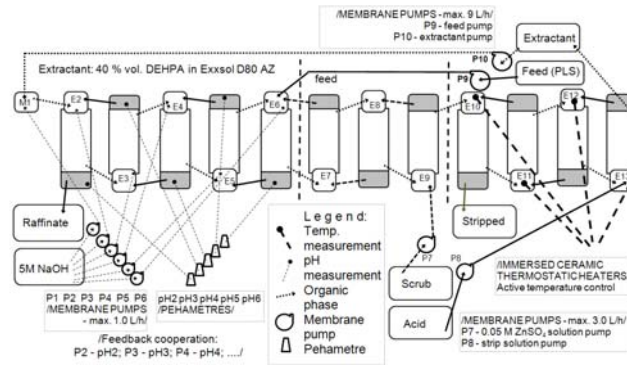


Fig. 1. Diagram of extraction, scrubbing and stripping system applied for recovery of zinc from preliminary prepared post-leaching solutions

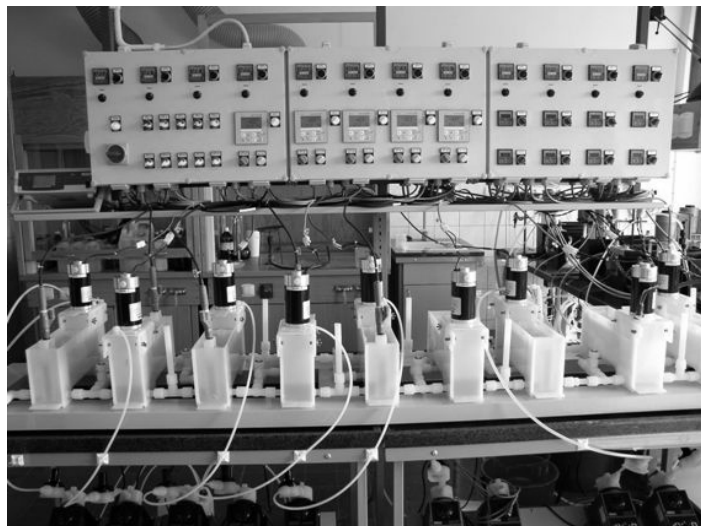


Fig. 2. Laboratory equipment, consisting of a set of mixer-settlers with systems of their feeding and control

3. Results and discussion

3.1. Leaching and solution purification

Composition of all solution used for extractive experiments are shown in Table 1. After applying the described leaching conditions, then the two steps of solution purification (oxyhydrolysis and Zn powder cementation), the solutions ‘b’ are ready

for further extractive treatment, even though the levels of some contaminants (e.g. Cd, Cu) are different.

The origin of the solutions was diversified as indicated below Table 1. Almost all of the solutions before extraction were routinely diluted with water or recycled from previous extraction experiments raffinates /RR/ to the values of 15-20 g Zn/dm³, to adjust zinc(II) concentration to the level optimal for extraction.

Table 1. Composition of the solutions prepared for extractive zinc purification

*)	Sol. No.	Zn	Cd	Cu	Fe	Mn	Mg	Al	As	Sb	Na	K	Si	Cl	F	
1	1a	145.8	0.48	0.082	0.018	-	0.40	-	<0.001	<0.001	10.1	6.81	0.20	19.7	0.10	g/dm ³
	1b	146.1	0.0087	<0.0002	0.0006	-	0.40	-	<0.001	<0.001	10.1	6.81	<0.01	19.7	0.10	
2	2a	123.5	2.93	<0.001	0.36	-	0.53	-	0.028	0.005	0.91	1.62	-	3.64	0.006	
	2b	125.2	0.034	<0.001	0.0001	0.35	0.53	-	<0.001	<0.001	1.60	1.62	-	3.64	0.006	
	3a	113.3	2.90	<0.001	0.36	-	0.60	-	<0.005	0.005	0.80	1.40	-	3.50	0.02	
	3b	115.0	0.064	<0.001	0.0001	0.32	0.58	-	<0.001	<0.001	1.38	1.41	-	3.45	0.018	
	4b	107.0	0.010	0.010	<0.001	0.30	0.50	<0.01	<0.001	<0.001	0.20	1.10	<0.01	2.40	0.13	
	5b	116.6	0.013	<0.0005	<0.001	-	-	0.014	<0.001	<0.001	0.20	1.13	0.045	2.60	-	
1	6a	53.5	0.47	0.058	0.042	-	-	0.035	-	-	-	-	0.27	7.80	0.13	
	7b	88.6	0.027	<0.05	<0.001	-	-	0.11	<0.001	<0.001	-	5.39	0.028	2.50	-	
3	8a	51.0	1.12	0.051	0.0019	-	-	-	0.83	-	5.7	3.10	-	26.2	-	
In fully purified solutions 'b': Ni and Co < 0.001 g/L																

*) - origin of leached crude zinc oxides: 1 – steel industry; 2 - classical zinc hydrometallurgy (Waelz processing of RLE process residues); 3 - copper pyrometallurgy (dusts).

Solutions: 'a' - as produced by leaching; 'b' - after additional preliminary hydrometallurgical purification (oxyhydrolysis + Zn powder cementation).

3.2. Pilot plant extraction

The range of extraction schemes which were applied for zinc purification in their fully developed form covered different counter-current systems, from set of extractors of (0)-4-1-4 type, through (1)-5-3-4 (see Fig. 1) to (1)-3-3-6 type, where the figures (p)-x-y-z denote a number of reactors assigned for extractant preneutralization (p), extraction proper (x), scrubbing (y) and stripping (z), respectively. All the tested systems and their characteristics are listed in Table 2.

Experiments lasted several weeks and covered not only different extraction systems but also various feed solutions (see Table 1 and 2). At the beginning and at the end of this period crude, unpurified solutions (No. 1a and 8a) were used. A few experiments (No. 1-5) were performed at ambient temperature – close to 22-25 °C. In the experiments No. 6 through 11 the temperature of the stripping area was elevated to 45-50 °C.

Each experiment was conducted for at least 4-6 days and then collected stripped

solutions were separated and analyzed for their purity (concentrations of 18 elements). The results of the analyses are shown in Table 3.

Table 2. Characteristics of tested extractive systems

No. of exp.	System of counter-current zinc extraction				Feed solution			Temp.	
	Mixer-settlers config. ^{*)}	Solvent pretreatment	Autom. pH adjust.	Extractive process	No.	Predilution		Zn	
					**)		agent	g/L	°C
1	(0)-4-1-4	no	no	natural	1a	yes	water	15.60	ambient
2	(0)-3-3-3	no	no	natural	1b	yes	water	14.62	
3	(0)-5-3-3	no	no	natural	1b	yes	water	14.62	
4					2b	yes	water	12.35	
5	(0)-3-3-5	no	no	natural	3b	no	RR ^{***)}	115 ^{***)}	
6	(0)-5-3-4	no	no	natural	5b	yes	water	14.6	45-50 (strip)
7					6a	no	none	53.5	
8					5b	yes	neutr. RR	20.3-22.5	
9					(1)-5-3-4	yes	yes	active: steady	
10	7b	yes	water	15.0					
11	(1)-3-3-6	yes	yes	pH ≥2.0	8a	yes	RR	13.8-15.0	

^{*)} - figures (p)-x-y-z denote the number of reactors in the counter-current set of devices assigned for extractant preneutralization (p), extraction proper (x), scrubbing (y) and stripping (z), respectively,

^{**)} - the number of mother feed solution as per Table 1; before extraction they were prepared (diluted) with water or recycled raffinate /RR/ to appropriate concentration,

^{***)} - mother solution systematically diluted with raffinate recycled internally, i.e. directly in mixer of the extractor, which receives feed solution, with aqueous phase, taken straight from its own settler.

The results are discussed in details in the Conclusion section. Almost all experiments gave positive results in a form of satisfactory pure zinc electrolytes. Only one of them (No. 7 in Table 2), in which solution 6a was used, resulted in a complete failure. Because of high silica content in the solution used as a feed material, after several hours of reaction all the organic solutions turned into extremely viscous, very slowly flowing liquid, completely unfit for further operation. Mixing and/or pumping was still possible but further separation and transportation by gravity failed. The experiment ended with organics overflowed and spilled on the table under the extractors.

During the experiments temperature and pH in all settlers of extraction section were continuously measured and registered. The most interesting part of the pH measurements is shown in Fig. 3, where behavior of extraction system in the moment of the change from natural type extraction system No. 8 (no pH control) to the active pH control system No. 9 /see Table 2/ is presented.

The period from 0 to 130 minutes presents situation in five consecutive extractors, accomplishing experiment No. 8, where, without any external intervention,

pH within the settlers of extractors No. 1 to 5 has stabilized on the levels of about 1.0, 1.2, 1.3, 1.7, 2.0, respectively. Then (in 130 minute on the graph) electronic automation systems, coupling pumps of NaOH solution with pH-meters, adjusted with intention to sustain pH at the levels within the range of 2.0-2.2, were switched on. The full effect of that operation was observed not earlier then after 770 minute, which means that there was over ten hour period needed for the system to adapt to the new circumstances. After that period, even though the situation in the extractor No. 2 still isn't fully stable, the other ones (including the most important No. 5) operated quite correctly, according to the new conditions, i.e. sustaining pH values nearby expected point ≥ 2 .

Figures 4 and 5 present cross-sections of all extractors with the registered concentrations of zinc(II) and sulfuric acid in the state of equilibrium of the extractive system as reached after several days of operation.

Table 3. Composition of zinc electrolytes produced with different schemes of extraction

	*)	1	2	3	4	5	6	8**)	9	10	11	***)
Zn	g/dm ³	126.5	140.8	155.0	147.4	162.1	165.9	169.0	170.0	158.8	158.4	164.8
Ca	g/dm ³		-	-	-	-	0.011	0.028	0.022	0.024	0.004	0.235
K	g/dm ³	-	0.0006	0.0003	0.004	< 0.6	0.029	0.003	0.063	0.047	0.015	0.999
Na	g/dm ³	-	0.0001	0.0008	0.006	0.0025	0.095	0.0075	0.325	0.251	0.116	3.04
Cl	g/dm ³	0.001	0.001	0.0018	0.096	0.010	0.021	0.041	0.017	0.11	0.0002	< 0.3
Mg	mg/dm ³	20	20	30	2	1	13	1	8	6	1	7290
Mn	mg/dm ³	-	-	-	-	-	23	0.4	0.9	1.1	0.6	6410
Cd	mg/dm ³	7.7	< 0.1	< 0.1	< 0.1	1.12	0.15	0.12	0.13	0.11	0.78	0.52
Ni	mg/dm ³	3.4	< 0.2	< 0.2	< 0.2	< 0.2	0.040	0.075	0.27	0.33	0.11	0.025
Co	mg/dm ³	1.1	< 0.2	< 0.2	< 0.2	< 0.2	0.18	0.14	0.14	0.12	0.16	0.36
As	mg/dm ³	0.057	< 0.1	0.025	0.05	0.05	0.1	0.1	0.1	0.1	8.7	< 0.1
Ge	mg/dm ³	-	-	-	-	-	0.01	0.01	0.01	0.01	0.22	0.02
Sb	mg/dm ³	0.077	< 0.1	< 0.06	< 0.06	< 0.06	0.04	0.02	0.02	0.01	0.13	0.24
Fe	mg/dm ³	-	-	-	-	-	0.52	0.68	0.48	0.56	0.30	0.34
Sn	mg/dm ³	-	-	-	-	-	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1
Pb	mg/dm ³	-	-	-	-	-	0.62	0.78	0.60	0.74	0.78	0.96
Cu	mg/dm ³	10	< 0.2	< 0.2	< 0.2	< 1.0	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
F	mg/dm ³	< 0.6	0.09	0.22	0.18	0.15	2.2	0.6	2.8	1.6	3.4	3.6

*) - the number of the extraction system as in Table 2

***) - experiment No. 7 failed because of silica excess in feed solution

****) - composition of the sample of industrial zinc electrolyte

The graphs provide possibilities to compare two typical situations, which were observed during the testing with the counter-current sets of extractors. They evidently show difference between the two main systems of extraction – the natural one, without any pH regulations, and automatically controlled.

The natural extraction (Fig. 4) shows almost linear progress and a

moderate slope of zinc(II) concentration along the row of five counter-currently configured extractors.

The extractions conducted with the extractant promoted with NaOH solution, which was added at the beginning to organic phase of the extractant in a separate mixer (partial 60-70 % preneutralization) and then continuously supplied to the mixer-settlers, can be seen as more progressive (Fig. 5). Therefore, the number of reactors could be limited here from five to three or even two units of mixer-settler type. But in a continuously operating system even that type of extraction does not provide possibilities for easy and complete removal of zinc from raffinates.

Figures 4 and 5 provide additionally the possibilities to observe how long it lasts in these both particular cases to attain extraction equilibrium. In the pictures there are inserted concentrations profiles after 4-5 consecutive days of action of each of them.

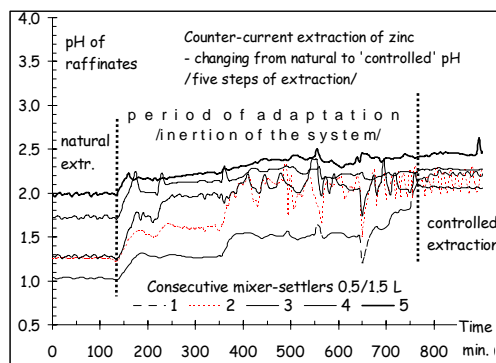


Fig. 3. pH variations in the period after switching from natural to automatically controlled pH of extraction

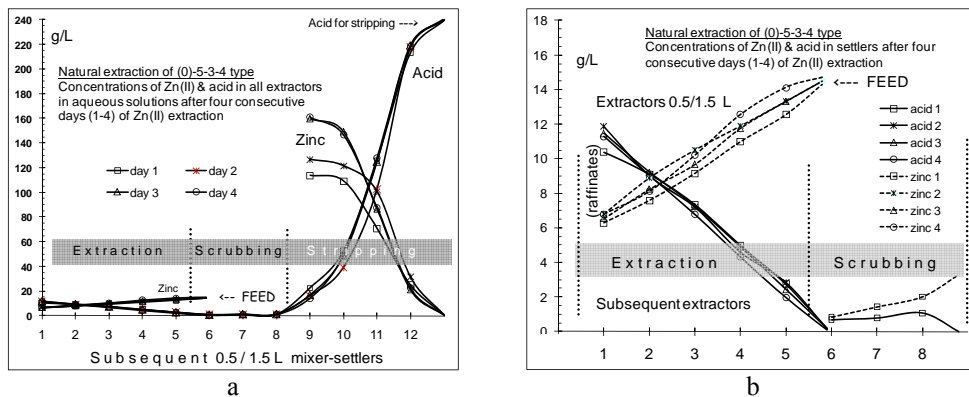


Fig. 4. Acid and Zn^{2+} concentration in consecutive extractors after over 50 hours of operation ((0)-5-3-4 system of counter-current zinc extraction): a) full range, b) extraction and stripping

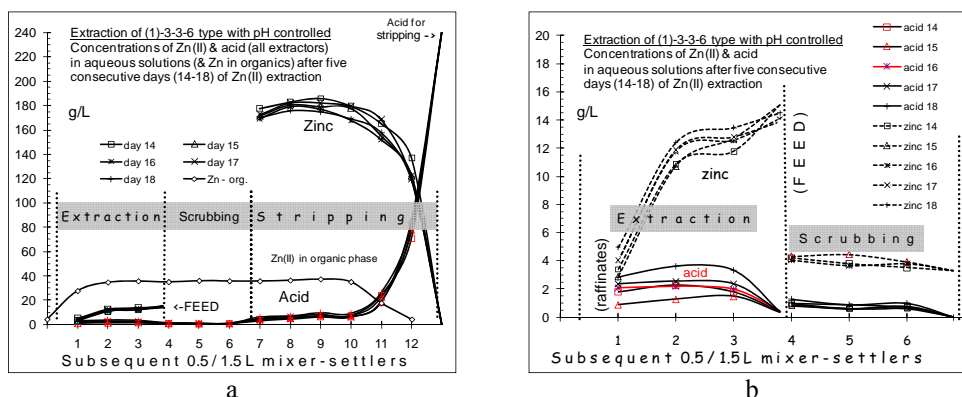


Fig. 5. Acid and Zn^{2+} concentration in consecutive extractors after over 50 hours of operation ((1)-3-3-6 system of counter-current zinc extraction): a) full range, b) extraction and stripping

4. Conclusions

The evaluation of technical results of the experiments, especially with regards to the composition of the produced zinc electrolytes (stripped solutions - Table 3), shows very low level of all technologically important contaminants. Only few of the samples can be qualified as solutions in which concentration of some, i.e. one or two, elements (Cu, Cd, Ni or As) very slightly exceeds the expected value. This especially applies to the solution No. 1 ('dirty' feed solution and too short scrubbing system), and to a lesser extent to solutions No. 5 and 11. The other are almost ready to be used as electrolytes in zinc electrolysis. To be fully accepted they should be only additionally treated for final removal of organic phase (e.g. by filtration through a layer of active carbon).

It is absolutely impossible to use the feed solution which contains colloidal SiO_2 (e.g. solution 6a in Table 1). This can lead to disastrous increase of organic phase viscosity. In such a situation the mixer-settlers and pumps are unable to operate properly.

Systems of zinc(II) extraction, promoted with current addition of alkali solution into each extractor, can be applied in very short (2-3 counter-current steps) extraction circuits, however they can be economically viable when using not expensive waste $NaOH/Na_2CO_3$ solutions only (even if contaminated, e.g. with $NaCl$). During such processes raffinates can be generated which contain mainly highly concentrated Na_2SO_4 . They can be used (in about 90 %) cyclically for dilution of next batches of rich in zinc mother liquor, especially prepared in a reasonably concentrated form (e.g. containing $120-150 \text{ g/dm}^3 \text{ Zn}^{2+}$) by leaching zinc-bearing materials at high solid-to-liquid ratio. The rest of the raffinate, some 10 % of the bleeding, which still contain small amounts of zinc, must be treated for further zinc recovery, e.g. by carbonate precipitation, before sending it to an effluent treatment plant or rather for Na_2SO_4 recovery in crystalline form.

Schematic flow sheet of proposed course of extractive technology based on such sort of extractive processes is depicted in Fig. 6.

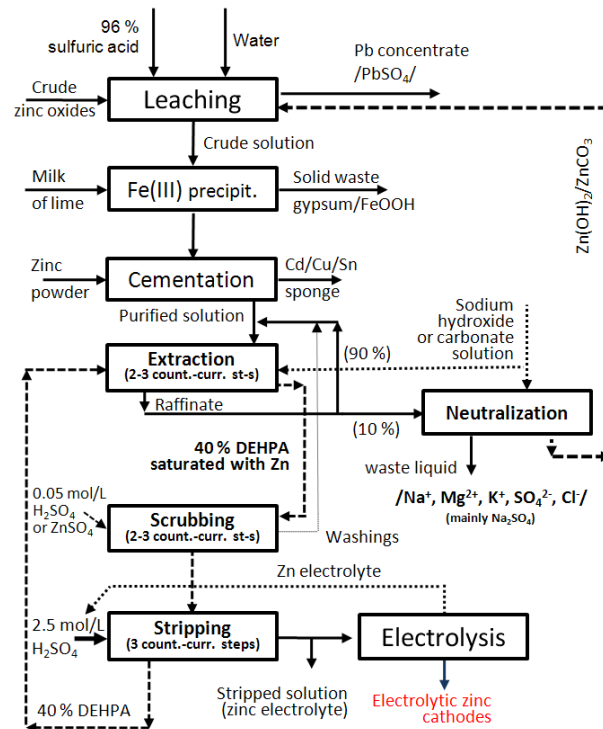


Fig. 6. Flow sheet of the proposed process for crude zinc oxide hydrometallurgical treatment based on promoted extraction of zinc(II)

The natural extraction is not as efficient as the promoted one, but it is performed without any additional reagents added currently to extraction, and these conditions (pH as low as naturally possible, even ≤ 1.0) favor higher zinc(II) extraction selectivity. Extractions can be organized and performed depending on Zn(II) concentration in PLS, i.e. the obtained acidic raffinates can be used again, in some 90%, alternatively:

- recycled as acidic lixivants for leaching of next batches of raw material (Alternative I for diluted PLS),
- recycled, but after their neutralization with lime stone powder, for PLS dilution, thus preparing it to be ready for direct zinc extraction (Alternative II for concentrated PLS).

Of course, in both cases, there is a need to bleed and treat a small fraction of the post-extraction solution (raffinate I) to recover the remainder of zinc(II) and other components (Cu, Cd), if they were not removed previously. Excessive acid can be earlier eliminated in a form of gypsum.

Both alternative raffinates I (i.e. their about 10% bleed) can be treated again by further additional extraction, however a significantly higher organic-to-aqueous ratio should be applied to reach higher efficiency of total zinc(II) extraction. The produced secondary raffinates II should be treated with limestone and/or milk of lime to separate zinc-containing and recyclable to the leaching stage sediments, and then disposed of to an effluent plant. A flow sheet of the proposed process for crude zinc oxide treatment with natural extraction involved, is shown in Fig. 7.

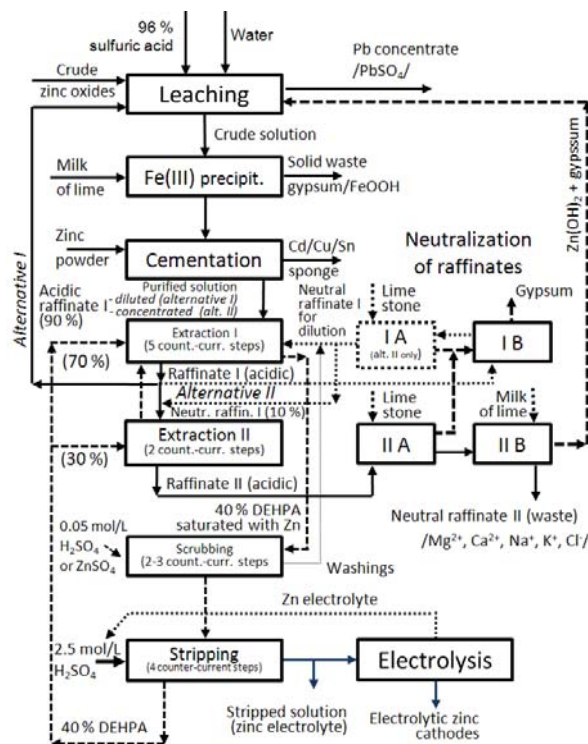


Fig. 7. Flow sheet of the proposed process for crude zinc oxide hydrometallurgical treatment based on natural extraction of zinc(II)

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