Analysis of Flue Dust from Hot-Dip Galvanization

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https://doi.org/10.29227/IM-2026-02-02-005

Submission date: *2026-06-09* | Review date: *2026-21-09*

Abstract

The contribution deals with the analysis of two samples of flue dust, considered hazardous waste, which, alongside bottom dross, salmiac skimmings, zinc ash, spent degreasing bath, spent pickling bath, and spent fluxes, belong among the main wastes from hot-dip galvanizing. The both dried samples of flue dust were subjected to XRF, ICP-MS, CHNS-analysis, and XRD. So as to major elements the samples 1 and 2 contain mainly 34.88% and 35.79% Cl, 24.91% and 25.38% Zn, 10.35% and 10.78% N, respectively, followed by 3.56% and 4.02% H, 2.79% and 2.68% Mg, 2.42% and 1.59% C, 0.90% and 1.03% Al, 0.45% and 0.40% Fe, 0.10% and 0.33% S, 0.16% and 0.10 % Ca, 0.16% and 0.06% Si, 0.05% and 0.05 % Mn, respectively. Minor elements in samples 1and 2 are represented by 110 ppm and 73 ppm Cu, 110.4 ppm and 49.6 ppm As, 74.7 ppm and 80.3 ppm Bi, 16.3 ppm and 26.1 ppm Ni, and 1.5 ppm and 1.22 ppm Cd, respectively. The results of the X-ray diffraction analysis can be summarized as follows: in both samples 1 and 2, unnamed minerals, i.e. orthorhombic Ammonium Zinc Chlorides, specifically $(NH_4)_2ZnCl_4$ and $(NH_4)_3ZnCl_5$, respectively, were identified as the dominant phases. As accompanying phases in samples 1 and 2, two variants of an unnamed orthorhombic compound Zinc Ammine Chloride $(NH_3)_2ZnCl_2$ were identified, which differ slightly in their unit cell dimensions, as well as in the position and intensity of their peaks in the diffractogram. All these substantially represented phases, both dominant and accompanying, overlap the peaks of other minor phases that may be present in these samples, e.g. unnamed minerals $NH_3(OH)Cl$ and γ-$ZnCl_2$, followed by simonkolleite $Zn_5(OH)_8Cl_2•H_2O$, salammoniac NH_4Cl, etc.

Keywords: *zincing, flue dust, ammonium zinc chlorides*

1. Introduction

The corrosion of metals is a spontaneous physicochemical process in which metals gradually deteriorate due to their reaction with the surrounding environment, i.e. it converts a refined metal into a more chemically stable oxide. The result is metal degradation and a change in its mechanical and physical properties [1].

The corrosion causes direct loss on the level of 3–4 % of global GDP (gross domestic product) [2,3]. It is estimated that indirect costs can attain up to 6% of GDP [4,5,6].

So, the zincing (or zinc galvanizing) is one of the most common and effective methods used worldwide to protect steel and iron against rust and corrosion.

As for zinc, it is the 24th most abundant element in Earth's crust. An average Zn content in continental rust is running 73 ppm [7]. Sphalerite, cubic ZnS (zinc sulphide) or Zn0.95Fe2+0.05S (Zn 64.01 %, Fe 2.88 %, S 33.06 % [8] is main ore mineral in the world. Zinc annual production is around 12 million tonnes [9, 10,11]. According to data for 2024, the largest zinc producers (in million metric tonnes/share in %) are China (3.95/32.19), Peru (1.27/10.35), Australia (1.09/8.92), Mexico (1.01/8.22), India (0.86/6.98), USA (0.76/6.18), Bolivia (0.52/4.22), Kazakhstan (0.36/2.96), Russia (0.29/2.36) and Iran (0.288/2.35) [9]. Thus, the production of the top ten countries accounts for 84.74% of global zinc production. According to USGS data, the price of zinc in 2025 was about 130 cents per pound, or $2,866 per ton [11].

Distribution of zinc consumption worldwide in 2024, by end use is as follows galvanizing 60 % (Anti-rust protective coating for sheet metal, beams, pipes, structural steel, car bodies, and household appliances.), die casting alloys 15% (refined zinc alloyed with aluminum, magnesium, and copper is injected into molds under high pressure, the automotive industry - door handles, logos, engine parts, hardware, and consumer electronics.), oxides and other chemicals 11% (zinc dust and zinc oxide (ZnO) are widely used in rubber vulcanization, especially for tire manufacturing, the ceramics industry, agriculture - fertilizers, cosmetics - UV-protective creams, and the pharmaceutical industry), brass and bronze 9% (zinc is added to copper to produce brass. This material is crucial for plumbing pipes, valves, electrical terminals, and musical instruments), semi-manufacturers 4% (rolled zinc, zinc

roofing sheets, gutter systems, and coin blanks), other 1% (new technologies, zinc-ion batteries for energy storage, and nutritional supplements) [12, 13]. As to industrial sectors, zinc consumption is as follows: construction and infrastructure (66), automotive industry and industrial machinery (28%), consumer goods and electrical appliances (23%) and general engineering (7%) [14].

In Slovakia, there are approximately 40 active galvanizing plants in total, ranging from large-scale facilities to small workshop-scale companies. The large-scale sector consists primarily of hot-dip galvanizing plants, represented by approximately 10 companies operating 13 production facilities, 2 companies galvanize only their own products. The remaining about 30 companies perform electro-galvanizing [15, 16]. The differences between galvanic and hot-dip galvanizing are introduced in Table 1 [17, 18, 19].

Tab. 1. Comparison of galvanic and hot-dip galvanizing in a nutshell.

property	electro-galvanizing	hot-dip galvanizing
process	an electrochemical process in which a thin layer of zinc is applied to the surface of a steel object. this process takes place in an electrolytic bath, where a protective layer is created by a current between the anode (zinc) and the cathode (object)	immersion of a steel object into molten zinc at a temperature of around 450 °c.
layer thickness	5–15(30) μm (thin)	50–150 (200) μm (thick)
appearance	smooth, shiny	coarser, dull
corrosion resistance	low, suitable for mild climates and interiors, dry environments	high, suitable for exteriors, industrial areas or marine environments
application	small parts, screws, nuts, decorative elements	large structures, bridges, fences, masts, pipes, car bodies
lifespan	short / medium-term lifespan (units to decades), generally 1–10 years according to the environments	long (decades), 20–40 years in let v corrosive industrial areas or marine environments and 50–100 years in less corrosive environments

Solid wastes from hot dip galvanization are described in [20, 21]. The authors recognized: i) bottom skimming (or bottom dross, also hard zinc) containing over 90 % Zn, 1–6 % Fe, other metals below 1 % (Si, Al, Ni, Mg...), ii) top skimming (or top dross, also zinc ash), with 60–85 % Zn, 1–20 % oxides and chlorides of Zn and other accompanying metals, iii) zinc flue dust (or galvanizing flue dust GFD), it occurs when a steel part is immersed in molten zinc, creating so-called white smoke due to the decomposition of the flux $ZnCl_2$ a NH_4Cl, it is formed by dusty particles of Zn and flux, and within the frame of gas exhaust it is then captured on a filter, iv) salmiac skimming (or flux skimming), it is generated by reaction of molten zinc and flux, in contain about 46 % Zn, 26–33 % Cl, below 1 % other elements, such as Al, Fe, Pb.

The properties of galvanizing flue dust (GFD) were studied by [22]. They analyzed 3 samples of GFD and they found out that, GFD contains 26.9–28 % Zn, 0.32–0.35 % Fe, 0.06–0.07 % Pb, 0.38–1.03 % Al, 0.05–0.17 % Ca. The biggest differences were in the chlorine content, which was: 23.40 %, 28.37 %, and 42.56 %. Regarding the phase composition, the following main phases were determined $(NH_4)_2ZnCl_4$ and/or $(NH_4)_2ZnCl_2$.

2. Materials and Methods

The both dried samples of flue dust were subjected to XRF, ICP-MS, CHNS-analysis, and XRD. Before analyses the samples were subjected to grain size reduction below 100 μm using planetary vibratory mill Pulverisette 6 (Fritsch, Germany) equipped by agate cells with agate balls.

Optical observations were performed by monocular microscope Levenhuk DXT TV (magnification max. 30x)Major elements were determined using a SPECTRO XEPOS X-ray fluorescence spectrometer model XEPO3, range of elements: $_{11}Na–_{92}U$, scattering targets: Mo, Co, Al_2O_3, Pd, HOPG-crystal, X-ray lamp (type VF50): Pd with Be window, resolution: 145 keV on line Kα Mn. 5 g of sample were homogenized with 1 g of Clariant micro powder C (CEREOX BM-0002-1) and then pressed under 15 t to a pellet with a 32 mm diameter.

Carbon, hydrogen, nitrogen and sulfur were determined using a CHNS Vario MACRO Cube analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) equipped with a thermal conductivity detector. Helium (purity 99.995 %, intake pressure 2 bar) was chosen as a carrier gas in all analyses. The purity of oxygen for combustion was 99.995 % with intake pressure of 2 bar. The combustion tube was set at 1150ºC, the reduction tube at 850ºC. The sulfanilamide (C = 41.81 %, N = 16.26 %, H = 4.65 %, S = 18.62 %) was used as the CHNS standard.

Minor elements were assayed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using the device Agilent 7700 (Agilent Technologies, Inc. Wilmington, USA) for detection of elements in the range 2-260 amu, possibility of ultratrace analysis with sensitivity in ppt unit.

X-ray powder diffraction study was performed using D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany), working with Cu $K\alpha_1$ radiation at voltage 30 kV and current 40 mA. The data were collected over the angular range $5° < 2\theta < 80°$ with measuring steps 0.03° and a counting time 5s. X-ray diffractograms were evaluated using the DIFFRAC.SUITE EVA software (Bruker AXS, Karlsruhe, Germany).

3. Results

The grains of flue dust are documented in Fig. 1. Chemical composition of flue dust is summarised in Tables 2–4. All identified phases including their symbols in the diffractograms are listed in Table 5. The diffractograms are depicted in Figs. 2–4.

Tab. 2. Major elements in %.

sample	Cl	Zn	Na	Mg	Al	Fe	Ca	Si	Mn
1	**34.88**	**24.91**	**18.63**	2.79	0.90	0.445	0.163	0.16	0.05
2	**35.79**	**25.38**	**14.48**	2.68	1.03	0.399	0.099	0.06	0.05

Fig. 1. Flue dust, agglomerates and finer grains (bottom right mm scale).

Tab. 3. C, H, N and S in %.

sample	C	H	N	S
1	2.42	3.56	**10.35**	0.10
2	1.59	4.02	**10.78**	0.33

Tab. 4. Minor elements in ppm.

sample	Cu	As	Bi	Ni	Cd
1	110.0	110.4	74.4	16.3	1.50
2	73.0	49.6	80.3	26.1	1.22

Tab 5. Symbols of minerals/unnamed phases in XRD patterns

	reference code	mineral / unnamed phase	chemical formula	crystal system	main peak	
					d [Å]	I [%]
A	**00-012-0304**	**Ammonium Zinc Chloride**	**$(NH_4)_2ZnCl_4$**	**orthorhombic**	**5.190**	**100**
B	00-024-1435	Zinc Ammine Chloride	$(NH_3)_2ZnCl_2$	orthorhombic	5.860	100
C	**00-030-0069**	**Ammonium Zinc Chloride**	**$(NH_4)_3ZnCl_5$**	**orthorhombic**	**3.165**	**100**
D	01-074-0506	Zinc Ammine Chloride	$(NH_3)_2ZnCl_2$	orthorhombic	3.897	100
E	00-016-0869	Zinc Chloride	β-$ZnCl_2$	monoclinic	5.140	100
F	01-088-1160	Hydroxylammonium Chloride	$NH_3(OH)Cl$	monoclinic	2.984	100
G	00-016-0850	Zinc Chloride	γ-$ZnCl_2$	tetragonal	3.490	100
H	01-072-1444	Simonkolleite – Zinc Chloride Hydroxide Hydrate	$Zn_5(OH)_8Cl_2•H_2O$	trigonal	7.880	100
J	00-007-0007	Salammoniac – Ammonium Chloride	NH_4Cl	isometric	2.740	100
K	01-084-4386	Hydroxyl Ammonium Chloride	$NH_3(OH)Cl$	monoclinic	2.952	100
L	04-011-3051	Sodium Perchlorate Hydrate	$NaClO_4•H_2O$	monoclinic	3,445	100
M	00-020-1436	Ashoverite – Zinc Hydroxide	$Zn(OH)_2$	tetragonal	2.902	100
N	00-036-1474	Nitratine – Sodium Nitrate	$NaNO_3$	trigonal	3.030	100
P	00-024-1460	Zinc Nitrate Hydroxide Hydrate	$Zn_5(OH)_8(NO_3)_2•2H_2O$	monoclinic	9.790	100

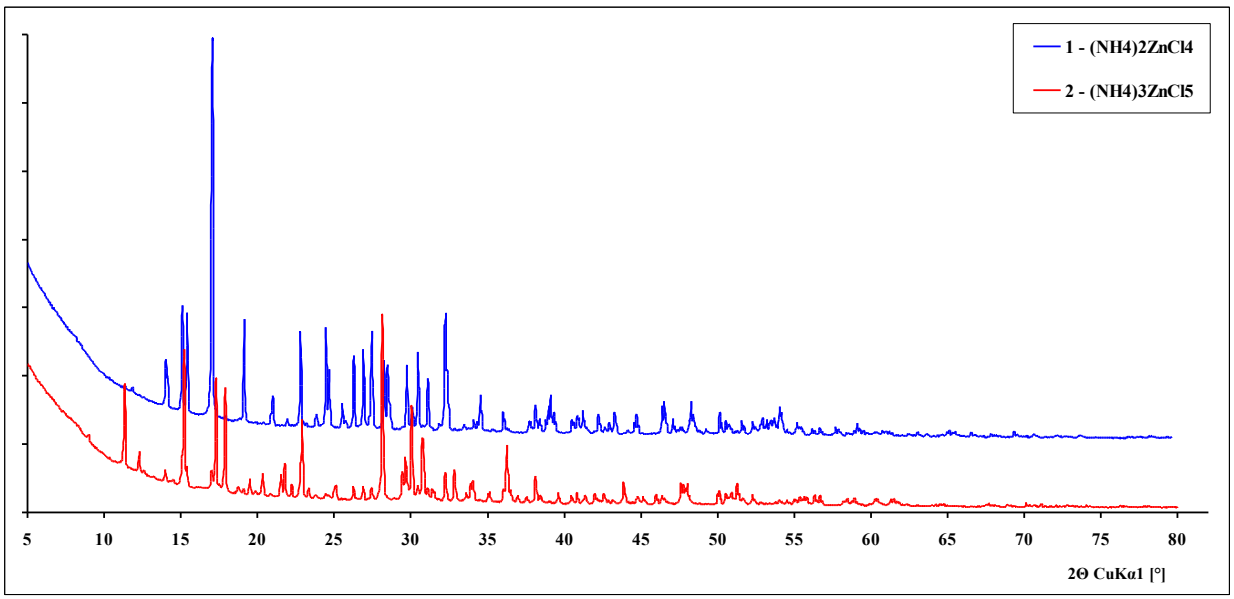

Fig. 2. Comparison of diffractograms

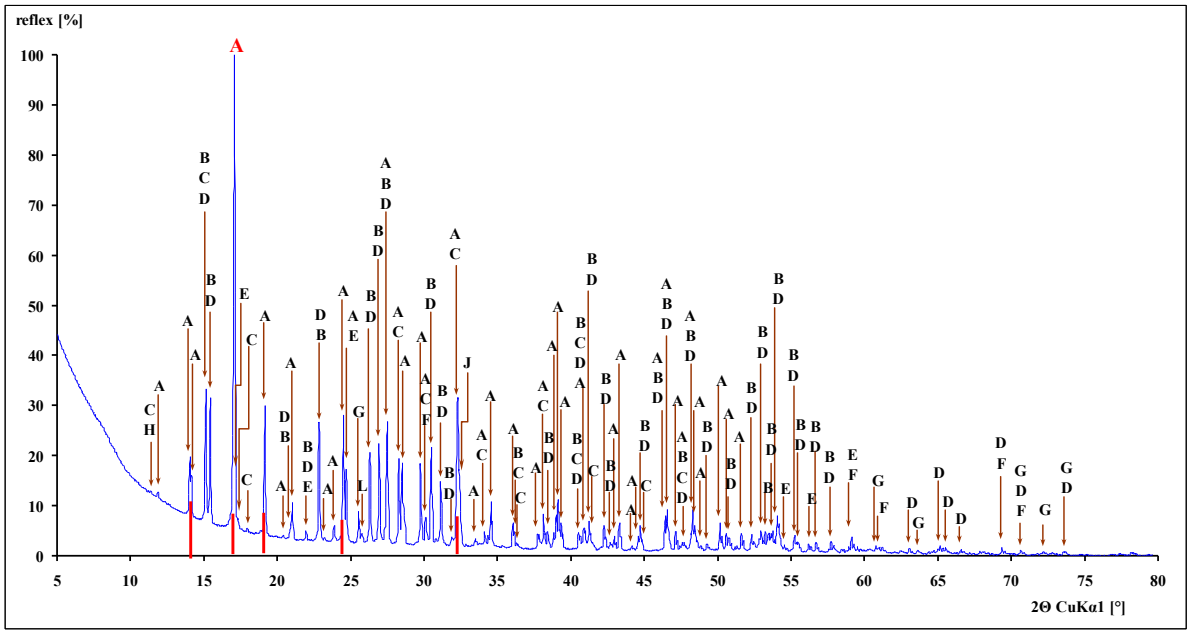

Fig. 3. XRD pattern of sample 1 – dominant phase A - $(NH_4)_2ZnCl_4$ (after Tab. 4)

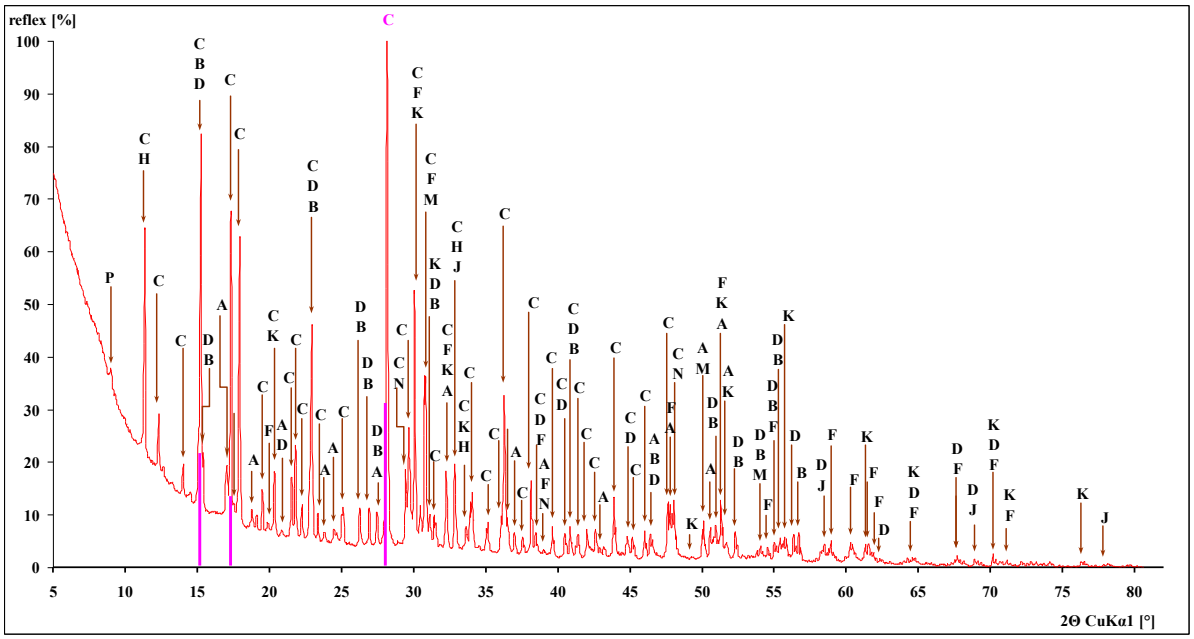

Fig. 4. XRD pattern of sample 2– dominant phase C - $(NH_4)_2ZnCl_5$ (after Tab. 4)

4. Conclusion

It has been shown that elements such as chlorine (34.88–35.79 %), zinc (24.91–25.38 %), sodium (14.48–18.63 %) and nitrogen (10.35–10.78 %) dominate in terms of chemical composition.

The results of the X-ray diffraction analysis can be summarized as follows: in both samples 1 and 2, unnamed minerals, i.e. orthorhombic Ammonium Zinc Chlorides, specifically $(NH_4)_2ZnCl_4$ and $(NH_4)_3ZnCl_5$, respectively, were identified as the dominant phases. As accompanying phases in samples 1 and 2, two variants of an unnamed orthorhombic compound Zinc Ammine Chloride $(NH_3)_2ZnCl_2$ were identified, which differ slightly in their unit cell dimensions, as well as in the position and intensity of their peaks in the diffractogram. All these substantially represented phases, both dominant and accompanying, overlap the peaks of other minor phases that may be present in these samples, e.g. unnamed minerals $NH_3(OH)Cl$ and γ-$ZnCl_2$, followed by simonkolleite $Zn_5(OH)_8Cl_2•H_2O$, salammoniac NH_4Cl, etc.

Acknowledgments

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-23-0055. This work was also supported by the Slovak Grant Agency for Science projects VEGA No. 2/0052/25 and No. 2/0116/23. This work was supported by the EU NextGenerationEU through the Recovery and Resilience Plan for Slovakia under the project No. 09I03-03-V03-00083.

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