Research Article

XPS and FT-IR Characterization of Selected Synthetic Corrosion Products of Zinc Expected in Neutral Environment Containing Chloride Ions

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ZnO, Zn(OH)2, Zn5(OH)8Cl2·H2O, ZnCO3, and Zn5(CO3)2(OH)6 synthetic powders were prepared by chemical or solid-state method. Their crystalline phase structure, thermal behavior, and morphology were examined. Characteristic infrared absorbance bands were estimated by means of FT-IR ATR spectroscopy. X-ray photoelectron spectroscopy (XPS) allowed to calculate the modified Auger parameters (α′) thereof to 2010.2, 2009.3, 2009.4, 2009.7, and 2009.8 eV, respectively for ZnO, Zn(OH)2, Zn5(OH)8Cl2·H2O, ZnCO3, and Zn5(CO3)2(OH)6. Finally, comparison of surface composition may be crucial to evaluation of the unknown experimental spectra of corrosion products formed on the surface of zinc alloy coatings exposed in NaCl solution.

1. Introduction

Zinc-based alloys which contain molybdenum can be the potential substitute for toxic cadmium coatings or additional Cr(VI)-based conversion coatings, due to the low harmfulness of Mo(VI) compounds present in the plating baths and the ability of molybdenum to form stable passive layer preventing chloride attack. The addition of molybdenum to zinc alloy coatings with the iron group metal seems to be interesting, and even in the 80s of twentieth century was undertaken research about the addition of Mo to binary zinc alloy coatings to form ternary Zn–Co–Mo [1] alloys.

In the more actual research [2, 3], the optimal conditions of the deposition of Zn–Co–Mo coatings have been defined. Recent work has been dedicated to determining the corrosion resistance of bright and homogeneous ternary Zn–Co–Mo alloy coatings in NaCl solution [3]. It has been demonstrated that the coatings with a content of about 2.7 wt.% Mo and 3.8 wt.% Co possess significantly better corrosion resistance than that of pure zinc coatings [3]. X-ray photoelectron spectroscopy (XPS) study revealed that the beneficial effect on the corrosion resistance of Zn–Co–Mo coatings has a passive layer which, initially, is composed of Zn(OH)2, ZnO, Mo(IV) oxide, and hydroxide and small amounts of Co3O4 [3]. For this reason, an attempt was made to investigate the corrosion mechanism of these coatings in a solution containing chloride ions, using the following techniques: infrared spectroscopy (FT-IR), the aforementioned XPS technique [4], and X-ray diffraction (XRD).

Further, own research led to the replacement of cobalt(II) compounds in electroplating baths with less harmful iron(II) compounds. Thanks to this, a method of obtaining Zn–Fe–Mo alloy coatings was successfully developed [5], and an effort was undertaken to investigate the mechanism of formation of passive layer and the layer of corrosion products [6].

It is well known that the layer of corrosion products can modify the kinetic of either anodic or cathodic reactions. Therefore, research studies focused on the analytical determination, chemical behavior, and properties of corrosion products are essential for understanding the corrosion mechanism of zinc alloy protective coatings with molybdenum. For
detailed study on the corrosion of zinc and zinc alloy coatings, several analytical techniques should be used to get an insight into the bulk and the surface of the corrosion product layer. Generally, after short exposure in corrosive environment, the amount of corrosion products is often too low to be determined by X-ray diffraction, infrared spectroscopy, or Raman microscopy, and this was the problem encountered during the study of the surface composition of corroding Zn–Fe–Mo coatings. It was noted in our preliminary tests that the corrosion process of Zn–Fe–Mo coatings in 0.05 mol·dm$^{-3}$ solution of NaCl is slow enough that the use of XRD and FT-IR techniques does not provide any information on the chemical composition of corrosion products. For this purpose, X-ray photoelectron spectroscopy (XPS) is commonly used [7]. However, the correct determination of the chemical states of the elements needs reference spectra of the expected compounds. According to the literature [8], during exposure in chloride environment, the layer of corrosion products may be formed by compounds such as ZnO, Zn(OH)$_2$, ZnCO$_3$, and Zn$_5$(OH)$_8$Cl$_2$H$_2$O, wherein zinc hydroxide predominates in the chloride-containing medium [9]. However, the presence of both oxide and hydroxide forms and more complex structures of zinc were discussed in the literature [10]. In the XPS analysis, a specific marker of a chemical state of zinc in its corrosion products is the modified Auger parameter ($\alpha'$). It is noticeable that the values of $\alpha'$ strongly vary among different literature references. Dake et al. [11] estimated for zinc hydroxide the $\alpha'$ to be 2009.2 eV. Deroubaix and Marcus [12] revealed for this compound the values 2009.9 eV and 2010.4 eV. It is interesting that the same authors reported similar $\alpha'$ for zinc oxide (2010.2–2010.4 eV). All these literature discrepancies lead to the conclusion that zinc hydroxide is not stable during XPS analysis. Zinc hydroxide is well known to easily decompose to zinc oxide even at relatively low temperatures. Thus, this effect is more pronounced by the specific ultrahigh vacuum environment required for XPS analysis. This supposition is in agreement with the work of Duchoslav et al. [13] and our own study [4].

The main purpose of this work was gathering and comparing the characteristic XPS and IR spectra of synthetic ZnO, Zn(OH)$_2$, Zn$_5$(OH)$_8$Cl$_2$H$_2$O, ZnCO$_3$, and Zn$_5$(CO$_3$)$_2$(OH)$_6$ powders, as corrosion products of zinc coatings that can be formed in the chloride environment. X-ray diffraction, thermogravimetric analysis (TG/DTA), and scanning electron microscopy (SEM) were applied to characterize the synthesized zinc compounds. Finally, the recorded infrared spectra, photoelectron, and Auger electron spectra may be found to be of great importance in the future for an accurate IR and XPS evaluation of zinc corrosion products formed in NaCl environment on the surface of ternary zinc alloy coatings containing molybdenum, and for further investigation of the corrosion mechanism thereof.

2. Materials and Methods

2.1. Synthesis of the Powders. Zinc oxide, ZnO, was prepared by the precipitation method at elevated temperature. Firstly, the solution of zinc sulfate (50 cm$^3$ and 1 mol·dm$^{-3}$) was heated to about 60°C. Then, a portion of 2 mol·dm$^{-3}$ NaOH solution was added with continuous stirring until the mixture reached pH~13. Stirring was continued for 30 min, and then, the mixture was aged (without stirring) for 2 hours. The precipitate was subsequently filtered, washed several times with redistilled water in order to remove the soluble sulfates, and then dried at 50°C for 96 hours.

Zinc hydroxide, Zn(OH)$_2$, was prepared by the precipitation method, based on the work of Shaporev et al. [14]. To the aqueous solution of the precipitant (sodium hydroxide, 50 cm$^3$ and 0.15 mol·dm$^{-3}$), a portion of 0.45 mol·dm$^{-3}$ zinc nitrate solution was added. A precipitation agent was used in a tenfold molar excess relative to zinc ions. The obtained mixture was vigorously stirred for about 30 min at room temperature. The obtained white precipitate was filtered and washed several times with redistilled water and subsequently dried overnight at 50°C.

Zinc hydroxide chloride, Zn$_5$(OH)$_8$Cl$_2$H$_2$O, was obtained by the precipitation method based on the experiment of Zhang et al. [15]. Aqueous solutions of zinc chloride (50 cm$^3$ and 1 mol·dm$^{-3}$) and 2 mol·dm$^{-3}$ sodium hydroxide were prepared. The NaOH solution was added in portions to the ZnCl$_2$ solution until pH~6. The mixture was heated up to 50°C, stirred for 30 min, and then aged for 2 hours. The precipitate was then filtered, washed several times with redistilled water, and dried at 50°C for 96 hours.

Anhydrous zinc carbonate, ZnCO$_3$, was prepared by solid-state reaction at room temperature based on the experiment of Wu and Jing [16]. In this case, ZnSO$_4$·7H$_2$O, NH$_2$HCO$_3$, and polyethylene glycol were used as reactants. The components have been ground for 1 hour in a mortar. The obtained mixture was hygroscopic and absorbing moisture from the air took the form of a paste. Before drying (1 h, 110°C), the mixture was washed several times with redistilled water, to remove SO$_4^{2-}$ ions, and then by a small amount of an anhydrous ethanol.

Zinc hydroxide carbonate, Zn$_5$(CO$_3$)$_2$(OH)$_6$, was synthesized by precipitation from aqueous solution of zinc sulfate as the zinc ion source (3 mol·dm$^{-3}$). The mixture of 3 mol·dm$^{-3}$ NH$_4$HCO$_3$ and 1 mol·dm$^{-3}$ NH$_2$OH was used as the precipitation agent. The precipitation process was conducted at room temperature. Substrates were placed on magnetic stirrer and mixed for 30 min (the final pH was 7.2). After that, the precipitate was filtered, washed several times with redistilled water, and dried at 50°C for 96 hours.

2.2. Characterization of the Powders. X-ray diffraction (XRD) was used to determine the phase structure of the synthesized particles. X-ray diffraction measurements at room temperature were performed with a Siemens D 5000 diffractometer using CuK$\alpha$ radiation (scanning rate of 3–6 min$^{-1}$ and an angle range of 28°–80°).

Thermal analysis (TG/DTA) was carried out with a derivatograph type 3427 (MOM, Hungary), from 20°C to 1100°C under air (heating rate: 7.5°C min$^{-1}$, reference material: alumina, platinum crucibles, Pt/PtRh10 thermocouple).

The morphology of the synthesized powdered samples was examined using a VEGA III (TESCAN) scanning electron microscope. All the samples were sputter-coated with a thin (~10 nm) layer of carbon.
X-ray photoelectron spectroscopy was done using a SPECS PHOIBOS 100 spectrometer and nonmonochromatic Al anode (1486.7 eV) operating at 250 W for high-resolution spectra. The analyzed surface was of about 8 × 8 mm². Before analysis, the surfaces were cleaned by Ar⁺ sputtering with low beam energy (3 keV, 5 μA cm⁻², 60 s). Spectra were processed and fitted by SPECLAB software using Gaussian–Lorentzian curve profile and Shirley baseline. The spectrometer energy scale was calibrated with Au 4f/2, Ag 3d/2, and Cu 2p/2 lines at 84.2, 367.9, and 932.4 eV, respectively. The accuracy of the reported binding energies was ±0.1 eV. C 1s peak at 284.8 eV, as a contamination carbon, was used as reference for all spectra.

Infrared spectra of the synthesized powders were recorded using a PerkinElmer Frontier FT-IR spectrometer with PerkinElmer Universal ATR sampling accessory (diamond window) in the range of wavenumber from 4000 to 400 cm⁻¹. 128 scans, and at a resolution of 4 cm⁻¹. All spectra were ATR corrected.

### 3. Results and Discussion

#### 3.1. Phase Structure and Thermal Behavior of Synthesized Particles

The XRD patterns of zinc oxidation species synthesized by chemical method are shown in Figure 1. Presented diffractograms confirmed almost all synthesized particles to be predominantly crystalline. Dominant diffraction peaks were assigned to the major crystalline phases from the JCPDS-ICDD database. The crystalline size of the prepared powders for the main diffraction peaks were calculated using the Scherrer equation [17] with the Scherrer constant K = 0.94 and λ = 0.15406 nm (the wavelength of the radiation) in the Match! Software. As can be seen in the diffractogram for zinc hydroxide chloride sample (simonkolleite (Zn₅(OH)₈Cl₂·H₂O)) corresponds to ICDD card number 36-1451. Other diffraction patterns of synthetic forms of zinc corrosion products observed. Zn(OH)₂ phase crystallizes in the hexagonal structure (ICDD card number 36-1451). Due to the low crystallinity (11 nm calculated from the Scherrer equation) of this compound, the diffractogram was presented on a 2:1 scale in relation to the other diffractograms. For this sample (Figure 1(e)), diffraction peaks correspond well to hydrozincite (Zn₅(CO₃)₂(OH)₆·H₂O) phase (ICPD-ICDD 19–1458). The identification of obtained phases/powder was confirmed by further TG/DTA analysis and FT-IR spectroscopy.

The thermal behavior of obtained powders was investigated by TG/DTA heating in a temperature range from 20 to 1100°C (Figure 2). The DTA curve for the ZnO sample (Figure 2(a)) features neither exothermic nor endothermic peaks in the whole temperature range. As seen from TG curve, no mass loss was observed during the heat treatment process. Therefore, it can be concluded that no phase transformation appears when heating this sample as well as the ZnO powder is not hydrated. On the DTA curve for the Zn(OH)₂ sample (Figure 2(b)), distinct endothermic peak at about 140°C appears. This peak is accompanied by a mass loss, which amounted to 30 mg. Due to the fact that this thermal effect starts at about 100°C, it can be stated that it corresponds to hydroxide decomposition and transformation to zinc oxide which is more stable. No further effects were present at the TG/DTA curve (Figure 2(b)). The TG/DTA thermogram for Zn₅(OH)₈Cl₂·H₂O sample is more complicated (Figure 2(c)). At least three endothermic effects are present on the DTA curve. These effects are accompanied by corresponding mass losses (TG curve in Figure 2(c)). First one of them takes place between 100°C and 190°C with the weight loss amounted to −12 mg (6.3%). The second endothermic peak occurs between 190°C and 210°C. This effect is accompanied by a loss in mass of approx. 6 mg (3.1%). The last one occurs at the temperature above 500°C with the mass loss about 18 mg (9.5%). Based on the study of thermal decomposition of Zn₅(OH)₈Cl₂·H₂O [18], reaction in still atmosphere at a heating rate of 10°C min⁻¹ proceeds as follows:

$$
Zn_5(OH)_8Cl_2 \cdot H_2O \xrightarrow{145-192°C} 2\beta-Zn(OH)Cl + 3ZnO + 4H_2O↑
$$

[theoretical weight loss 13%] $$
\xrightarrow{192-219°C} \left[ ZnCl_2 + \frac{1}{2}H_2O \right] + 4ZnO + \frac{1}{2}H_2O↑
$$

[theoretical weight loss 1.6%] $$
\xrightarrow{219-602°C} \left[ \frac{1}{2}ZnCl_2 + HCl \right] \frac{1}{2}ZnO + 4ZnO
$$

[theoretical weight loss 19%] $$\equiv 4.5ZnO$$

Based on the thermogram shown in Figure 2(c), it can be concluded that, between 100°C and 190°C, transformation to β-Zn(OH)Cl and ZnO occurs. Next, above 190°C, the β-Zn (OH)Cl phase dehydroxylates to ZnCl₂ and ZnO. Above 220°C, under these experimental conditions (heat rate 7.5° min⁻¹), slightly larger amounts of both ZnCl₂ and H₂O are removed.
A smaller fraction of ZnCl₂ is hydrolyzed to ZnO, which was observed as the last endothermic peak at the TG/DTA curve. Finally, at 530 °C, TG and DTA curves stabilize yielding a residue of ZnO, with an overall experimental weight loss at about 20.5 %.

The DTA curves for ZnCO₃ and Zn₅(CO₃)₂(OH)₆ are similar, and both exhibit one distinct endothermic peak at about 250 °C. This effect is related to the reactions (2) and (3), and those can be written as follows:

\[
\text{ZnCO}_3 \xrightarrow{250^\circ C} \text{ZnO} + \text{CO}_2 \uparrow \quad \text{[theoretical weight loss 35.2%]} \\
\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6 \xrightarrow{240^\circ C} 5\text{ZnO} + 2\text{CO}_2 \uparrow + 3\text{H}_2\text{O} \uparrow \quad \text{[theoretical weight loss 26%]} 
\]
Figure 2: Continued.
In both cases, the weight loss increased slowly in the temperature interval up to 200°C, whereas above this temperature, the thermal decomposition rate became fast. Greater weight loss occurs during decomposition of zinc carbonate as indicated from (2) and (3)The molar ratio of the solid to the gaseous phase (CO₂) formed during ZnCO₃ decomposition is 1 : 1, and theoretical calculated mass loss is 35.2%, while from one mole of Zn₅(CO₃)₂(OH)₆ is created 5 moles of gaseous products and theoretical calculated mass loss is ~26%. The experimental weight loss is close to the theoretical value, and for Zn₅(CO₃)₂(OH)₆, it amounted to ~28%. On the basis of the TG curve for ZnCO₃, weight loss amounted to 36.5%. Above the thermal decomposition temperature, no mass change was detected at the TG curve for both samples (Figures 2(d) and 2(e)).

3.2. Microscopic and Spectroscopic Studies of the Synthesized Particles

3.2.1. Morphology. SEM analysis revealed the synthesized particles to vary in morphology, crystal shape, and size (Figure 3). Zinc oxide powder has loose structure and is composed of fine fiber or plate-like particles, few hundred of nanometers in size (Figure 3(a)). The particles of wulfingite (ε-Zn(OH)₂) have a granular shape and are covered by a fine deposit (Figure 3(b)). SEM microphotographs for simonkolkeite (Zn₅(OH)₈Cl₂·H₂O) show that the obtained sheets have hexagonal structure, while the average size of these particles amounts to 1 µm (Figure 3(c)). Smithsonite (ZnCO₃) particles have nodular shape. Most of them have nanometric scale, but larger agglomerates are also visible (Figure 3(d)). Large and massive precipitates of hydrozincite (Zn₅(CO₃)₂(OH)₆) have been formed by a number of loosely bonded nanoparticles (Figure 3(e)).

3.2.2. FT-IR Spectroscopy. ATR-IR spectra of the synthetic zinc alloy corrosion products are shown in Figure 4, while the main peaks of zinc compounds and corresponding vibration bonds, described based on current literature data, are listed in Table 1. Spectrum “a” in Figure 4 shows bands at about 570 and 403 cm⁻¹ attributed to the formation of the stretching vibration of metal-oxygen (Zn–O) bonds. Typically, infrared spectra show characteristic bands of ZnO in the region from 680 up to 300 cm⁻¹, which can be used for qualitative characterization and confirmation of the shape of ZnO particles [19].

The presence of bands at about 3390 cm⁻¹ was characteristic for the stretching vibration of intermolecular hydrogen bond (OH) existing between the adsorbed water molecules. Also, the bond characteristic for OH stretching vibration appears at about 3200 cm⁻¹ on the ATR spectrum for zinc hydroxide (spectrum “b” in Figure 4). Other modes originating from OH such as ZnOH bending and OH libration are observed at lower wavenumbers (1100–750 cm⁻¹). The bands in the range from 1000 to 1120 cm⁻¹ could be interpreted as motion of hydrogen atoms perpendicular to the connection line of the two nearest metal ions in type OM₂H unit, whereas the bands in the range from 700 to 800 cm⁻¹ could be interpreted as those parallel in relation to tangential to this line [20]. Zinc hydroxide chloride spectrum shows
characteristic peaks at about 1040, 900, and 715 cm$^{-1}$, which have also previously been described by Srivastava and Secco [21].

The bands for translational/lattice modes are visible below 600 cm$^{-1}$ in Figure 4, spectrum “c”. In this case, the hydrogen bonds are formed between H$_2$O molecules (hydrogen bond donors) and the OH groups (hydrogen bond acceptors). This could be manifested by the appearance of splitting and broadening of the band at approximately 3450 cm$^{-1}$. In the ATR spectra of zinc carbonate, the very strong bands occurred at about 1400 cm$^{-1}$, whereas for hydrozincite, two bands are observed (at about 1500 and 1390 cm$^{-1}$). These bands may be assigned to $\nu_3$ (CO$_3$)$_2$$^{-2}$ antisymmetric stretching modes. As explained by Hales and Frost [22], the difference of number of bands in this spectral region (between zinc carbonate and hydrozincite) is due to the symmetry reduction of the hydrozincite. The mode for $\nu_2$ (CO$_3$)$_2$$^{-2}$ for zinc carbonate is slightly shifted towards higher values of wavenumber (~870 cm$^{-1}$). Multiple bands are observed for $\nu_4$ (CO$_3$)$_2$$^{-2}$ in the hydrozincite spectrum (spectrum “e” in Figure 4), while for zinc carbonate, only one band is present in the spectrum. Similarly, as for previously described compounds, bands below 600 cm$^{-1}$ could be assigned to lattice modes. The band characteristics for OH stretching vibration are very weak for zinc carbonate, whereas for hydrozincite, very broad band is observed at 3300 cm$^{-1}$. This value is in accordance with previously described findings in the literature [23, 26]. Other strong intensity bands are observed at about 1040 and 950 cm$^{-1}$ and may be assigned to OH librations.

Figure 3: SEM microphotographs of ZnO (a), Zn(OH)$_2$ (b), Zn$_5$(OH)$_4$Cl$_2$·H$_2$O (c), ZnCO$_3$ (d), and Zn$_5$(CO$_3$)$_2$(OH)$_6$ (e) powders prepared by the precipitation or solid-state (ZnCO$_3$) method.
3.2.3. XPS Surface Analysis. The identification of chemical bonds between zinc and oxygen in oxidation products of zinc is the main problem in qualitative and quantitative surface analysis by means of X-ray photoelectron spectroscopy. This research task is not difficult, when two completely different (in terms of binding energy) oxidized zinc forms are considered, for example, ZnO and Zn(OH)$_2$. When compounds with more complex structure, for example, hydroxychlorides, hydroxycarbonates, and so on, are present in addition to the abovementioned ZnO and Zn(OH)$_2$, their quantitative differentiation begins to be really difficult. This situation occurs during corrosion of zinc coatings in the real systems, that is, chloride-containing environment where corrosion products are a mixture of zinc: oxide, hydroxychloride, hydroxycarbonate, and hydroxide [9]. Therefore, very useful would be knowledge of standard photoelectron spectra of individual oxidized zinc compounds.

![Figure 4: FT-IR ATR spectra of ZnO (a), Zn(OH)$_2$ (b), Zn$_5$(OH)$_8$Cl$_2$·H$_2$O (c), ZnCO$_3$ (d), and Zn$_5$(CO$_3$)$_2$(OH)$_6$ (e) powders prepared by the precipitation method.](image-url)
In order to solve this problem, both XPS core-level spectra and Auger spectra for synthetic zinc oxidation products were recorded. O 1s photoelectron spectra for synthetic ZnO and Zn(OH)₂ powders (Figure 5) show that their surface is not homogeneous. For ZnO powder, which was analyzed “as received,” the spectrum O 1s was deconvoluted taking into account the presence of three components: (1) dominant lattice oxide—ZnO, (2) Zn(OH)₂, and (3) surface and/or crystal water. On the O 1s spectrum of Zn(OH)₂ synthetic powder, the OH− component predominates. However, the peak asymmetry towards lower BE suggests the presence of remnants of ZnO. Therefore, the accurate determination of zinc-oxygen binding energy in Zn(OH)₂ was achieved by Ar⁺ sputtering. After Ar⁺ sputtering, the component “ZnO” became more intense (Zn(OH)₂ to ZnO photoreduction phenomenon). This fact made the deconvolution easier (Figure 5(b)). What is interesting is that Ar⁺ sputtering of the surface of ZnO synthetic powder did not result in a significant loss of OH− component (photoreduction was not observed this time).

Zinc shows only a small binding energy shift in the Zn 2p½ region (1021 eV–1023 eV). Besides, peak width may broaden when more than one Zn species are present. Therefore, the correct identification of zinc chemical bonds performed only on the main Zn 2p½ line is unreliable.

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These spectra in Figure 6 were deconvoluted on the basis of previously estimated (by means of O 1s spectra) ZnO: Zn(OH)₂ ratios. Also, in this case, the Ar⁺ sputtering of the surface was useful in determining the binding energy of Zn 2p½ photoelectron bonds (Table 2). As it was mentioned earlier, chemical state differentiation by XPS on the basis of Zn 2p½ main line only can be difficult or even impossible due to a small binding energy shift between Zn⁰, ZnO, Zn(OH)₂, ZnCO₃, and Zn₅(OH)₈(ClO₄)₂ especially occurring at the same time. For that reason, the interpretation of the Auger Zn L₃M₄5M₄5 main lines might be useful (spectra not included) because of larger chemical shifts (CS—L₃M₄5M₄5). The utility of Zn LMM spectral line becomes obvious if zinc

| Compound                        | Band assignment                  | Peak center (cm⁻¹) | Literature peak region (cm⁻¹) |
|--------------------------------|----------------------------------|--------------------|------------------------------|
| ZnO                            | OH stretching vibration          | 3393.4 (m)         | 3620–2950 [19]               |
|                                | C=O stretching vibration         | 1637.8 (vw)        | 1635 [19]                    |
|                                | C=O stretching vibration         | 898.8 (m)          | 875 [19]                     |
|                                | Zn–O lattice                     | 570.8 (s)          | 300–650 [19]                 |
|                                | Zn–O lattice                     | 402.9 (s)          |                               |
| Zn(OH)₂                         | OH stretching vibration          | 3218.7 (vs)        | 3250–3100 [20], 3260 [21]    |
|                                | OH librations                    | 1086.4 (vs)        | 1115–1060 [20], 1080 [21]    |
|                                | OH librations                    | 1028.9 (vs)        | 1040 [20], 1025 [21]         |
|                                | OH librations                    | 933.5 (m)          | 947 [20]                     |
|                                | OH librations                    | 847.3 (s)          | 844 [20], 830 [21]           |
|                                | OH librations                    | 774.1 (m)          | 772 [20], 750 [21]           |
|                                | OH librations                    | 715.1 (vs)         | 739 [20], 715 [21]           |
|                                | Zn–O asymmetric stretching       | 478.3 (vs)         | Below 550 [20]               |
| Zn₅(OH)₈Cl₂·H₂O                 | OH stretching vibration          | 3567.5 (s)         | 3600–3260 [21]               |
|                                | OH stretching vibration          | 3482.1 (vs)        | 3588 and 3570 [22]           |
|                                | H₂O bending                      | 3451.1 (vs)        | 3495–3545 [21, 22]           |
|                                | OH librations                    | 3330.7 (s)         |                               |
|                                | OH librations                    | 1604.1 (m)         | 1601 [22]                    |
|                                | OH librations                    | 1041.2 (s)         | 1035 [21]                    |
|                                | ZnOH librations                 | 901.2 (vs)         | 895 [21], 906 [22]           |
|                                | ZnOH librations                 | 714.9 (vs)         | 715 [21], 717 [22]           |
|                                | Zn–O lattice mode                | 569.2 (s)          | Below 570 [22]               |
|                                | Zn–O lattice mode                | 532.7(s)           |                               |
| ZnCO₃                          | CO₃ v₁                          | 1402.9 (vs)        | 1485–1320 [23]               |
|                                | CO₃ v₂                          | 865.4 (vs)         | 890–850 [23]                 |
|                                | CO₃ v₄                          | 737.8 (s)          | 750–710 [23]                 |
| Zn₅(CO₃)₃(OH)₆                 | OH stretching vibration          | 3295.4 (vs)        | 3560–2750 [23], 3402 [24]    |
|                                | CO₃ v₁ component 1              | 1505.2 (vs)        | 1600–1200 [25], 1503 [24], 1395 |
|                                | CO₃ v₁ component 2              | 1360.9 (vs)        | [24], 1383 [23],             |
|                                | OH bending                      | 1046.7 (s)         | 1070–1035 [23], 1046 [24]    |
|                                | OH bending                      | 950.4 (vs)         | 949 [23], 951 [24]           |
|                                | CO₃ v₂                          | 833.5 (vs)         | 832 [23], 833 [24]           |
|                                | CO₃ v₃                          | 737.8 (m)          | 737 [23]                     |
|                                | CO₃ v₄                          | 707.6 (vs)         | 707 [23], 708 [24]           |
|                                | Zn–O lattice mode               | 465.9 (vs)         | 469 [25], 483 [24]           |

*Peak intensity: vs, very strong; s, strong; m, moderate; w, weak; vw, very weak.
is buried (under carbon, for example). Then, Zn LMM peak may be observed even if Zn 2p is not visible. Similarly, Zn 3p (of very high kinetic energy) may be observed even if Zn 2p is not visible. These statements result from the sampling depth of Zn 2p3/2, Zn LMM, and Zn 3p photoelectrons. These values, conventionally calculated in XPS as $3\lambda_{x,y}$ (where $x$ is the photoelectron and $y$ is the medium in which the electron moves), are respectively $3\lambda_{Zn2p3}^{ZnO} = 2.4$ nm, $3\lambda_{ZnLMM}^{ZnO} = 6$ nm, and $3\lambda_{Zn3p}^{ZnO} = 8$ nm [27]. The values of KE for Zn L$_M$M$_M$M$_G$ as well as modified Auger parameter ($\alpha'$) are shown in Table 2.

Auger parameter is very useful energy parameter for identifying the chemical state of elements where chemical shift is very small or comparable with the energy resolution of the instrument. This modified Auger parameter ($\alpha'$) is independent of the X-ray energy used as well as independent of charging effect. This property makes it easier to compare the results from the work of other authors, and what has been done in the current work. The calculated $\alpha'$ parameter values indicate very high compliance with the literature data (Table 2).

To our knowledge, the data for Zn$_5$(OH)$_8$Cl$_2$·H$_2$O as typical corrosion product of zinc are presented here for the first time. The Zn 3p spectra are no longer as significant as Zn 2p, due to the almost 6-fold lower value of the relative sensitivity factor (RSF), greater full width at half maximum (FWHM), and, in particular, overlapping of 3p3/2 and 3p1/2 doublet components. However, the interpretation of zinc bonds, based on the Zn 3p spectra, becomes a necessity if, for example, zinc is buried under carbon (which is often the case with thicker layers of corrosion products). As stated above, large differences in the kinetic energies of Zn 2p and Zn 3p photoelectrons cause the sampling depth of the latter to be over three times greater. This allows to identify zinc bonds even when the Zn 2p main lines are not at all visible. For these purposes, the values of Zn 3p3/2 binding energies are presented in Table 2. During deconvolution of Zn 3p spectra (spectra not included here), earlier results of Zn 2p3/2 spectra deconvolution were used, getting their full compatibility.

O 1s and Zn 2p3/2 photoelectron spectra for ZnCO$_3$ are presented in Figure 7. The shape of the spectra and their FWHM values testify to high homogeneity of synthesized ZnCO$_3$ powder. The binding energies of O 1s, Zn 2p3/2, and C 1s photoelectrons were estimated at 532.2, 1022.49, and 290.0 eV, respectively.
Table 2: Binding and kinetic energies for selected photoelectrons and Auger electrons estimated on the basis of experimental spectra for ZnO, Zn(OH)$_2$, Zn$_5$(OH)$_8$Cl$_2$·H$_2$O, ZnCO$_3$, and Zn$_5$(CO$_3$)$_2$(OH)$_6$ powders.

| Compound                | Zn 2p$_{3/2}$ (eV) | Zn LMM (eV) | Modified Auger parameter ($\alpha'$) | Zn 3p$_{3/2}$ (eV) | O$_{\text{binding}}$ (eV) | Reference |
|------------------------|--------------------|-------------|-------------------------------------|-------------------|-----------------|-----------|
| Zinc foil$^*$          | 1021.18            | 992.65      | 2013.83, 2013.8                      | 87.88             | —               | This work [11, 28] |
| ZnO                    | 1021.47            | 988.75      | 2010.22, 2010.1, 2010.4             | 88.18             | 530.2           | 531.4      | [28, 29] [30] |
| Zn(OH)$_2$             | 1021.81            | 987.5       | 2009.31, 2009.2, 2009.6             | 88.49             | 530.1           | 531.4      | This work [11] [28] [29] |
| Zn$_5$(OH)$_8$Cl$_2$·H$_2$O | 1022.21          | 987.22      | 2009.43                              | 89.13             | 530.1           | 531.89     | This work |
| ZnCO$_3$               | 1022.49            | 987.23      | 2009.72, 2009.7                      | 89.1              | —               | —          | This work [11, 28] |
| Zn$_5$(CO$_3$)$_2$(OH)$_6$ | 1021.88          | 987.9       | 2009.78, 2009.7, 2009.6              | 88.68             | 530.05          | 531.35     | 532.05 | This work [11] [28] |

$^*$ Zinc foil (Sigma-Aldrich, Zn 99.99%) for reference only.

Figure 7: O 1s and Zn 2p$_{3/2}$ photoelectron spectra for Zn$_5$(OH)$_8$Cl$_2$·H$_2$O, ZnCO$_3$, and Zn$_5$(CO$_3$)$_2$(OH)$_6$ after Ar$^+$ sputter cleaning.
The gained knowledge about XPS spectra for ZnO, Zn(OH)₂, and ZnCO₃ proved to be crucial in understanding the more complex spectra of real zinc corrosion products like Zn₅(OH)₈Cl₂·H₂O (simonkolleite) and Zn₂(CO₃)₃(OH) (hydrozincite) (Figures 7–9). On the O 1s spectrum of Zn₅(OH)₈Cl₂·H₂O dominates the component characteristic for the binding energy of oxygen in a hydroxyl group (maximum at 531.9 eV). In contrast, in the O 1s spectrum for Zn₂(CO₃)₃(OH)₆, the highest (and comparable) share belongs to the component characteristic of the hydroxyl and carbonate groups. Similarly, in the Zn 2p₃/₂ spectra, the relevant components of zinc bonds with OH⁻, CO₃²⁻, and Cl⁻ groups were distinguished (Figure 7).

The C 1s spectra were used to properly balance particular bonds in the analyzed compounds. In the case of ZnCO₃ and Zn₅(CO₃)₃(OH)₆ deconvolution of C 1s spectra (Figure 8), taking into account the existence of the two (main) components: the carbon originating from carbonates (CO₃) and contamination carbon (C–C), allowed to estimate the content of “carbonate” carbon in ZnCO₃ and Zn₅(CO₃)₃(OH)₆ to 19.6 and 9.8 at.%, respectively (Table 3). For comparison, the C 1s spectrum of ZnO does not contain any component of the “carbonate” on the side of higher binding energies (Figure 8). The carbonate component was also not found on the surface of Zn₅(OH)₈Cl₂·H₂O, proving the high surface purity of the obtained standard (Figure 9). The spectral documentation of Zn₅(OH)₈Cl₂·H₂O was supplemented with Cl 2p spectrum and assigned BE = 198.74 and 200.34 eV in 2p₃/₂ and 2p₁/₂ doublet, respectively, characteristic of alkali chloride.

XPS surface composition of ZnO, Zn(OH)₂, Zn₅(OH)₈Cl₂·H₂O, ZnCO₃, and Zn₅(CO₃)₃(OH)₆ powders prepared by the precipitation method and the shares of oxygen and zinc bonds based on deconvolution are shown in Table 3. In each case, the results of the deconvolution were correlated to the stoichiometry of the studied compounds, whose structure was previously documented by XRD and FT-IR analysis.

4. Conclusions
In this work are summarized and compared the XPS and IR spectra for the chosen and the most common synthetic corrosion products of zinc in NaCl environment. The basic
The conclusion from the present research is that the surface composition of the investigated synthetic oxidation products: ZnO, Zn(OH)2, Zn5(OH)8Cl2·H2O, ZnCO3, and Zn5(CO3)2(OH)6, corresponds well with their stoichiometry despite the presence of surface contamination. Another important conclusion is also that obtaining the standard spectra of pure (Zn(OH)2 free) zinc oxide and other (ZnO-free) zinc hydroxyl compounds is in practice extremely difficult, even though the XRD phase analysis indicates the phase purity of these substances. It has been shown that despite the complexity of the recorded photoelectron spectra, after the adoption of certain assumptions, one can estimate the corrosion products of zinc coatings. This work collects the binding energies of Zn 2p3/2, O 1s, and Zn 3p photoelectrons, together with Zn LMM kinetic energies, modified Auger parameters (a′), and corresponding characteristic infrared absorbance bands. Therefore, it can be helpful in the interpretation of corrosion processes of zinc alloy coatings in environment containing chloride ions.

### Data Availability

Raw measurement data will be available (ASCII format) for the reader upon request.

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