

REPROCESSING OF ZINC GALVANIC WASTE SLUDGE BY SELECTIVE PRECIPITATION

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Multi-step selective precipitation method was tested for processing zinc waste galvanic sludge. This method involved acid leaching of sludge in sulphuric acid, purification of sulphate leach liquors using a sequence of hydroxide, sulphide, and fluoride precipitation to remove trivalent metals, Cu, Cd, Ca, Mg, and Si, oxidative precipitation to remove Mn, and finally precipitation of Zn as zinc carbonate. The solids were separated from leach liquors after each precipitation step, and their phase composition was determined by X-ray powder diffraction and elemental composition by AAS. The flowsheet proposed yielded relatively pure Zn-precipitate, suitable for possible production of raw materials for ceramic, metallurgical, or pigment industry, however, due to incomplete leaching of the sludge and co-precipitation of Zn to hydroxides of trivalent metals and Cu, Cd-sulphides, the overall recovery efficiency was only 63-65 %.

INTRODUCTION

The simplest way of treating rinse waters and concentrates from the metal plating industry (Zn, and Ni, Cr plating of metals, Cu plating of metals and plastics), descaling Cu or their alloys, and printed circuit production is their neutralisation with lime, usually after addition of Fe(III) salts as flocculant. The neutralisation sludge contains gypsum and hydroxides of heavy metals in concentrations comparable or exceeding those in metallurgical raw materials. The metals of interest, which might be obtained from the sludge, are nickel, copper, zinc, and possibly chromium, are present in concentration 5-10 wt.%. They hence represent a possible subject of recovery of heavy metals, or better of producing their compounds. The current level of utilisation of neutralising sludge as secondary raw material is unsatisfactory. The sludge is transported and disposed of in special landfills as dangerous waste. In Czech Republic, only highly concentrated waste is reprocessed, namely several hundred tons of dross from dip hot zinc plating is annually used in pigment manufacturing by Silchem Ltd. (Neštětice, Czech Republic). In order to reduce environmental hazards and to recover heavy metals for industrial reuse, several hydrometallurgical technologies based on leaching and selective separation of metals from the solutions have been pro-

posed using ion exchange, liquid-liquid separation, and electrolysis. However, application of the modern technologies is limited due to high investment and operational cost [1] that could only be economical at a large scale (>100 tons per year). In a common Czech plant producing Cu, Ni, or Zn galvanic waste, the annual production of waste corresponds to several tens tons of pure metal. That amount is economically insufficient for operating a specialised chemical or metallurgical plant, because such amount is below the limit of profitability at the current price of these metals in world market. The exception regards reprocessing of more valuable CoO from fly ash of manufacturing Co coloured glass by a simple hydrometallurgical technology [2]. On the other hand, any investment to further technologies is beyond the economical possibilities of the waste producers, because both galvanic plants still suffer from the decrease of engineering industry in the 1990's. This economical condition together with a lack of legislative regulations of dangerous waste disposal lead to situation, which is in a direct contradiction to the requirement of sustainable development.

A possible solution of this situation could be introduction of hydrometallurgical waste processing that could be operated in water neutralisation stations of the waste producers without a need of huge investments to sophisticated devices or buying know-how. This was the

reason of a procedure that has recently been tested in a laboratory scale with Cu and Zn bearing sludge [3-4], which is based on limited miscibility of metal impurities in CuO and ZnO and on the large dissolution reactivity of these two oxides [5].

On the base of findings described in our previous studies [6-7], we propose a multi-stage precipitation method of processing zinc waste galvanic sludge, which was verified on laboratory scale. This method was designed to contain only simple technological steps: leaching, precipitation in solution, and solid-liquid separation. For purification of the final product, the metal and non-metal impurities were removed as hydroxides, sulphides, fluorides, and oxides. The objective of this investigation was to determine the phase composition of individual precipitates and to utilise this knowledge for more detailed understanding of the refining processes applied.

EXPERIMENTAL

The sludge originated from one of the biggest Czech chemical landfills of hazardous wastes (GEAM Dolní Rožinka).

Leaching and precipitation experiments were carried out in closed 4-6 dm³ glass reaction vessels, stirred with an impeller, and immersed in a thermostatically controlled water bath connected with a water cooler. *pH* and redox potentials of the solutions were continuously monitored with Benchtop 525A *pH*/ISE meter. Samples of the suspension were withdrawn at regular intervals. The concentrations of metals in the filtrates were determined using flame AAS. The leach residues, precipitates and the final zinc products were filtered, washed with water, dried at 80°C and weighed. The oxidation precipitation of Mn was performed at *pH* = 3.5 by addition of (NH₄)₂S₂O₈, or H₂SO₅ at 70-100°C for 30 min, then the solution was left to cool for 8-10 h [8].

The phase compositions of individual solid samples were investigated by X-ray diffraction, and the concen-

tration of metals was determined by flame AAS. The qualitative and semi-quantitative phase analysis has been performed using PDF2 database. The X-ray diffraction analysis was performed at the ambient temperature with the horizontal diffractometer DRON-UM-1 using CuK α radiation with Ni filter on the diffracted beam, scan step 0.02° and speed 1°/min. Difpatan [9] program was used to evaluate powder patterns.

RESULTS AND DISCUSSION

The scheme of sludge processing is shown in figure 1. Chemical composition of zinc galvanic sludge processed, acid leaching residues, individual precipitates and the final zinc carbonate are given in tables 1 and 2. Composition of the solids based on X-ray powder diffraction and supported by elemental analysis is summarised in table 3.

Zinc waste galvanic sludge consisted mainly of amorphous metal hydroxides and several crystalline phases: quartz, SiO₂ (PDF2 card 46-1045), gypsum, CaSO₄·2H₂O (PDF2 card 33-311) and calcite, CaCO₃ (PDF2 card 5-586). This composition is quite typical for neutralization sludge of Zn galvanic plating.

The waste material was first leached with sulphuric acid at two different acid-to-waste ratios. The first one included leaching up to *pH* = 1, and the second up to *pH* = 3.9. The yield of zinc into the solutions was 96 % (*pH* = 0.9-1.0) and 72 % (*pH* = 3.9-4.0). The leach residue from the leaching up to *pH* = 1, whose weight was 66-68 % of the initial weight of the sample of galvanic sludge, was mainly formed by the crystalline phases, quartz and gypsum. It means, that almost entire amorphous part including metal hydroxides was dissolved in the liquor. The leach residue from the leaching up to *pH* = 3.9 consisted of both the residues of the amorphous and crystalline phases. In the latter case the weight of the leach residue was by about 2-3 % higher than the initial weight of galvanic sludge processed, probably due to oxidation of Fe(II) to Fe(III) and for-

Table 1. Elemental composition of the original sludge and leaching residues (gangues) (wt.%).

Solid	Zn	Fe	Cr	Ni	Cu	Mn	Cd	Pb	Ca	Mg	Al	Si
dry sludge (weight loss 47 %)	8.7	10.4	0.9	0.5	0.4	0.3	<0.1	0.1	7.3	0.7	1.1	9.8
leaching residue (<i>pH</i> = 1.0)	0.4	3.6	0.1	<0.1	0.1	<0.1	0	0.4	9.1	0.1	0.5	13.6
leaching residue (<i>pH</i> = 3.9)	2.6	9.5	0.9	0.5	0.4	0.3	<0.1	0.1	8.9	0.7	<0.1	10.6

Table 2. Elemental composition of the solids formed by multi-stage precipitation. Results in wt.%. Composition of Zn hydroxide obtained according to refs. [4, 11] is included for comparison.

precipitate	Zn	Fe	Cr	Ni	Cu	Mn	Cd	Pb	Ca	Mg	Al	Si	Na
1a (hydroxides)	7.2	15.2	2.7	0.2	1.1	0.4	0.05	0.05	0.6	0.2	1.6	2.5	4.2
1b (hydroxides)	19.4	<0.01	1.8	1.1	2.4	0.3	0.05	0.01	1.5	0.7	3.7	7.3	1.6
2 (sulphides)	23.4	0	0	0.2	6.4	0.2	20.1	0	0.3	0	0	0.5	0.5
3 (fluorides)	3.6	0	0	<0.1	0	0.5	0	0	8.4	10.1	3.9	9.5	12.2
4 (Mn oxide)	8.6	0	0	0.13	0	38.6	0	0	<0.1	0	0	<0.1	2.9
5 (final product)	47	<0.01	<0.01	<1.0	<0.01	<0.05	<0.01	<0.01	<0.2	<0.1	<0.1	<1.5	3-7
Zn-hydroxide [11]	39	0.002	0.02	0.26	3.5	0.003	0.03	n. d.	0.03	0.02	0.05	5.3	n. d.

n. d.: not determined

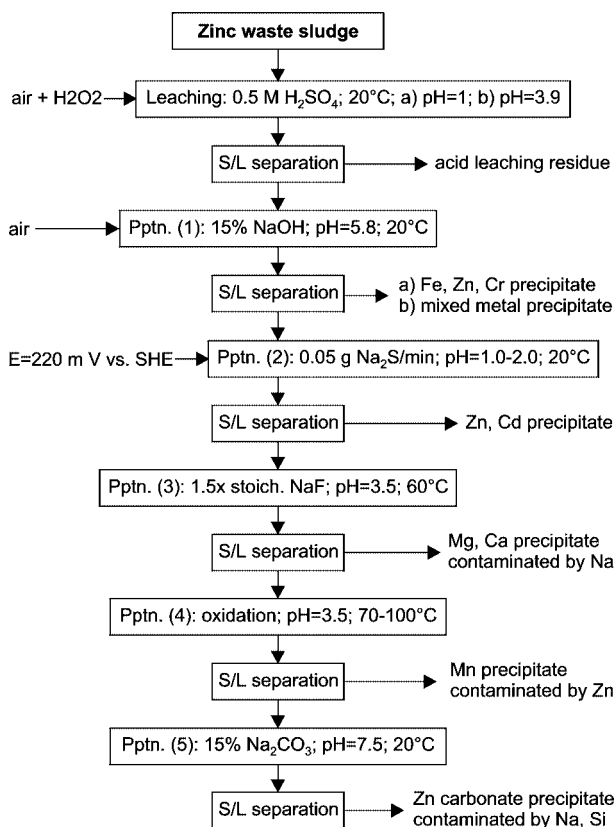


Figure 1. Tentative flowsheet of the Zn sludge processing.

mation of gypsum from calcite. However, the incompletely dissolved amorphous phase including zinc hydroxides caused low efficiency of Zn dissolution. Identical crystalline phases in the gangue after leaching up to $pH = 1$ (1a) and 3.9 (1b) indicated that all CaCO_3 was converted to CaSO_4 , yielding gypsum in solid phase and saturated solution of the calcium sulphate in liquor.

The subsequent processing of both leach liquors was performed under the same conditions. Due to the different composition of leach liquors of 1a and 1b the composition and the amount of hydroxide precipitates were substantially different. An amorphous phase was only found in the hydroxide precipitate 1a, in which the trivalent metals, mainly Fe, are presented. However, the precipitate 1a contained besides the amorphous phase also the crystalline phase $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The amount of the precipitate 1a was 3.3 times larger than the amount of the precipitate 1b. The zinc loss in this first precipitation step was 24 % in solid phase 1a and only 12 % in the solid phase 1b. The filtration of the leaching gangue and the first precipitation step removed approximately 99 % Fe and Cr, 92 % Al and Cu, 27 % Zn, 32 % Ni, 15 % Mn and Mg and 10 % Ca. The completion of the first precipitation step resulted in the practically equal composition of the both filtrates.

The results of X-ray and chemical analyses of the product of the second precipitation step, sulphide precipitate, revealed a subsequent unexpected zinc loss.

According to the precipitation diagrams constructed for ideal solutions [10] we assumed that at $pH = 1-2$ only copper and cadmium would be separated from solution. However, from the real multi-component solution a part of the Zn excess was co-precipitated. Hence, instead of pure hawleyite, CdS (PDF2 card 10-454) and covellite, CuS (PDF2 card 6-464), observed in X-ray diffraction patterns, the phases formed were actually mixed sulphides $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ and $\text{Zn}_x\text{Cu}_{1-x}\text{S}$ according to the elemental analysis (table 3). In this way more than 98% Cu and Cd was separated from refined solutions.

In the fluoride precipitation step 3, 95-98 % Al, Mg, Ca and Si were removed from solutions as two crystalline phases: $\text{CaMg}_2\text{Al}_2\text{F}_{12}$ (PDF2 card 25-152) and malladrite, Na_2SiF_6 (PDF2 card 33-1280).

The oxidation of Mn(II) to an insoluble birnessite-like phase $\text{Mn}_7\text{O}_{13} \cdot 5\text{H}_2\text{O}$ (PDF2 card 23-1239) by addition of peroxodisulphate (step 4) ensured its efficient removal from zinc sulphate solution without any significant co-precipitation of zinc.

The final product of processing waste galvanic sludge, zinc carbonate, was precipitated in the last step 5. In this precipitate Zn is partly bounded as $\text{Na}_2\text{Zn}_3(\text{CO}_3)_4 \cdot 3\text{H}_2\text{O}$ (PDF2 card 1-457), whose amount depends on the content of sodium in the purified leaching solutions.

The purity of the final Zn product can be compared to the purified hydroxide obtained from a similar raw waste by the calcination-dissolution procedure described in refs. [4, 11], which, instead of selective precipitation uses calcination to bind metal impurities to very slowly soluble oxides. As it is shown in table 2, the precipitate 5 obtained by the selective precipitation was purer, particularly with respect to lower content of Cu and Si. In calcination-dissolution procedure Si, formed easily soluble willemite (Zn_2SiO_4) [4,11], and Cu partly entered into the lattice of easily soluble zincite (ZnO) [5] and partly formed CuO that was dissolved simultaneously with zincite. In the selective precipitation procedure according to figure 1, Cu and Si were separated as insoluble sulphide and fluorosilicate, respectively. In both methods efficiency of Zn recovery from the waste was based on the same processes and hence were comparable.

Table 3. Phase composition of solid phases according to X-ray powder diffraction and elemental analysis.

solid	
sludge	a. p., SiO_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, CaCO_3
leaching residue ($pH = 1.0$)	SiO_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
leaching residue ($pH = 3.9$)	a. p., SiO_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
1a (hydroxides)	amorphous phase
1b (hydroxides)	a. p., traces $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
2 (sulphides)	$\text{Zn}_x\text{Cd}_{1-x}\text{S}$, $\text{Zn}_x\text{Cu}_{1-x}\text{S}$
3 (fluorides)	$\text{CaMg}_2\text{Al}_2\text{F}_{12}$, Na_2SiF_6
4 (Mn oxide)	$\text{Mn}_7\text{O}_{13} \cdot 5\text{H}_2\text{O}$
5 (final product)	a. p., traces $\text{Na}_2\text{Zn}_3(\text{CO}_3)_4 \cdot 3\text{H}_2\text{O}$
a. p.: amorphous phase	

CONCLUSION

From the results obtained it is obvious that the developed multi-step selective precipitation method provides efficient processing of zinc waste galvanic sludge. The purity of the zinc carbonate precipitate the composition of which is given in table 2, is sufficient for its possible utilisation in the metallurgical and ceramic industry. The total zinc yield ranged from 63 to 65 %. The significant zinc losses were observed in the leaching step (in the case of leaching up to $pH = 3.9$) or in the hydroxide precipitation stage (in the case of leaching up to $pH = 1.0$). The purity of the final zinc product does not depend on the initial composition of the leach liquor.

Among the impurities in the final Zn precipitate (table 3, precipitate 5), Ni and Na should be mentioned. Ni presence is highly undesirable if the product should be calcined to obtain ZnO white. However, Ni is not a common admixture in Zn galvanic sludge, and its presence in the sample processed probably represents a secondary contamination from the landfill in Dolní Rožínka. Si would probably not affect adversely the possible pigment application of ZnO.

Depending on the final pH value of leaching waste galvanic sludge the yield of zinc into the solution was 96 % ($pH = 0.9-1.0$) and 72 % ($pH = 3.9-4.0$). However, in the subsequent processing of strongly acid leach liquors the yield of zinc significantly declines. The total yield of zinc involving both zinc losses during leaching and processing of leach liquor with sodium hydroxide up to $pH = 5.8$ is practically equal. An advantage of leaching to higher pH values is the utilisation of neutralising capacity of the sludge for removal of most contaminants instead of using relatively expensive sodium hydroxide or carbonate.

The selective precipitation of the metal impurities does not require any special device, which should be exceptional in the wastewater treatment. That flowsheet proposed can hence be directly applicable in the plants producing the Zn-containing waste sludge.

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PŘEPRACOVÁNÍ ODPADŮ Z GALVANICKÉHO ZINKOVÁNÍ SELEKTIVNÍM SRÁŽENÍM

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Byla zkoušena metoda několikastupňového srážení pro přepracování odpadu z galvanického zinkování. Tato metoda zahrnuje kyselé loužení kalu v kyselině sírové, čištění sira-nového výluhu postupným srážením hydroxidů, sulfidů a fluoridů k odstranění trojmocných kovů, Cu, Cd, Ca, Mg, a Si, oxidačního srážení pro odstranění Mn, a konečně srážení Zn jako uhličitanu. Tuhé látky byly odstraňovány z každého matečného roztoku po srážení a jejich fázové složení bylo určováno rtg práškovou difrakcí a prvkové složení AAS. Navržené schéma dává relativně čistý uhličitán zinečnatý, vhodný pro výrobu surovin pro keramický a metalurgický průmysl a výrobu pigmentů, nicméně díky neúplnému loužení kalu, spolusrážení Zn do hydroxidů trojmocných kovů a sulfidů Cu a Cd byla celková účinnost přepracování jen 63-65 %.