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Characterization of Galvanizing Flue Dust and Recycling Possibilities

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Abstract: Waste generation is a part of every technological process, including galvanizing. The presented paper deals with the characterization of flue dust generated in the process of hot-dip galvanizing, and proposes possible methods for zinc recycling. The flue dust is released into the atmosphere as a white fume above the zinc bath, which is caused by the decomposition of ammonium chloride and zinc chloride present in the flux. This dust is classified as hazardous waste and is a material with a particle size below 90 µm. In addition to zinc and iron compounds, it contains water vapor and oils. The presented elemental, phase, and other characteristic methods of flue dust are important for the subsequent selection of a suitable method for processing the material. At present, this waste is not processed separately due to its low production, which is approximately 0.3 kg per 1 tonne of galvanized steel. The proposed hydrometallurgical recycling method enables the processing of flue dust on a small scale and enables the recovery of high-purity zinc in the form of metallic zinc or zinc oxide.

Keywords: galvanizing; flue dust; zinc; atomic absorption spectroscopy; X-ray fluorescence analysis; X-ray diffraction analysis; recycling; leaching; precipitation

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1. Introduction

There are several methods for protecting steel from corrosion. Hot-dip galvanizing is currently one of the most effective ways, with approximately 95% of galvanized steel products being hot-dip galvanized [1].

Zinc is widely used for the corrosion protection of steel due to its more negative redox potential compared to steel under the same conditions [2]. The use of zinc globally has an increasing trend every year, which is also reflected in its overall consumption. Worldwide, more than 50% of zinc is used for galvanizing every year, while in 2020, production of zinc was almost 13.7 million tons. China, Australia, and Peru maintain their leading positions in zinc production [3,4]. The world's total zinc reserves are estimated at 250 million tonnes, with Australia having the largest zinc reserves at 27%, China has 18%, and Peru and Mexico have 9%. Zinc is of high economic importance due to its widespread use in various industries [5]. Due to the high consumption of this metal, zinc reserves at open sites are expected to be sufficient only for the next 17 years. For this reason, it is necessary to recover zinc from zinc-containing waste, which includes the recycling of waste from hot-dip galvanizing plants.

Continuous and batch hot-dip galvanizing uses the immersion of steel parts into molten zinc. The entire process, from the surface preparation of the steel part to the formation of the zinc coating, is accompanied by the generation of waste. The largest

volumes of the waste produced are liquids. These are spent solutions from pre-treatment (degreasing, pickling, and flux). Solid top and bottom dross waste is also generated in the galvanizing bath. Gaseous wastes are generated during both pre-treatment and the immersion of steel parts in zinc melts. After the fumes are cooled, galvanizing flue dust is formed, which is captured on the filters [6–9].

Only a small part of the scientific publications deals with the characterization and processing of flue dust. A hydrometallurgical processing method is used to obtain various zinc and flux products [10,11]. The leaching of flue dust mainly takes place in hydrochloric acid [10], due to the high content of chloride compounds in the waste. Pyrometallurgical processing of galvanizing flue dust has been carried out to obtain pure zinc ingots [12].

According to the EPA (Environmental Protection Agency, European waste catalog and hazardous waste list, KO61), zinc flue dust is classified as hazardous waste [13] due to the high content of zinc (~20%), chlorine (~10%), ammonia, Fe, and other elements such as Pb, Cu, Al, Sn, Mg, Ca and Si [10–14], which come from the pretreatment and galvanizing process itself [11,15]. Despite the fact that galvanizing flue dust is classified as hazardous waste, it can also be considered a valuable secondary raw material due to its high zinc content.

Flue dust is released into the kiln atmosphere, producing fume that forms above the galvanizing bath. The main cause of fume production is the decomposition of zinc chloride and ammonium chloride present in the flux [16,17]. Generally, the mono, double, and triple salts of zinc ammonium chloride ($ZnCl_2$:xNH_4Cl) are most commonly used as the flux. The formation of white fume depends on the total value of ACN (Ammonium Chloride Number), which expresses the mathematical relationship between the ammonium chloride and zinc chloride in the flux solution, as seen in Equation (1).

$$\mathrm{ACN} = \frac{\mathrm{NH_4Cl}\ \%}{\mathrm{ZnCl_2}\ \%} \quad (1)$$

When the ACN value is under 1 (typical value for double salt is ACN 0.8), the fume tends to be brown or black. If the ACN value is above about 1.2 (typical value for triple salt or quadraflux is ACN 1.60), the fume is white. The greater the flux concentration, the more fume produced [18].

Other reasons for fume formation include relative humidity, the type of galvanized material, and the composition of the molten zinc. The aluminum content of the zinc melts, about 0.010%, has positive effects on the galvanizing process, while the recommended concentration of Al during bath galvanizing is in the range of 0.003 to 0.005% [19]. The higher the aluminum content, the greater the production of thick white fume containing the volatile aluminum chloride, as shown in Equation (2). Thus, it can be assumed that aluminum chloride will be present in the flue dust as well [18].

According to Equation (3), ammonium chloride decomposes into ammonia and hydrochloric acid, when in contact with the molten zinc in the bath. This decomposition is very reactive and forms chloride compounds with metals. Unreacted ammonia and acid are cooled above the bath to form solid NH_4Cl, which is part of the white fume. The binary diagram $ZnCl_2$-NH_4Cl confirms that with increasing NH_4Cl content, the evaporation temperature of NH_4Cl decreases. At about 2.5% of NH_4Cl, the sublimation temperature is lower than the kettle operation temperature of 450 °C. Sublimation at commonly used $ZnCl_2$:xNH_4Cl ratios already occurs at a temperature of 338 °C [20]. Approximately 90% of the white fume is produced as soon as the steel part is immersed in molten zinc, and the remaining 10% is released when the galvanized part is removed. The chloride compounds present in the fluxes react with both the zinc melts and the steel parts. Part of the fumes formed above the bath are also the compound $ZnCl_2$ originating from the flux and arising from the reaction between zinc in the bath and hydrochloric acid, as shown in Equation (4) [7,16,21,22].

$$6NH_4Cl + 2Al = 2AlCl_{3(g)} + 6NH_{3(g)} + 3H_{2(g)} \qquad \Delta G^{\circ}{}_{450} = -628{,}821\ \mathrm{KJ} \quad (2)$$

$$NH_4Cl = NH_{3(g)} + HCl_{(g)} \qquad \Delta G^{\circ}_{450} = -21{,}257\ KJ \tag{3}$$

$$Zn + 2HCl_{(ia)} = ZnCl_{2(g)} + H_{2(g)} \qquad \Delta G^{\circ}_{450} = -141{,}090\ KJ \tag{4}$$

In addition to the reactions above, during which fumes are formed above the zinc bath, zinc flue dust is produced according to reactions (5)–(7) between the zinc melt and the flux in the bath. These reactions are accompanied by the production of strong acids, which further cleanse and purify the surface of the steel part.

$$Zn(NH_4)_3Cl_5.4H_2O = Zn(NH_3)_2.Cl_2.2H_2O + [HCl(OH)_2]H_2 + 2HCl + NH_3 \tag{5}$$

$$ZnO + [ZnCl_2(OH)_2]H_2 = ZnO.ZnCl_2 + 2H_2O \tag{6}$$

$$Zn(NH_3)_2Cl_2.2H_2O = [ZnCl_2(OH)_2]H_2 + 2NH_3 \tag{7}$$

The waste generated in the process of batch hot-dip galvanizing (dry, wet) is in relatively low quantities (approximately 1 kg of flue dust per tonne of galvanized steel) compared to other solid waste, which causes its problematic processing. It is not processed separately but is disposed of in a hazardous waste landfill. However, flue dust can be treated hydrometallurgically or pyrometallurgically together with zinc ash, as this waste has a similar chemical composition.

Considering these facts, the main aim of this research was the characterization of flue dust and to determine its composition and mineral phases, as an indispensable preliminary step towards choosing the best available technology for recovery of metals. Based on the results of galvanizing flue dust analysis, the possibilities of galvanizing flue dust recycling are subsequently proposed.

2. Materials and Methods

Sample Preparation and Characterization

Flue dust samples A, B, and C, from three different local, dry, batch, hot-dip galvanizing plants, were used in this study. Flue dust samples captured on the filters in the galvanizing plants were collected during the one-month galvanizing period. The as-received samples were reweighed and subjected to quartering and dividing sample preparation methods to obtain representative samples of flue dust.

The observation of samples showed that samples A and C had similar color and particle size structure. Sample B differed not only in color, but also in particle size, which caused the formation of variously sized clusters. The sample was then milled in a disc vibrating mill (OPS, Prešov, Slovakia) for 1 min and then homogenized, quaternized, and divided to obtain a representative sample.

The surface area of the samples was measured with a nitrogen gas adsorption analyzer (Quantachrome-NOVA-1000; software NovaWin, version 10.01, Quantachrome Instruments, Boynton Beach, FL, USA). Before measuring, the samples (2–4 g) were degasified in a vacuum at a temperature of 30 °C for 24 h. The specific surface area (S_A) was determined by the Brunauer–Emmett–Teller (BET) method from the measured nitrogen adsorption ($p/po = 0.05–0.30$). $S_{A(mult)}$ informative value of density was calculated from the measured volume and weight of samples within the surface analysis.

Chemical analysis of flue dust samples was performed by the classical wet method using atomic absorption spectrometry (AAS) with a Varian SpectrAA20^{+}-type spectrophotometer (Varian, detection limit: 0.3–6 ppb; slit width 0.2–1 nm; wavelength 213.9–422 nm and lamp current 4–12 mA, Belrose, Australia). For analysis, 5 samples were taken from each representative sample and analyzed 10 times to determine the average values of the elements. Chlorides were determined by titration using silver nitrate $AgNO_3$ (0.1M) and K_2CrO_4 indicator (5%) of analytical purity.

The phases present in homogenized samples of Zn dust were identified by X-ray diffraction phase analysis (XRD). The samples were prepared according to the standardized panalytical backloading system, which provides nearly random distribution of the particles. The samples were analyzed using a Philips X'Pert PRO MRD (Co-Kα), range of measuring

(10–120° 2theta), scan step (0.0170°) diffractometer (Philips, Almelo, the Netherlands). The phases were identified using X´Per HighScore plus software. Samples were subjected to scanning electron microscopy (SEM) analysis along with energy-dispersive spectrometry (EDS), MIRA3 FE-SEM (resolution: 1.2 nm at 30 kV; 2.3 nm at 3 kV, TESCAN, Warrendale, PA, USA).

Leachability testing was performed according to the European standard EN 12457-1:2002. This standard deals with compliance testing in the leaching of granular waste materials, which includes galvanizing flue dust.

Thermodynamic calculations of proposed recycling methods were calculated by MEDUSA software (version 32-bit, 2010, Royal Institute of Technology, Stockholm, Sweden) and by HSC Chemistry (version 10.0., Outotec, Pori, Finland)

3. Results

3.1. Surface Analysis

From the achieved results of the specific surface area of the flue dust samples (Table 1), different values of $S_{A(mult)}$ can be observed. The highest value is achieved by sample C with 2.41 $m^2.g^{-1}$. At the same time, sample C achieves the highest loss on drying at about 1.2%. Sample B before/after crushing in the mortar reaches the lowest value $S_{A(mult)}$.

Table 1. Surface area of dust samples.

Sample	Degasified in Vacuum 30 °C/24 h	Specific Surface Area (m^2 g^{-1})	Density (g cm^{-3})
A—grey	≈1%	1.74	1.88
B [1]—brown	≈0.3%	0.28	1.72
B [2]—brown	0.3 + 0.3%	0.55	1.69
C—light gray	≈1.2%	2.41	1.85

[1] Agglomerates present in the sample. [2] Agglomerates crushed with a mortar and pestle.

3.2. The Chemical Composition Analysis

The contents of the main and trace elements in the studied samples are given in Table 2. The obtained results show that all three samples of flue dusts have a majority of Zn up to 28% and Cl^- around 43%. All three flue dust samples contain almost the same content of iron and calcium. Sample A has the highest content of aluminum and lead, about 1.03% and 0.07%, respectively, with lead traces represented in the other two samples (<LoD—detection limit). The contents of Cu, Si, and Sn were also determined. The content of these elements was below the detection limit of the method. The chemical composition shows that the flue dust contains a significant amount of zinc compared to the primary raw material (2–10% Zn). For this reason, flue dust from hot-dip galvanizing can be considered as a valuable secondary raw material.

Table 2. Content (%) of elements in samples, LoD—limit of detection in AAS methods.

Sample	Zn	Fe	Cu	Pb	Al	Si	Sn	Ca	Cl^-	Residue
A	27.49	0.34	<LoD	0.07	1.03	<LoD	<LoD	0.17	23.40	47.5
B	26.9	0.32	<LoD	0.06	0.38	<LoD	<LoD	0.05	28.37	43.98
C	28.0	0.35	<LoD	0.07	0.97	<LoD	<LoD	0.08	42.56	29.01

3.3. The Phase Analysis

The results of the XRD analysis (Figure 1) show that flue dust contains zinc and chlorides in various complex compounds, together with ammonia, in a different crystal structure, with the main mineral being $(NH_4)_2ZnCl_4$ resp. $(NH_4)_2ZnCl_2$. Sample B contains, in addition to the compounds mentioned, a simoncolleite phase $(Zn_5(OH)_8Cl_2.H_2O$ and $(NH_3OH)Cl$. However, XRD diffraction analysis did not confirm the presence of ZnO in

the samples, which according to [14], should be in the zinc dust. The presence of zinc in the compounds together with chlorides and ammonia indicates that this dust can be processed hydrometallurgically with the subsequent recovery of zinc compounds [10,23], or in the production of a new flux [11] applicable in the galvanizing pretreatment process.

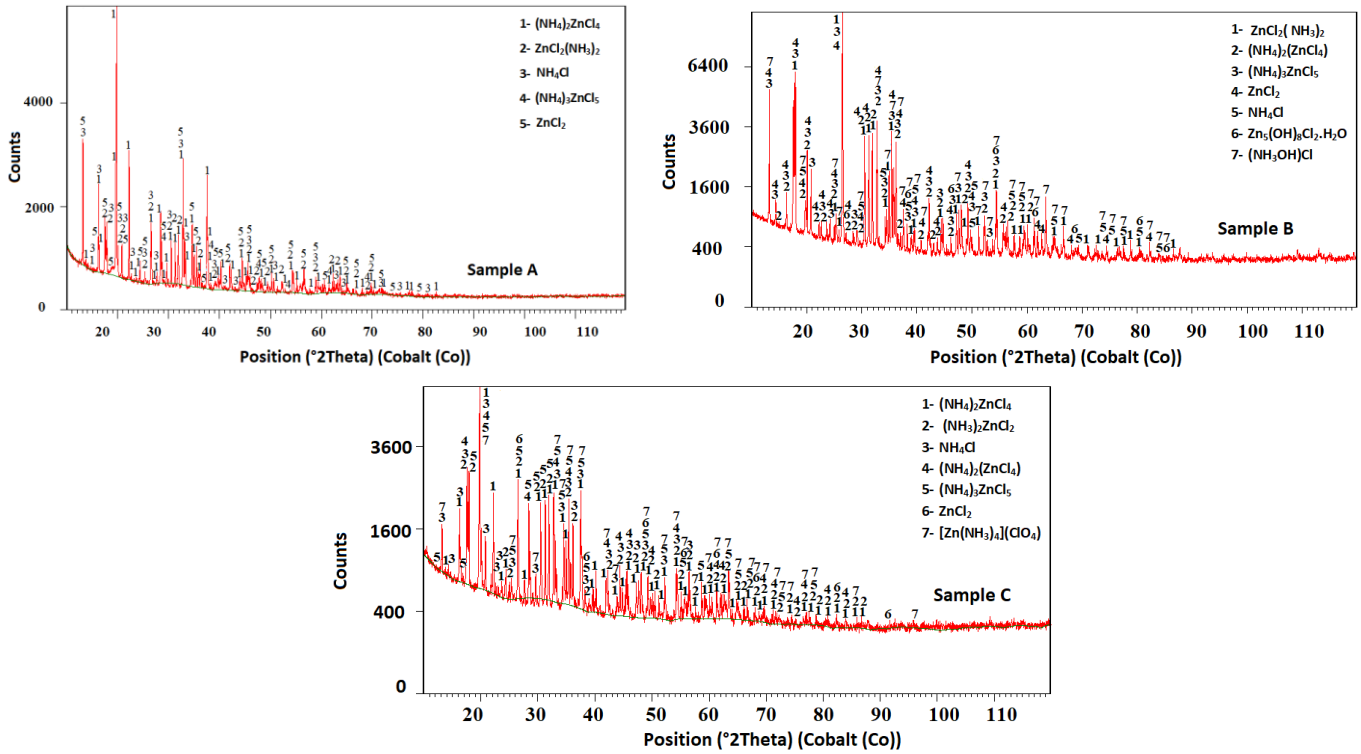


Figure 1. X-ray diffraction (XRD) patterns of Zn samples A, B and C.

3.4. Morphology of Samples

Figure 2 shows the morphology of flue dust samples using SEM. From the comparison of the mentioned flue dust samples, it is possible to highlight the difference in particle sizes. The smallest particles were observed in sample C. This observation confirms the results of the measurement of the measuring surface. The largest specific surface area was measured in this sample.

The EDS analysis of the flue dust samples A, B and C are shown in Figure 3a–c, respectively. The EDS analysis confirms that the samples of flue dust consist mainly of zinc and chlorine, which together make up from 70.8 to 94 wt.% by weight, which was confirmed by previous analysis of flue dust. The given analysis also determined a relatively high oxygen content (sample A and B), which in turn confirms the XRD analysis that zinc and aluminum can also be present in the sample in oxide or oxochloride compounds. The presence of Al, which was observed in samples of Zn dust in samples A and C, is in accordance with the literature reference [18]. The red color of the text represents elements that are less likely to occur.

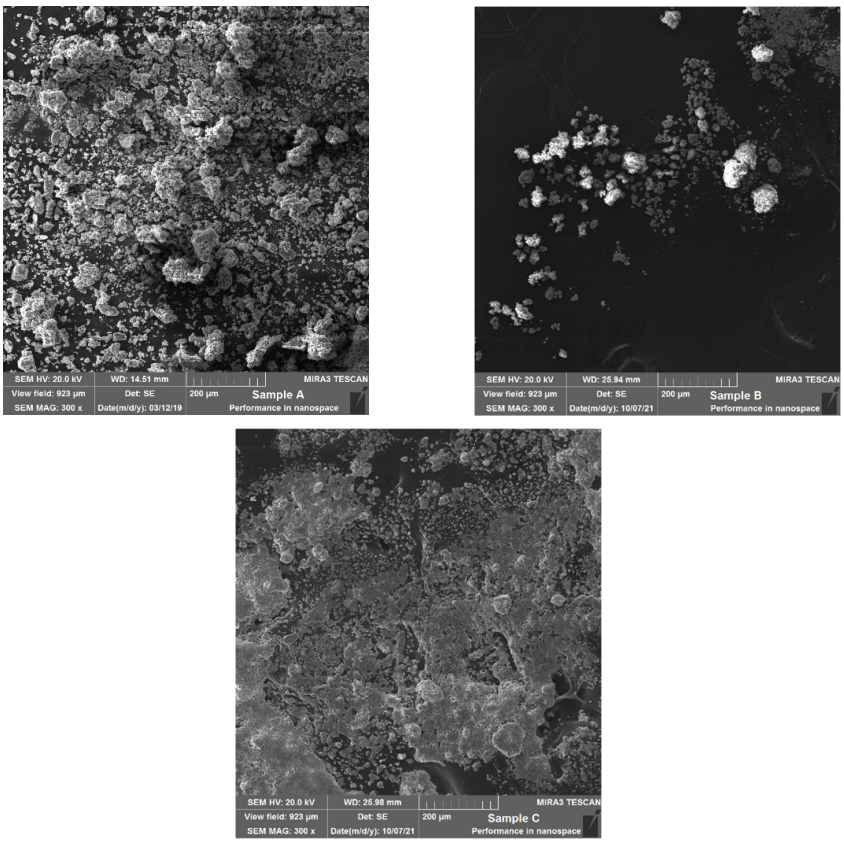
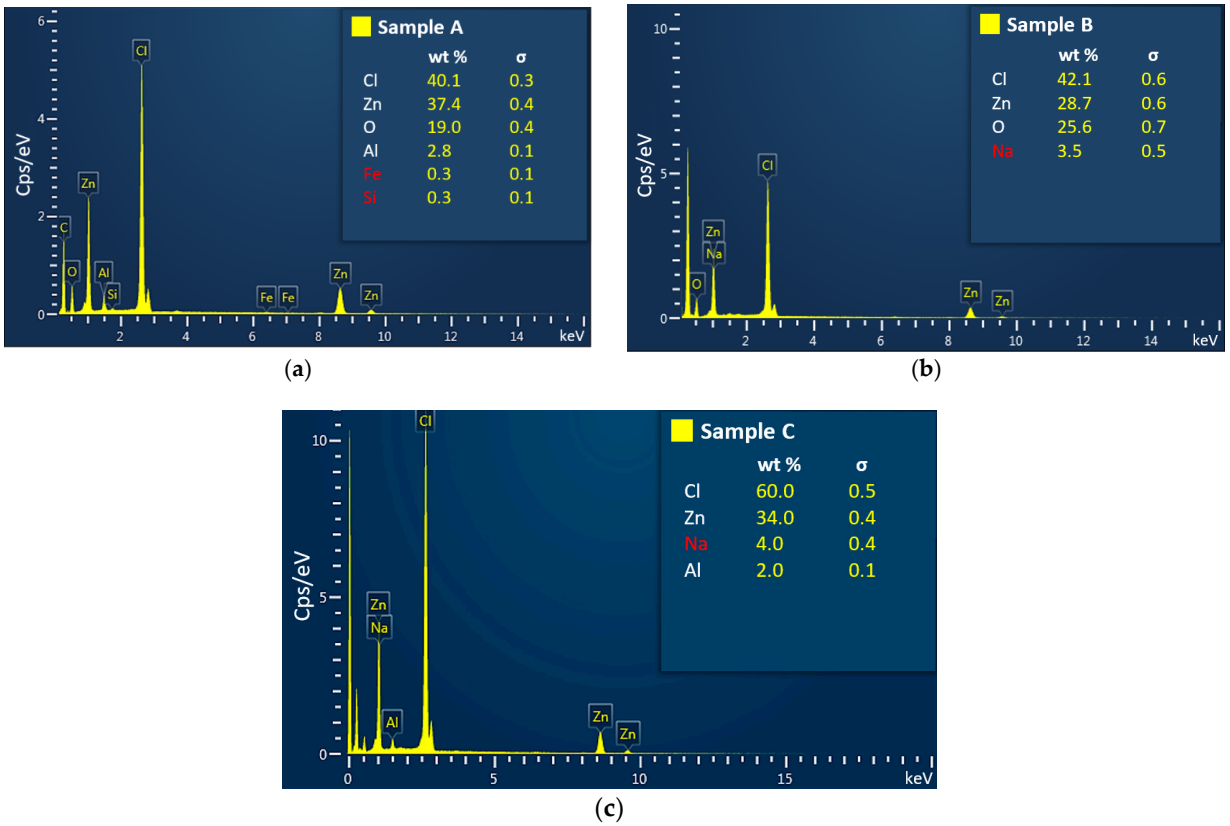


Figure 2. Particle morphology of zinc flue samples A, B, and C.



(**a**) (**b**)

(**c**)

Figure 3. EDS analysis of the Zn flue dust (**a**) sample A, (**b**) sample B, and (**c**) sample C.

3.5. Leachability Testing

The results of leachability tests by the European standard EN 12457-1:2002, for all three zinc dusts, are shown in Table 3. From the results it follows that concentrations are exceeded for cadmium, lead, zinc, and chlorides. According to the limits, all three dusts must be disposed of in landfills for hazardous waste.

Table 3. Results of Leachability Testing.

Sample	Concentration ($mg.l^{-1}$)									
	Al	**As**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mo**	**Ni**	**Pb**
A	2.118	<LoD	0.5041	0.025	<LoD	1.76	0	0	0.7561	41.225
B	1.952	<LoD	0.5233	0.010	<LoD	1.05	0	0	0.6542	39.013
C	2.206	<LoD	0.5122	0.026	<LoD	1.43	0	0	0.8241	40.325
Sample	**Concentration ($mg.l^{-1}$)**									
	Sb	**Se**	**Sn**	**V**	**Zn**	**Cl^-**	**F-**	**SO_4^{2-}**	**pH**	
A	0	0	<LoD	0	80,145	43,024	1.52	50	5.872	
B	0	0	<LoD	0	72,750	37,871	1.23	48	5.682	
C	0	0	<LoD	0	87,780	47,123	1.01	43	5.914	

4. Recycling Possibilities

This chapter summarizes the conclusions drawn from the characterization of flue dust and discusses the possibilities of waste treatment with the aim of obtaining a marketable product. The results of the AAS analysis confirmed the high content of Zn (27.46%) in the flue dust. Impurities, which could affect the quality of the obtained Zn, are Al (0.38–1.03%), Fe (0.33%) and Pb (0.07%). Both results of the phase analysis and the subsequent leachability test confirm that most of the Zn in the waste is present as water-leachable phases. The remaining solid phase should be ZnO, which was confirmed by EDS analysis (Figure 3).

4.1. Proposed Two-Step Leaching Recycling Method

The water leachability test performed at a liquid-to-solid ratio L/S of = 2 confirmed Zn leaching efficiency ranging from 54.09% to 62.70%. In addition to Zn, Pb was leached into the solution with an efficiency of 12% and Al was leached with an efficiency from 0.04% to 0.1%. Fe concentration in the water-leaching step was below the level of AAS detection. In further research of flue dust treatment, it is necessary to determine the maximum Zn leaching efficiency at different L/S ratios, since a ratio of 2 is low for practical usage.

In order to recover remaining Zn from solid non-water-leachable phases, it is necessary to use leaching solution such as HCl, H_2SO_4, or others. According to ΔG° values of Equations (8) and (9), both leaching reagents should be suitable to leach the remaining Zn from predicted ZnO phase.

$$ZnO_{(s)} + H_2SO_4 = ZnSO_4 + H_2O \qquad \Delta G^\circ_{293.15} = -95.692\ KJ \tag{8}$$

$$ZnO_{(s)} + 2HCl = ZnCl_2 + H_2O \qquad \Delta G^\circ_{450} = -24.349\ KJ \tag{9}$$

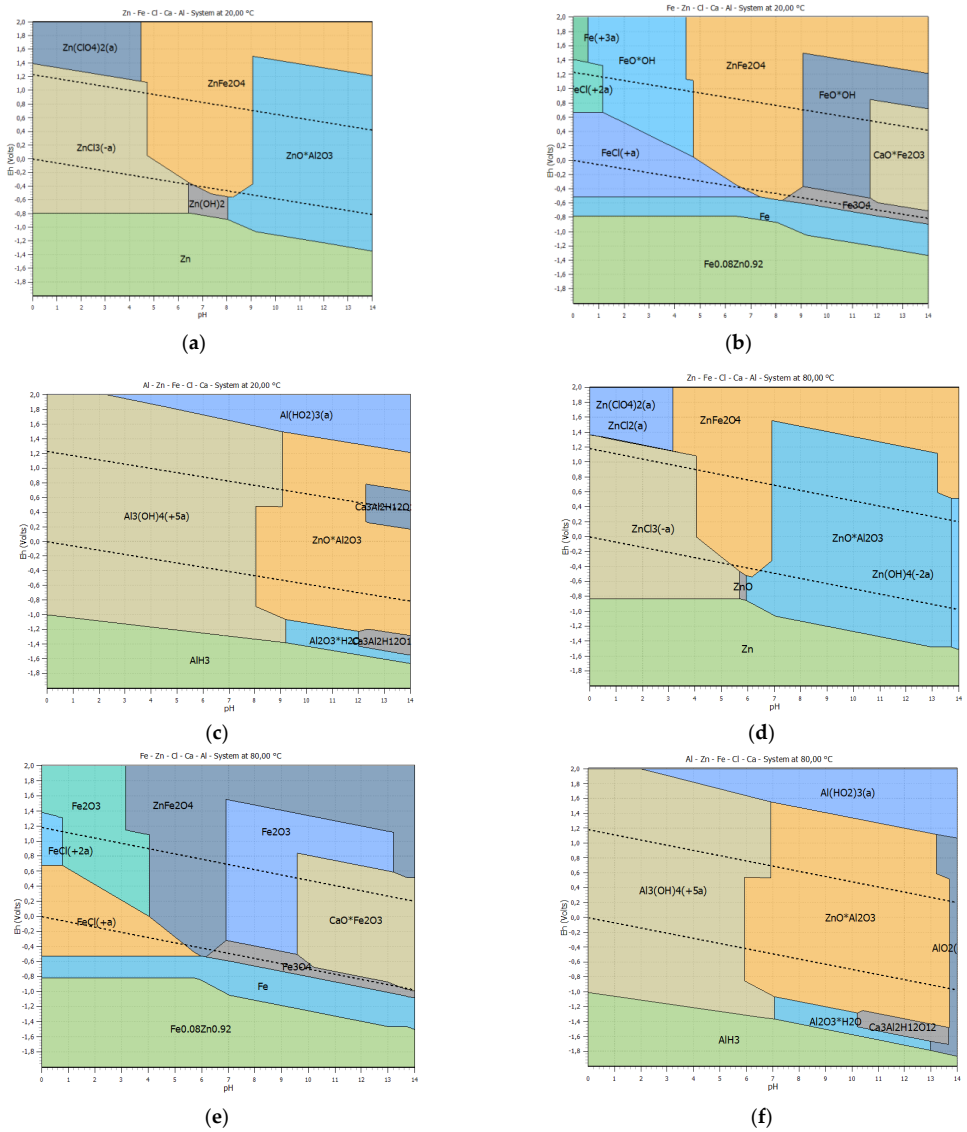
Based on the above findings, a two-stage leaching is therefore proposed. The first stage is leaching in water and the second stage is leaching the resulting solid residue in suitable acid. The results of the leachability test show that leaching in water provides the advantages of obtaining high Zn concentration and relatively high leaching selectivity. The disadvantage could be the presence of chlorides, which makes zinc electrowinning with the use of lead anode less suitable. The second acidic leaching step should be sufficient to dissolve the remaining (~40%) Zn, but an acidic solution will also dissolve other present impurities.

4.2. Proposed Solution Refining and Zinc Recovery

Depending on the proposed method, the recovery of Zn from acidic solutions may be affected by the presence of impurities.

If sulfuric acid is used for the second leaching step, direct Zn recovery could be possible by electrowinning due to the fact that the lead anode does not dissolve in this solution and none of the impurities (nor Al or Fe) are reduced together at the cathode surface with Zn [24].

If hydrochloric acid is used, solution refining is necessary to obtain pure zinc carbonate precipitate. The proposed solution-refining method consists of the precipitation of Fe and Al prior to Zn precipitation. Solution refining consisting of hydroxide precipitation may be performed by addition of NaOH. Figure 4 shows Eh-pH diagrams of Zn, Fe and Al in Zn-Fe-Al-Cl-Ca-H_2O systems at 20 and 80 °C. Iron will co-precipitate with Zn as $ZnFe_2O_4$ by an increase of pH to 4 at 20 °C or pH increase to 5 at 80 °C, and further increase of pH to 6 at 80 °C or to 8 at 20 °C will result in $ZnO{\cdot}Al_2O_3$ precipitation. Both precipitations will cause undesirable zinc losses [25]. Removal of Fe should also be possible by an increase in oxidation potential in the system at pH range from 1.2 to 4.6 at 20 °C and at range from 0.8 to 4.0 at 80 °C.



(**a**) (**b**) (**c**) (**d**) (**e**) (**f**)

Figure 4. Eh-pH diagram for Zn-Fe-Cl-Ca-Al-H_2O system: (**a**) Zn 20 °C; (**b**) Fe 20 °C; (**c**) Al 20 °C; (**d**) Zn 80 °C; (**e**) Fe 80 °C and (**f**) Al 80 °C. Molarity: (Zn) = 1.85 M, (Fe) = 0.0475 M, (Cl) = 2.00 M and (Ca) = 0.017, (Al) = 0.0877 M.

The next proposed step is the recovery of the Zn in the form of insoluble compounds from both acidic and neutral solutions. Zinc precipitation is possible in the form of carbonates, as the $K_{sp\ ZnCO3}$ is 1.46×10^{-10}. Suitable reagents for precipitation are Na_2CO_3 Equation (10) or $(NH_4)_2CO_3$ Equation (11).

$$Na_2CO_3 + ZnCl_2 = ZnCO_{3(s)} + 2NaCl \qquad \Delta G^{\circ}{}_{293.15} = -81.327\ KJ \tag{10}$$

$$(NH_4)_2CO_3 + ZnCl_2 = ZnCO_{3(s)} + 2NH_4Cl \qquad \Delta G^{\circ}{}_{293.15} = -80.959\ KJ \tag{11}$$

Figure 5 shows a fraction diagram for Zn precipitation. Minimum theoretical pH for high Zn precipitation efficiency is 7, but practical pH necessary to precipitate Zn will be higher due to ionic strength of the solution which promotes the formation of complex compounds [26,27]. The carbonate can be further calcined to form zinc oxide and carbon dioxide, according to Equation (12). Based on the above, a recycling process is proposed, the individual steps and operations of which are shown in Figure 6.

$$ZnCO_3 = ZnO + CO_{2(g)} \qquad \Delta G^{\circ}{}_{473.15} = -13.577\ KJ \tag{12}$$

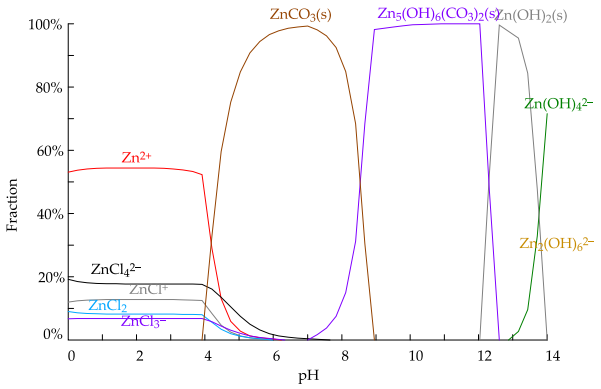


Figure 5. Phase diagram of $ZnCO_3$ precipitation. Molarity: $(ZnCl_2)$ = 1.00 M, (Na_2CO_3) = 1.00 M.

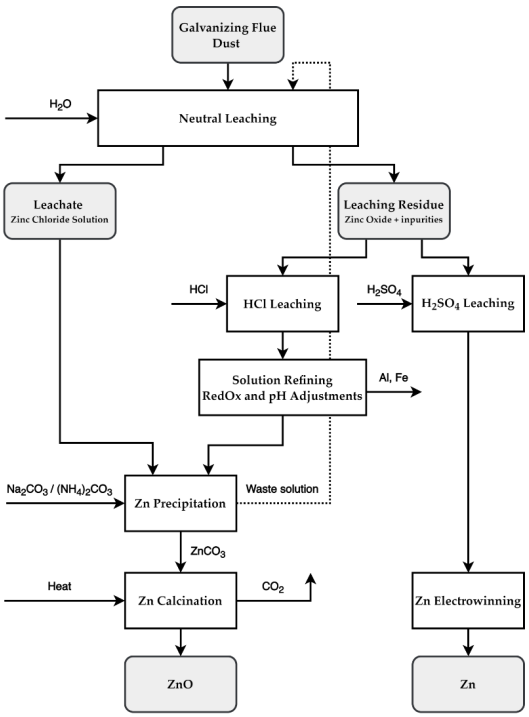


Figure 6. Proposed recycling method of Zn from galvanizing flue dust.

5. Conclusions

The hot-dip galvanizing process is accompanied by the production of various types of waste, which are often classified as hazardous. One of them is the flue dust generated above the bath. Despite the high zinc content, the treatment of said waste is not carried out. Given this fact, the main aim of this study was to obtain basic information about waste for reuse in the industry. The characterization of the delivered dust samples was performed as an important step in the selection of suitable methods used in the design of possible recycling methods. Phase $(NH_4)_2ZnCl_2$ and $(NH_4)_2ZnCl_4$ are the main mineral phases. The obtained results indicate that for economic and environmental benefits, the most suitable processing method appears to be a hydrometallurgical process aimed at obtaining metallic zinc, zinc oxide or a flux based on $ZnCl_2$:xNH_4Cl, which can be reused in the dry bulk galvanizing process. Leaching as the first step of hydrometallurgical processing should be performed in two steps. The first is neutral leaching in water, where zinc is selectively leached from the waste (~60%). The second is acid leaching, where the remaining zinc is leached (~40%) with other metal impurities present in the flue dust. One of the options for Zn recovery from the solution is a combination of solution refining by pH adjustment, carbonate precipitation and calcination to zinc oxide. The second method should be especially applicable to zinc sulphate solutions, from which direct reduction to zinc metal by electrowinning should be possible. In future research, it is necessary to experimentally verify the proposed methods for the recycling of zinc flue dust.

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