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DETERMINATION OF THE FORMATION MECHANISM OF ZINC AND NICKEL LAYERED DOUBLE HYDROXIDES

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The object of the study – the formation mechanism of Zn-Al nitrate, Zn-Al tripolyphosphate, Ni-Al carbonate and Ni(II)-Ni(III) carbonate layered-double hydroxides (LDHs).

To calculate the composition of the precipitate at the LDH formation stage, the following hypotheses were proposed:

1) basic salt hypothesis (BSH): all cations completely precipitate, then OH- ions replace the anions;

2) variable cation composition hypothesis (VCCH): the precipitate is formed by a saturated "guest" cation, and subsequently the amount of the "host" cation increases.

Potentiometric titration with a glass electrode was used to determine the LDH formation mechanism.

A two-stage formation mechanism was observed for Zn-Al-NO_3 LDH. At the first stage, aluminum hydroxide forms (pH = 6.47) via the formation of the hydroxo salt $Al(OH)_{0,667}(NO_3)_{2,333}$ (pH = 4.98). At the second stage, LDH formation proceeds through intermediate stages: at pH = 7.36, the is composition $Zn_{0,8}Al_{0,2}(OH)_{1,20}(NO_3)_{1,00}$ (BSH) or $Zn_{0,667}Al_{0,333}(OH)_2(NO_3)_{1,667}$ (VCCH), at pH = 9.35, the composition is $Zn_{0,8}Al_{0,2}(OH)_{1,93}(NO_3)_{0,27}$ (BSH) or $Zn_{0,793}Al_{0,207}(OH)_2(NO_3)_{0,204}$ (VCCH).

A two-stage mechanism is characteristic of Zn-Al-P_3O_{10} LDH. At pH = 6.25, the hydroxo salt $Al(OH)_{2,66}(P_3O_{10})_{0,067}$ is formed, whereas at pH = 9.25, LDH with the composition $Zn_{0,8}Al_{0,2}(OH)_{2,00}(P_3O_{10})_{0,040}$ is obtained. For Zn-Al LDH, a pH range of 7–10 is recommended.

It was found that during the formation of Ni-Al-CO_3 LDH, the stage of Al hydroxocompound formation is absent due to the complete irreversible hydrolysis of Al3+ in the presence of At pH = 6.5, the precipitate $Ni_{0,8}Al_{0,2}(OH)_{1,066}(CO_3)_{0,567}$ (BSH) or $Ni_{0,624}Al_{0,376}(OH)_2(CO_3)_{0,376}$ (VCCH) is formed, which is transformed into LDH upon further alkalization. The synthesis of Ni-Al-CO_3 LDH should be carried out at pH = 8–11.

A single-stage formation mechanism is determined for Ni(II)-Ni(III)-CO_3 LDH, with a recommended synthesis pH range of 10–11.

Comparative analysis shows that the VCCH better describes the change in the precipitate composition during LDH formation

Keywords: potentiometric titration, formation mechanism, Zn-Al LDH, Ni-Al LDH, Ni(II)-Ni(III) LDH

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1. Introduction

Layered double hydroxides (LDHs) are 2d-anion exchange materials widely used in various fields [1]. In terms of crystal structure, LDHs represent the α-form of the hydroxide of a "host" cation (mainly M^{2+}), in which a portion of the host cations is substituted ed by "guest" cations (M^{3+} or M^{4+}) [2]. To compensate for the excess charge arising in the crystal

lattice, various anions are intercalated, which can be divided into three groups:

1) anions of precursor salts [3];

2) anions that stabilize the LDH crystal structure, such as carbonate anions [4];

3) and functional anions [5, 6].

It should be noted that some authors refer to LDHs as nanocomposites [7] or hybrids [8]. However, this description introduces some inaccuracy, since true composites [9] are polyphasic and consist of a matrix-forming material and a filler, with interfaces between them. LDHs, with rare exceptions, are single-phase substances.

LDHs intercalated with functional anions are widely used as pharmaceuticals [10], cosmetic agents [11], antiretardants [12], and as catalysts and photocatalysts [13], including in the oxide form after calcination [14].

The most promising LDHs are those based on nickel hydroxide and zinc hydroxide. Ni-based LDHs are widely used as electrochemically active substances in alkaline batteries [15], hybrid supercapacitors [16], electrochromic [17, 18], and electrocatalytic [19] devices. Zinc-based LDHs are widely used, primarily due to their intercalated functional anions, for example as anticorrosive pigments (with inhibitor anions intercalated) [20] and as color pigments (with dye anions intercalated) [21, 22]. In addition, the possibility of extracting lycopene (a lipophilic carotenoid) as a nanocomposite with Zn-Al LDHs was demonstrated in [23].

To summarize, it should be noted that LDHs are materials with a wide range of applications, particularly as nanocontainers for various functional ions, confirming the high potential of this class of compounds. Given the dependence of LDH composition on production conditions, studying the formation mechanism of various LDHs is relevant. A targeted strategy for the synthesis of layered double hydroxides with predetermined characteristics for specific applications was developed in [1]. To implement this strategy, in terms of an informed choice of synthesis method, it is essential to determine the mechanisms of LDH formation, particularly LDHs based on nickel and zinc hydroxides.

2. Literature review and problem statement

The synthesis method and conditions critically affect the properties of the resulting LDHs [24]. The most promising method for LDH synthesis is considered coprecipitation. One of the most important parameters of this method is the synthesis pH. In most cases, the synthesis pH is selected arbitrarily or based on literature data.

Several studies have been conducted to more effectively select the pH. For example, [25] examined the effect of pH on the properties of glutamate-intercalated LDHs, while [26] examined its influence on the characteristics of Zn-Al and Cu-Al LDHs. The main drawback of these and similar studies is that the effect of pH is determined by changes in the characteristics of the synthesized LDHs. This approach is indirect and essentially implements the "black box" method, allowing for the establishment of dependencies without taking into account the mechanisms of LDH formation. However, such dependencies are relevant only within the range of conditions for their determination. A similar approach was adopted in [27], where the effect of pH on the formation of Mg-Al LDH was investigated. In addition to the indirect method for determining the mechanism, this work has another significant drawback: the pH range of 10.0–13.2 was selected for the study. However, in general terms, the chemical mechanism of LDH formation is described as a two-stage process [1]. In the first stage, the hydroxide form of the "guest" metal cation is formed. In the second stage, the resulting precipitate of the hydroxo form of the "guest" metal cation interacts with the cations of the "host" metal, excess OH- ions, and intercalated anions to form LDHs. For this study, pH = 10.0–13.2 is in the zone of complete formation of Mg-Al LDH, and, therefore, the data on the formation mechanism are partial.

The most direct and reliable method for investigating LDH formation mechanisms is pH-metric titration (titration using a glass electrode). In [28], the formation mechanism of Ni-Fe and Mg-Fe LDHs were studied, using both conventional and differential titration curves. When discussing the formation mechanism, the authors pointed to the formation of a primary phase, most likely one of the Fe^{3+} hydroxo forms. However, this study focused on LDHs where Fe^{3+} acts as the "guest" cation.

Important studies of LDH formation using pH-metric titration were conducted by Braterman et al. [29]. In [30], the formation of a wide range of LDHs, including those based on Zn^{2+} and Ni^{2+} as the "host" metal cations, was investigated, and both conventional and differential titration curves were obtained. However, it should be noted that the primary objective of this work was to determine the stability of various LDHs, rather than to elucidate their formation mechanisms. Furthermore, it should be noted that the authors viewed LDH formation from a crystallographic perspective as the direct formation and growth of crystals. However, this view is erroneous, as due to the extremely high rate of nucleation, formation proceeds through the formation of amorphous primary particles. This likely led the authors to the incorrect conclusion that LDHs are less stable than the mixture of metal cation hydroxides that comprise the LDH. This conclusion was subsequently refuted.

In summary, it should be noted that the mechanisms of LDH formation have not been sufficiently studied. Furthermore, pH titration studies should be conducted for LDHs containing specific intercalated ions. Such targeted investigations have not been identified in the available literature.

Based on the above, it is necessary to identify the LDHs for which the formation mechanism should be investigated. According to previous studies, Zn-Al-NO_3 (as a base matrix for intercalation) [3] and Zn-Al-P_3O_{10} (as an anticorrosive pigment) [31] are promising for zinc LDHs. Ni-Al-CO_3 and Ni(II)-Ni(III)-CO_3 are promising for nickel LDHs [32]. The formation mechanisms for these types of LDHs have remained virtually unexplored, and the latter LDH was first reported in [33]. Therefore, elucidating the formation mechanisms of these LDHs is of significant importance.

3. The aim and objectives of the study

The aim of the study is to determine the formation mechanism of Zn-Al, Ni-Al, and Ni-Ni LDHs using pH-metric titration, as well as to identify rational pH ranges for their synthesis. This will subsequently make it possible to develop technologies for producing highly efficient and highly active LDHs. To achieve this goal, the following objectives were defined:

– conduct pH-metric titrations of Zn^{2+} and Al^{3+} nitrate solutions to study the formation mechanism of individual zinc and aluminum hydroxides;

– conduct pH-metric titrations of Zn^{2+} + Al^{3+} nitrate solutions to study the formation mechanism of Zn-Al-nitrate and Zn-Al-tripolyphosphate LDH, calculating the precipitate compositions according to two hypotheses;

– conduct pH-metric titrations of Ni^{2+} + Al^{3+} nitrate solutions and a Ni^{2+} nitrate solution both in the presence and absence of sodium hypochlorite to study the formation mechanism of Ni-Al-carbonate and Ni(II)-Ni(III)-carbonate LDHs, calculating the precipitate compositions according to two hypotheses.

4. Materials and methods

4. 1. The object and hypothesis of the study

The object of this study is the formation mechanism of Zn-Al nitrate, Zn-Al tripolyphosphate, Ni-Al carbonate, and Ni(II)-Ni(III) carbonate layered double hydroxides. The hypothesis of the study assumes that the formation mechanism is two-stage and proceeds via the formation of basic salts. Two hypotheses are proposed to calculate the precipitate composition at the LDH formation stage.

The basic salt hypothesis is based on the complete incorporation of both cations into the precipitate and, due to an insufficient amount of hydroxyl anions, charge compensation occurs through the incorporation of precursor salt anions or specially introduced anions.

The variable cation composition hypothesis is based on the assumption that the U(NaOH)/U(Me) ratio is maintained in the precipitate by varying the amount of incorporated "host" metal cations. In this case, the precursor salt anions or specially introduced anions compensate for the excess charge of the "guest" metal cation.

It is assumed that the use of differential pH-metric titration curves allows a comprehensive investigation of LDH formation. In this study, it is further assumed that other synthesis parameters, particularly temperature, do not significantly affect LDH formation process. Therefore, titration is carried out at room temperature.

4. 2. Sample preparation method

For the experiments, crystalline hydrates of nickel nitrate, zinc nitrate, aluminum nitrate, sodium carbonate, and sodium tripolyphosphate of analytical grade were used. For potentiometric titration with a glass electrode, solutions of individual nitrates (Zn^{2+}, Al^{3+}, and Ni^{2+}) as well as solutions of mixed nitrates (Zn^{2+} + Al^{3+} and Ni^{2+} + Al^{3+}) were prepared. The total amount of metal cations in the titrated solution for determining the LDH formation mechanisms was 0.0015 mol. The molar ratio of "host" and "guest" metal cations was 4:1. A 0.1 N NaOH solution prepared from Fixanal was used for titrating individual zinc and aluminum nitrates, as well as for determining the mechanism of Zn-Al nitrate LDH formation. For titrations to determine the LDH formation mechanism intercalated with tripolyphosphate or carbonate ions, the required amount of carbonate or tripolyphosphate was calculated based on the "guest" metal cation content and introduced into the 0.1 N NaOH solution during preparation.

Potentiometric titration was carried out by sequentially adding 1 ml of titrant (0.1 N NaOH), with pH recorded after 2 minutes. The titration was performed under continuous stirring using a magnetic stirrer with heating to maintain a temperature of 20°C. A pH meter AD8000 (Hungary) equipped with a universal glass electrode Ad1131 (Hungary) was used for potentiometric titration.

A steady-state titration was also used, where the pH was recorded after no change in value was observed for 2 minutes. In such cases, the designation "steady-state" was included in the labeling. The labels for the titrations performed are listed in Table 1.

Table 1

Titration labels

Designation	LDH (hydroxide) typer	Type of salt anion	Intercalated anion	Additional anion	Additional condition
Zn-NO3	$Zn(OH)_2$	NO_3^-	NO_3^-	No	No
Al-NO3	$Al(OH)_3$	NO_3^-	NO_3^-	No	No
Zn-Al-NO3	Zn-Al-nitrate	NO_3^-	NO_3^-	No	No
Zn-Al-NO3-steady-state	Zn-Al- nitrate	NO_3^-	NO_3^-	No	Stationary conditions *
Zn-Al-NO3-P3O10	Zn-Al-tripoly-phosphate	NO_3^-	$P_3O_{10}^{5-}$	No	No
Ni-Al-CO3	Ni-Al-carbonate	NO_3^-	CO_3^{2-}	No	No
Zn-Al-CO3-ClO	Ni-Al-carbonate oxidized	NO_3^-	CO_3^{2-}	ClO^-	No
Ni-Ni-CO3-ClO	Ni(II)-Ni(III)-carbonate	NO_3^-	CO_3^{2-}	ClO^-	No

Based on the titration results, a titration curve was plotted using the coordinates pH = f(U(NAOH) / U(Me)), where U(NAOH) / U(Me) is the molar ratio of NaOH to the total amount of metal cations. A differential titration curve was also constructed using the coordinates d(pH) / d(U(NAOH) / U(Me)) = f(U(NAOH) / U(Me)). Peaks on the differential titration curve indicate the occurrence of specific processes. For each peak, the corresponding pH, the value of d(pH) / d(ν(NaOH) / ν(Me)), and the calculated composition were determined and recorded in tables. The identified peaks were numbered from 1 to 6, where peaks 1 and 2 corresponded to aluminum hydroxide formation, peaks 3 and 4 – to zinc hydroxide formation or Zn-based LDH formation, and peaks 5 and 6 – to nickel-based LDH formation.

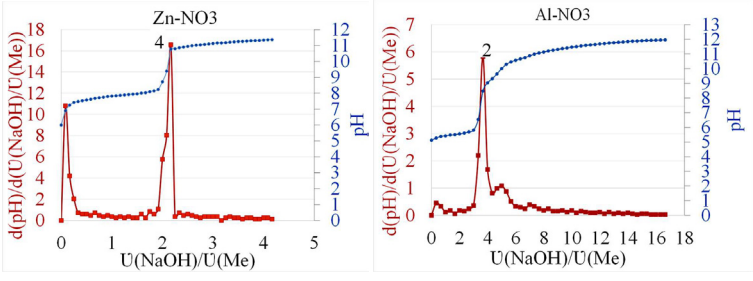
5. Results of determining the formation mechanism of hydroxides

5. 1. Formation mechanism of individual zinc and aluminum hydroxides

Fig. 1 shows the titration curves of zinc hydroxide (Zn-NO_3) and aluminum hydroxide (Al-NO_3).

First, it should be noted that the differential titration curves exhibit a peak upon the addition of the first portion of alkali. This peak is associated with the initial neutralization of the acid formed due to hydrolysis of zinc and aluminum

cations. This peak is not labeled or considered in the further discussion. The differential titration curves in both cases exhibit a single distinct peak, which is shown in Table 2.



a *b*

Fig. 1. Titration curves for studying the formation mechanisms of individual hydroxides: *a* – **Zn-NO3**; *b* – **Al-NO3**

Table 2

Peak parameters of differential titration curves in studying the formation mechanism of individual zinc and aluminum hydroxides

Peak	Data type	Zn-NO3	Al-NO3
1	pH	No peak	No peak
	U(NaOH)/U(Me)	No peak	No peak
	Formula	Impossible to calculate	Impossible to calculate
2	pH	No peak	8.48
	U(NaOH)/U(Me)	No peak	3.658
	Formula	Impossible to calculate	Impossible to calculate
3	pH	No peak	No peak
	U(NaOH)/U(Me)	No peak	No peak
	Formula	Impossible to calculate	Impossible to calculate
4	pH	10.77	No peak
	U(NaOH)/U(Me)	2.167	No peak
	Formula	Impossible to calculate	Impossible to calculate

When titrating a Zn^{2+} solution, a peak on the differential curve is observed at pH = 10.77 with a molar ratio OH-:Zn^{2+} = 2.167, which exceeds the theoretical ratio in $Zn(OH)_2$. For titrating an Al^{3+} solution, a single peak is observed at pH = 8.48 with a molar ratio OH-:Al^{3+} = 3.658, which exceeds the theoretical ratio in $Al(OH)_3$.

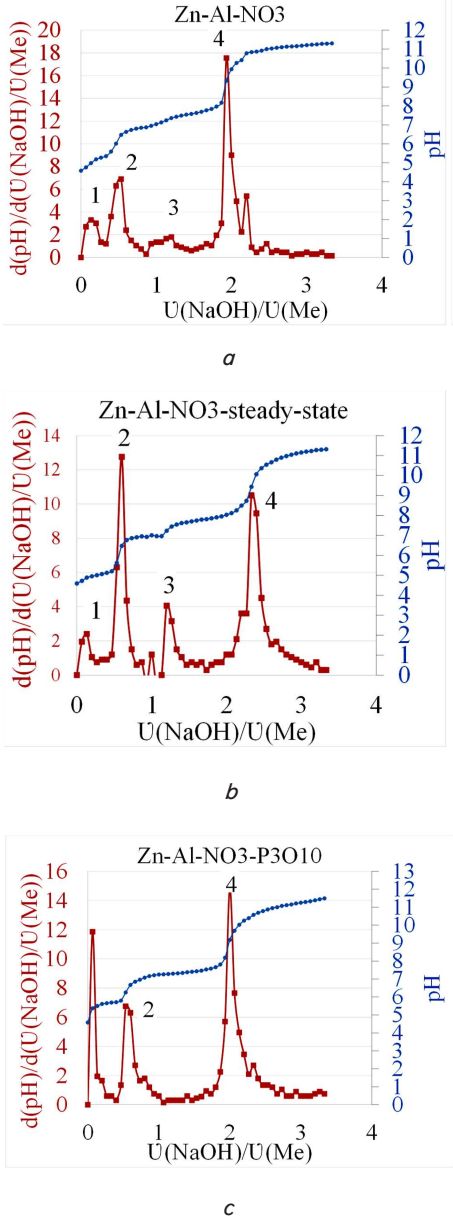
5. 2. Formation mechanism of nitrate and tripolyphosphate Zn-Al layered double hydroxides

Fig. 2 shows the titration curves obtained for studying the formation mechanism of Zn-Al nitrate and Zn-Al tripolyphosphate LDHs. The peak data derived from these curves are summarized in Table 3 for Zn-Al-NO_3, Zn-Al-NO_3-steady-state, and Zn-Al-NO_3-P_3O_{10}.

The titration curve of Zn-Al-NO_3 in studying the formation mechanism of Zn-Al-nitrate LDH (Fig. 2, *a*) exhibits four peaks. LDH formation proceeds via sequential formation of a basic aluminum salt with the formula $Al(OH)_{0.667}(NO_3)_{2.333}$ (at pH = 4.98), followed by a second basic aluminum salt with a lower nitrate content, $Al(OH)_{2.66}(NO_3)_{0.34}$ (at pH = 6.47). After this, the formation of Zn-Al LDH begins through the formation of a compound with the formula $Zn_{0.8}Al_{0.2}(OH)_{1.20}(NO_3)_{1.00}$ (calculated according to the basic salt hypothesis) (pH = 7.36) or with the formula $Zn_{0.667}Al_{0.333}(OH)_2(NO_3)_{1.667}$ (calculated according to the variable cation composition hypothesis).

This compound then, at pH = 9.35, transforms into a compound with the formula $Zn_{0.8}Al_{0.2}(OH)_{1.93}(NO_3)_{0.27}$ (calculated according to the basic salt hypothesis) or with the formula $Zn_{0.793}Al_{0.207}(OH)_2(NO_3)_{0.204}$ (calculated according to the variable cation composition hypothesis).

Transition to steady-state titration conditions (Fig. 2, *b*, Zn-Al-NO_3-steady-state) yields a similar pattern with high reproducibility. Peak 1 for steady-state titration conditions is completely consistent with conventional titration. However, peak 2 shows the formation of complete aluminum hydroxide $Al(OH)_3$ (peak 2).



a

b

c

Fig. 2. Titration curves for Zn-Al LDH formation: *a* – **Zn-Al-NO3**; *b* – **Zn-Al-NO3-steady-state**; *c* – **Zn-Al-P3O10**

Table 3

Peak parameters of differential titration curves for Zn—Al LDH formation

Peak	Data type	**Zn-Al-NO3**	**Zn-Al-NO3-steady-state**	**Zn-Al-NO3-P3O10**
1	pH	4.98	4.88	No peak
	U(NaOH)/U(Me)	0.133	0.133	No peak
	Formula	$Al(OH)_{0.667}(NO_3)_{2.333}$	$Al(OH)_{0.667}(NO_3)_{2.333}$	Impossible to calculate
2	pH	6.47	6.47	6.25
	U(NaOH)/U(Me)	0.533	0.600	0.533
	Formula	$Al(OH)_{2.66}(NO_3)_{0.334}$	$Al(OH)_3$	$Al(OH)_{2.66}(P_3O_{10})_{0.067}$
3	pH	7.36	7.23	No peak
	U(NaOH)/U(Me)	1.200	1.200	No peak
	Formula (basic salt hypothesis)	$Zn_{0.8}Al_{0.2}(OH)_{1.20}(NO_3)_{1.00}$	$Zn_{0.8}Al_{0.2}(OH)_{1.20}(NO_3)_{1.00}$	Impossible to calculate
	Formula (variable cation composition hypothesis)	$Zn_{0.667}Al_{0.333}(OH)_2(NO_3)_{0.333}$	$Zn_{0.667}Al_{0.333}(OH)_2(NO_3)_{0.333}$	Impossible to calculate
4	pH	9.35	9.49	9.18
	U(NaOH)/U(Me)	1.93	2.33	2.0
	Formula (basic salt hypothesis)	$Zn_{0.8}Al_{0.2}(OH)_{1.93}(NO_3)_{0.27}$	Impossible to calculate	$Zn_{0.8}Al_{0.2}(OH)_{2.00}(P_3O_{10})_{0.040}$
	Formula (variable cation composition hypothesis)	$Zn_{0.793}Al_{0.207}(OH)_2(NO_3)_{0.207}$	Impossible to calculate	$Zn_{0.8}Al_{0.2}(OH)_{2.00}(P_3O_{10})_{0.040}$

At the final stage of LDH formation (peak 4), the formula of the compound cannot be calculated, since the molar ratio U(NAOH)/U(Me) = 2.33 exceeds the theoretical value of 2.

The titration curve of **Zn-Al-NO3-P3O10** in studying the Zn-Al-tripolyphosphate LDH formation mechanism (Fig. 2, *c*) contains only two peaks. Peak 2 corresponds to the formation of the aluminum hydroxide phase (formula $Al(OH)_{2.66}(P_3O_{10})_{0.067}$). Peak 4 corresponds to the formation of Zn-Al-tripolyphosphate LDH. The calculated formula of the substance for this peak, $Zn_{0.8}Al_{0.2}(OH)_{2.00}(P_3O_{10})_{0.040}$, corresponds to the theoretical formula of LDH.

5. 3. Formation mechanism of carbonate Ni-Al and Ni(II)-Ni(III) layered double hydroxides

Fig. 3 shows the titration curves obtained for studying the formation mechanism of Ni-Al-carbonate LDH, Ni-Al-carbonate LDH synthesized in the presence of hypochlorite anion, and Ni(II)-Ni(III)-carbonate LDH synthesized in the presence of hypochlorite anion. Peak data from these curves are summarized in Table 4 for **Ni-Al-CO_3, Ni-Al-CO_3-OCl**, and **Ni-Ni-CO_3-OCl.**

It should be noted that the titration curves for **Ni-Al-NO_3-CO_3** and **Ni-Al-NO_3-CO_3-OCl** exhibit two peaks, both corresponding to the formation of Ni-Al LDH. This is confirmed by the fact that U(NaOH)/U(Me) for the first peak exceeds the theoretical value of 0.600. That is, peaks corresponding to the formation of an aluminum hydroxy compound are not observed. Ni-Al-carbonate LDH (**Ni-Al-NO3-CO3**) is formed via the formation at pH = 6.5 of the compound $Ni_{0,8}Al_{0,2}(OH)_{1,066}(CO_3)_{0,567}$ (calculated according to the basic salt hypothesis) or the compound $Ni_{0,624}Al_{0,376}(OH)_2(CO_3)_{0,376}$ (calculated according to the variable cationic composition hypothesis) followed by LDH formation at pH = 10.43.

The formation of Ni-Al-carbonate LDH in the presence of an oxidizing agent **(Ni-Al-NO_3-CO_3-OCl)** follows a similar pathway. At pH = 6.75, a compound with the formula $Ni_{0.8}Al_{0.2}(OH)_{0.799}(CO_3)_{0.700}$ (calculation based on the basic salt hypothesis) or with the formula $Ni_{0.498}Al_{0.502}(OH)_2(CO_3)_{0.256}$ (calculation based on the variable cationic composition hypothesis) is formed. This compound is subsequently transformed at pH = 9.74 into Ni-Al-carbonate LDH with composition $Ni_{0.8}Al_{0.2}(OH)_{1.932}(CO_3)_{0.134}$ (calculation based on the basic salt hypothesis) or $Ni_{0.792}Al_{0.208}(OH)_2(CO_3)_{0.104}$ (calculation based on the variable cationic composition hypothesis).

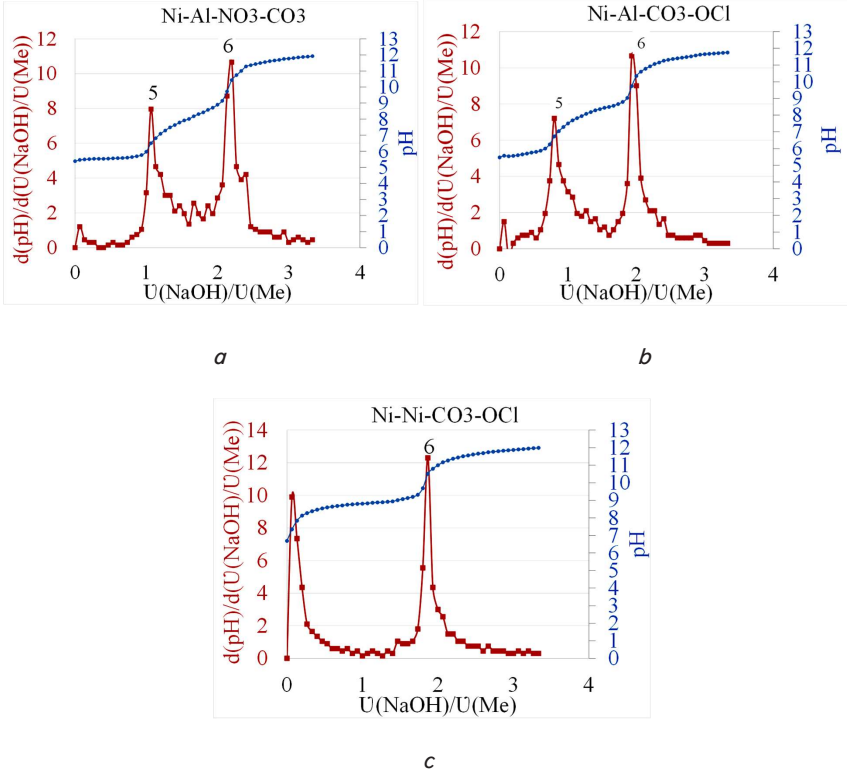


Fig. 3. Titration curves for Ni-Al and Ni(II)-Ni(III) LDH formation: *a* — **Ni-Al-CO3**; *b* — **Ni-Al-CO3-OCl**; *c* — **Ni-Ni-CO3-OCl**

Table 4

Peak parameters of differential titration curves for Ni-Al and Ni(II)-Ni(III) LDH formation

Peak	Data type	**Ni-Al-NO3-CO3**	**Ni-Al-NO3-CO3-Ocl**	**Ni-Ni-NO3-CO3-OCl**
1	pH	No peak	No peak	No peak
	U(NaOH)/U(Me)	No peak	No peak	No peak
	Formula	Impossible to calculate	Impossible to calculate	Impossible to calculate
2	pH	No peak	No peak	No peak
	U(NaOH)/U(Me)	No peak	No peak	No peak
	Formula	Impossible to calculate	Impossible to calculate	Impossible to calculate
5	pH	6.5	6.73	Absent
	U(NaOH)/U(Me)	1.066	0.799	Absent
	Formula (basic salt hypothesis)	$Ni_{0.8}Al_{0.2}(OH)_{1.066}(CO_3)_{0.567}$	$Ni_{0.8}Al_{0.2}(OH)_{0.799}(CO_3)_{0.700}$	Impossible to calculate
	Formula (variable cation composition hypothesis)	$Ni_{0.624}Al_{0.376}(OH)_2(CO_3)_{0.186}$	$Ni_{0.498}Al_{0.502}(OH)_2(CO_3)_{0.251}$	Impossible to calculate
6	pH	10.43	9.74	10.51
	U(NaOH)/U(Me)	2.198	1.932	1.867
	Formula (basic salt hypothesis)	Impossible to calculate	$Ni_{0.8}Al_{0.2}(OH)_{1.932}(CO_3)_{0.134}$	$Ni_{0.8}Ni_{0.2}(OH)_{1.866}(CO_3)_{0.167}$ *$Ni_{0.885}Ni_{0.115}(OH)_{1.866}(CO_3)_{0.124}$
	Formula (variable cation composition hypothesis)	Impossible to calculate	$Ni_{0.792}Al_{0.208}(OH)_2(CO_3)_{0.104}$	$Ni_{0.8}Ni_{0.2}(OH)_{1.866}(CO_3)_{0.167}$ *$Ni_{0.885}Ni_{0.115}(OH)_{1.866}(CO_3)_{0.124}$

*Note: * – the Ni^{3+} content is taken for Ni-Ni LDH synthesized at pH = 10 [32].*

The titration curve of nickel nitrate with a NaOH solution in the presence of sodium carbonate and hypochlorite (Ni-Ni-NO_3-CO_3-OCl) exhibits a single peak corresponding to the formation of Ni(II)-Ni(III)-carbonate LDH via formation of a substance with the formula $Ni_{0\cdot8}Ni_{0\cdot2}(OH)_{1\cdot866}(CO_3)_{0\cdot167}$.

6. Discussion of the results on the formation mechanisms of hydroxides

Formation mechanism of individual zinc (as the "host" metal cation) and aluminum (as the "guest" metal cation) hydroxides.

The chemical mechanism of layered double hydroxide formation [1], accepted by most researchers, is a two-stage process. At the first stage, the hydroxide of the "guest" metal cation is formed; at the second stage, the hydroxide of the "guest" metal cation interacts with the "host" metal cation, excess hydroxyl ions, and intercalating anions to form a layered double hydroxide. However, both trivalent "guest" metal cations and divalent "host" metal cations can form hydroxides via the basic salts' formation.

Analysis of the titration curves of **Zn-NO3** (Fig. 1, *a*) and **Al-NO3** (Fig. 1, *b*) reveals only single inflection point and, accordingly, a single peak on the differential curves. For the **Zn-NO3** curve, the peak on the differential curve is characterized by U(NaOH) / U(Me) = 2.167, while for the **Al-NO3** curve it is U(NaOH) / U(Me) = 3.658. In both cases, these values exceed the values for the complete hydroxide: U(NaOH) / U(Me) =2 for $Zn(OH)_2$ and U(NaOH) / U(Me) = 3 for $Al(OH)_3$. This can be attributed to the adsorption of additional hydroxide ions as well as the incorporation of the mother liquor into the precipitate. It can be concluded that, during the formation of both zinc hydroxide and aluminum hydroxide from nitrate solutions, potentiometric titration with a glass electrode does not reveal the formation of a precipitate of basic salts. This is most likely due to the very high rate of interaction of both cations with hydroxyl anions. To clarify the formation mechanism of individual zinc and aluminum hydroxides, additional studies combining potentiometric titration with, for example, conductometry are required, as previously demonstrated for nickel hydroxide in [33].

Formation mechanism of Zn-Al-nitrate and Zn-Al-tripolyphosphate LDHs. The differential titration curve of a mixture of zinc and aluminum nitrates (**Zn-Al-NO3**, Fig. 2, *a*) reveals four peaks. The first two peaks (peak 1 and peak 2) correspond to the formation of Al^{3+} hydroxo compounds, while the next two peaks (peak 3 and peak 4) correspond to the formation of LDHs themselves. This confirms the two-stage formation mechanism of Zn-Al LDHs. The first stage involves the formation of the "guest" metal cation hydroxide via the formation of a basic aluminum salt with the formula $Al(OH)_{0\cdot667}(NO_3)_{2\cdot333}$ at pH 4.98, which is less basic than aluminum monohydroxonitrate. This basic salt, when the pH increases to 6.47, transforms into an aluminum hydroxy compound with a lower nitrate content, $Al(OH)_{2\cdot66}(NO_3)_{0\cdot34}$ (peak 2), which can be considered either as a basic aluminum salt or as nitrate-doped aluminum hydroxide. The observation of two stages in the formation of aluminum hydroxy compounds during titration of the mixture (Zn^{2+} and Al^{3+}) and the absence of recorded stages during titration of the Al^{3+} solution indicates a decrease in the rate of interaction between the aluminum cation and hydroxyl anions, probably due to the adsorption of the Zn^{2+} cation when it is in excess. Under slower titration conditions (steady-state titration, **Zn-Al-NO3-steady-state**, Fig. 2, *b*), the peak of the

first stage of the Al hydroxo compounds formation (peak 1, Table 3) is completely reproduced with the same parameters: $Al(OH)_{0.667}(NO_3)_{2.333}$. However, with steady-state titration, the basic aluminum salt at the same pH = 6.47 (peak 2) is transformed into complete aluminum hydroxide $Al(OH)_3$. It can therefore be concluded that the minimum pH required for the synthesis of Zn-Al-nitrate LDH is 7.

Following the formation of aluminum hydroxo compounds, the formation of Zn-Al layered double hydroxide begins. Two hypotheses were formulated to calculate the precipitate compositions.

The basic salt hypothesis is based on the assumption that basic salts also possess a double layered lattice. Moreover, basic salts are also used to intercalate functional anions such as herbicides [34], emulsifiers, luminescence activators, catalysts, etc. The composition calculation based on the basic salt hypothesis is based on the assumption that both cations have already been incorporated into the precipitate, and the missing charges are compensated by the salt anions. In this case, two peaks are recorded on the differential curve (Zn-Al-NO_3, Fig. 2, *a*). According to the basic salt hypothesis, a compound of the composition $Zn_{0.8}Al_{0.2}(OH)_{1.20}(NO_3)_{1.00}$ (peak 3, Table 3) initially is formed at pH 6.47, followed by $Zn_{0.8}Al_{0.2}(OH)_{1.93}(NO_3)_{0.27}$ (peak 4, Table 3) at pH 9.35. Thus, according to the basic salt hypothesis, a basic salt with a higher nitrate content is initially formed, and then, as hydroxyl anions are introduced, they replace the nitrates.

The variable cation composition hypothesis assumes that the total number of metal cations is exactly equal to half the number of hydroxyl ions, while the salt anions merely serve to compensate the excess charge of the "guest" metal cation. In fact, initially a precipitate saturated with "guest" metal cations is formed (with a minimal "host" to "guest" cation ratio). Upon further addition of OH^- ions, the precipitate becomes saturated with "host" metal cations simultaneously with the incorporation of hydroxyl ions, and the "host" to "guest" cation ratio increases. When calculating according to the variable cation composition hypothesis, peak 3 corresponds to the formula $Zn_{0.667}Al_{0.333}(OH)_2(NO_3)_{1.667}$ (the molar ratio of Zn^{2+} :Al^{3+} is 2:1), and peak 4 corresponds to the formula $Zn_{0.793}Al_{0.207}(OH)_2(NO_3)_{0.207}$ (the molar ratio of Zn^{2+}:Al^{3+} is 0.793:0.207, which is very close to the ratio Zn^{2+} :Al^{3+} = 4:1).

Steady-state titration of the same system (**Zn-Al-NO3-steady-state**, Fig. 2, *b*, Table 3) shows a very similar pattern. Peaks 1 and 3 are completely reproduced in terms of the U(NaOH)/U(Me) value, although all peaks appear at lower pH values. Peak 2 corresponds to the formation of aluminum hydroxide, while peak 4 has U(NaOH)/U(Me) = 2.33, indicating the formation of Zn-Al-nitrate LDH with an excess of adsorbed and entrapped hydroxyl anions in the precipitate.

For the complete formation of Zn-Al-nitrate LDH, the recommended pH range is 9–10. It should be noted that in [3], the authors hypothesized a change in the formation mechanism of Zn-Al-nitrate LDHs at pH 9–10. The full possible pH range for synthesis is 7–10.

Analysis and comparison of the basic salt hypothesis and the variable cationic composition hypothesis for Zn-Al-nitrate LDH shows the preference for the variable cationic composition hypothesis. When using the basic salt hypothesis for peak 3 (Table 3) at U(NaOH) / U(Me) = 1.2 (i.e., at an alkali content of 60%), it seems unlikely that zinc will be completely incorporated into the precipitate in the absence of anions that form poorly soluble compounds. Furthermore, the variable cationic composition hypothesis is supported by the ratio of zinc and aluminum cations calculated for the compositions of peak 3 and peak 4: Zn^{2+}:Al^{3+} = 2:1 and Zn2+:Al^{3+} = 4:1, which fall within the LDH stability range reported in the literature [1, 2, 6, 11–14]. It should be concluded that for Zn-Al LDHs intercalated with anions that do not form poorly soluble salts with LDH cations, the variable anionic composition hypothesis is more relevant.

The formation mechanism of Zn-Al tripolyphosphate LDH is characterized by two stages, as evidenced by two peaks on the titration curve of **Zn-Al-NO3-P3O10** (Fig. 2, *c*). Peak 2 (Table 3) at pH = 6.25 corresponds to the stage of precipitate formation of the aluminum hydroxide form with the formula $Al(OH)_{2.66}(P_3O_{10})_{0.067}$, which can be considered either as a basic salt or as tripolyphosphate-doped aluminum hydroxide. The absence of peak 1 and the formation of peak 2 are probably due to the fact that aluminum tripolyphosphate is a poorly soluble substance. Moreover, the values U(NaOH) / U(Me) = 0.533 for peak 2 are the same for the curves of **Zn-Al-NO3** and **Zn-Al-NO3-P3O10**. Another peak is peak 4, corresponding to the formation of Zn-Al-tripolyphosphate LDH with the formula $Zn_{0.8}Al_{0.2}(OH)_{2.00}(P_3O_{10})_{0.040}$, which corresponds to the theoretical formula.

The minimum pH for the synthesis of Zn-Al-tripolyphosphate LDH is 7; the full possible pH range for the synthesis is 7–10; for complete LDH formation, pH = 9–10.

For Zn-Al-tripolyphosphate LDH, both hypotheses (basic salt and variable cation composition) yield similar precipitate compositions.

Formation Mechanism of Ni-Al-Carbonate and Ni(II)-Ni(III)-Carbonate LDHs. It should be noted that the titration curves of **Ni-Al-NO3-CO3** and **Ni-Al-NO3-CO3-OCl** (Fig. 3, *a, b*) lack peaks corresponding to the aluminum hydroxo compounds formation. This is due to the fact that the simultaneous presence of Al^{3+} and CO_3^{2-} in solution leads to irreversible complete hydrolysis of the aluminum cation, with the precipitation of insoluble aluminum hydroxide. Therefore, during the synthesis of carbonate-intercalated LDHs with Al^{3+} as the "guest" metal cation, aluminum hydroxide is formed immediately. Ni-Al-carbonate LDH (**Ni-Al-NO3-CO3**, Fig. 3, *a*) is formed via the formation of the compound $Ni_{0.8}Al_{0.2}(OH)_{1.066}(CO_3)_{0.567}$ at pH 6.5 (calculation based on the basic salt hypothesis) or the compound $Ni_{0.624}Al_{0.376}(OH)_2(CO_3)_{0.376}$ with the ratio Ni^{2+}:Al^{3+} = 0.624:0.376 = 1.66 (calculation based on the variable cation composition hypothesis). The formation of the precipitate at such a low Ni^{2+}:Al^{3+} ratio is probably also associated with the influence of the carbonate ion, since nickel carbonates are also insoluble. The rapidly formed aluminum hydroxide sorbs nickel cations, carbonate and hydroxyl anions, which contributes to the early formation of such precipitates. Subsequently, upon addition of alkali at pH 10.43, LDH is formed.

The formation of Ni-Al-carbonate LDH in the presence of an oxidizing agent (**Ni-Al-NO3-CO3-OCl**) occurs via a similar mechanism. Peak 5 is revealed on the titration curve at pH 6.75, yielding a compound with the formula $Ni_{0.8}Al_{0.2}(OH)_{0.799}(CO_3)_{0.700}$ (calculated according to the basic salt hypothesis) or $Ni_{0.498}Al_{0.502}(OH)_{0.2}(CO_3)_{0.256}$ (calculated according to the variable cation composition hypothesis). In the latter case, the ratio Ni^{2+}:Al^{3+} = 0.498:0.502 = 0.993 = 1. Visual observations show that under conditions corresponding to the formation of peak 5, a dark-colored precipitate forms, indicating oxidation of $Ni^{2+} \rightarrow Ni^{3+}$. Most likely, it is the influence of the oxidizing agent that leads to the formation of

a precipitate with an equimolar ratio of nickel and aluminum cations. With further introduction of alkali at pH = 9.74, the precipitate is transformed into a Ni-Al-carbonate LDH with the formula $Ni_{0.8}Al_{0.2}(OH)_{1.932}(CO_3)_{0.134}$ (calculated according to the basic salt hypothesis) or $Ni_{0.792}Al_{0.208}(OH)_2(CO_3)_{0.104}$. (calculated according to the variable cation composition hypothesis). It should be noted that for Ni-Al-carbonate LDH, according to the variable cation composition hypothesis, the precipitate saturated with the "guest" metal cation has a molar ratio of Ni^{2+}:Al^{3+} = 1 and is subsequently transformed into a precipitate with a molar ratio of Ni^{2+}:Al^{3+} = 4:1.

The minimum pH for the synthesis of Ni-Al-carbonate LDH is 7.5, the total possible pH range for synthesis is 7.5–11, and the pH for complete LDH formation is 10–11.

For Ni-Al-carbonate LDH, complete incorporation of Ni^{2+} from solution into the precipitate at U(NaOH)/U(Me) = 1.07–0.8 (40–54% hydroxyl anions relative to the required value) also seems unlikely. This calls into question the relevance of the basic salt hypothesis. However, calculations based on the variable composition hypothesis yield a Ni^{2+}:Al^{3+} ratio of 1.66–1.0, which is outside the stability range of LDH. It should be noted that the carbonate anion forms insoluble salts with the nickel cation. Most likely, both hypotheses contribute to the formation mechanism of LDHs, intercalated by anions capable of forming poorly soluble salts with LDH cations. An accurate resolution of the influence of a particular hypothesis will require experimental determination of the precipitate composition at a given point.

The formation mechanism of Ni(II)-Ni(III)-carbonate LDH in the presence of sodium hypochlorite is characterized by a single-stage formation. The titration curve of nickel nitrate with a NaOH solution containing sodium carbonate and hypochlorite (**Ni-Ni-NO3-CO3-OCl**) reveals a single peak of formation of Ni(II)-Ni(III)-carbonate LDH via the formation of a substance with the formula $Ni_{0.8}Ni_{0.2}(OH)_{1.866}(CO_3)_{0.167}$. It was shown in [32] that during synthesis at a constant pH = 10, the oxidation rate of $Ni^{2+} \rightarrow Ni^{3+}$ exceeds the rate of hydroxide formation. As a result, Ni^{3+} may appear in solution as a "guest" metal cation, forming Ni(II)-Ni(III). Using the experimentally obtained ratio Ni^{2+}:Ni^{3+} = 0.885:0.115 taken from work [32], the formula corresponding to the peak on the differential curve of $Ni_{0.885}Ni_{0.115}(OH)_{1.866}(CO_3)_{0.124}$ is recalculated. This formula most likely corresponds to carbonate-doped Ni(II)-Ni(III)-carbonate LDH. It should be noted that it is possible that by combining pH-metric titration with other methods it will be possible to identify additional stages of the formation of this LDH. It should also be concluded that the minimum pH value for the synthesis of Ni(II)-Ni(III)-carbonate LDH using sodium hypochlorite is 9, the full possible synthesis range is 9–12.

It can be concluded that the objective of this study has been fully achieved: the formation mechanisms of Zn-Al, Ni-Al, and Ni-Ni LDHs have been determined, and the precipitate compositions for critical points have been calculated. The practical significance of this study is that knowledge of the mechanisms allows for a clear delimitation of the pH range of LDH synthesis (for which the mechanisms have been studied), which will enable an informed choice of synthesis pH and reduce technology development costs. Determining the formation mechanism of Zn-Al nitrate LDHs will allow for the prediction of the synthesis conditions for Zn-Al LDHs intercalated with other promising functional anions.

A limitation of this study is the use of only pH-metric titration to determine the formation mechanism of LDHs. A disadvantage of the study is that the precipitate composition has been calculated based on two hypotheses; the molar ratio of "host" metal cation to "guest" metal cation has not been experimentally determined. A further development of this study is the investigation of the formation mechanisms of these LDHs using both pH-metric and conductometric titration.

7. Conclusions

1. Potentiometric titration of Zn^{2+} and Al^{3+} nitrate solutions with a glass electrode demonstrates a single-stage mechanism for the formation of individual zinc and aluminum hydroxides.

2. Potentiometric titration reveals a two-stage formation mechanism for Zn-Al-nitrate LDH. At the first stage, aluminum hydroxide (pH 6.47) is formed via the formation of a hydroxo salt of the composition $Al(OH)_{0.667}(NO_3)_{2.333}$ (pH 4.98). At the second stage, LDH is formed via intermediate stages of precipitate formation. At pH 7.36, a precipitate of the composition $Zn_{0.8}Al_{0.2}(OH)_{1.20}(NO_3)_{1.00}$ (basic salt hypothesis) or $Zn_{0.667}Al_{0.333}(OH)_2(NO_3)_{1.667}$ (variable cation composition hypothesis) is formed. At pH 9.35, the precipitate composition changes to $Zn_{0.8}Al_{0.2}(OH)_{1.93}(NO_3)_{0.27}$ (basic salt hypothesis) or $Zn_{0.793}Al_{0.207}(OH)_2(NO_3)_{0.204}$ (variable cation composition hypothesis).

Potentiometric titration also determines a two-stage formation mechanism for Zn-Al tripolyphosphate LDH. At the first stage, at pH 6.25, an aluminum hydroxo salt of the composition $Al(OH)_{2.66}(P_3O_{10})_{0.067}$ is formed. At the second stage, at pH 9.25, an LDH of the composition $Zn_{0.8}Al_{0.2}(OH)_2(P_3O_{10})_{0.040}$ is formed.

Based on the identified mechanisms, Zn–Al LDH synthesis can be carried out in the pH range of 7–10, with complete formation achieved at pH 9–10.

3. Potentiometric titration with a glass electrode reveals that the formation mechanism of Ni-Al-carbonate LDH is a two-stage process; however, the stage of aluminum hydroxy compound formation is missing. This is due to the complete irreversible hydrolysis of the aluminum cation in the presence of the carbonate ion, forming aluminum hydroxide, which immediately undergoes further reaction. At pH 6.5, a precipitate of the composition $Ni_{0.8}Al_{0.2}(OH)_{1.066}(CO_3)_{0.567}$ (basic salt hypothesis) or $Ni_{0.624}Al_{0.376}(OH)_2(CO_3)_{0.376}$ (variable cation composition hypothesis) is formed, which is transformed into LDH upon further addition of alkali.

The formation mechanism of Ni-Al carbonate LDH in the presence of ClO- as an oxidizing agent is similar. However, the composition of the first-stage precipitate differs: $Ni_{0.8}Al_{0.2}(OH)_{0.799}(CO_3)_{0.700}$ (basic salt hypothesis) or $Ni_{0.498}Al_{0.502}(OH)_{0.2}(CO_3)_{0.256}$ (variable cation composition hypothesis). Based on the formation mechanism, the synthesis of Ni-Al carbonate LDH can be carried out at pH 7.5–11, with pH 10–11 required for complete formation.

A single-stage formation mechanism is established for Ni(II)–Ni(III) carbonate LDH, and its synthesis is recommended at pH 10–12.

Conflict of interest

The authors declare no conflict of interest regarding this article or the published results of the study, including finan-

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Data availability

The manuscript has no associated datasets. Any additional explanations and materials can be obtained from the corresponding author upon request.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies in the preparation of this work.

Authors' contributions

Vadym Kovalenko: Conceptualization, Writing – original draft, Supervision**; Anastasiia Borysenko:** Methodology, Validation, Investigation; **Dmytro Andreiev:** Investigation; **Anton Dopira**: Investigation; **Oleksii Demchenko:** Investigation; **Valerii Kotok:** Methodology, Validation, Visualization; **Volodymyr Medianyk:** Validation, Writing – review & editing; **Dnytro Sukhomlyn:** Validation, Writing – review & editing; **German Shuklin:** Formal analysis. Data Curation; **Volodymyr Verbitskiy:** Resources. Writing – review & editing.

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