

Influence of synthesis conditions over Simonkollite/ZnO precipitation

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Abstract

Simonkollite is a zinc layered hydroxide salt with the formula $Zn_5(OH)_8Cl_2 \cdot H_2O$. It has a platelet morphology and can be used for many applications, owing to both its layered structure and its nature as a hydroxide salt. It can be prepared via a simple precipitation from $ZnCl_2$ and NaOH in water thermostated at 50°C. Depending on the synthesis conditions, we could obtain different sizes and a hybrid containing parts of ZnO. We studied the influence of the OH:Zn molar ratio, the addition order, and the maturation time after the reaction was completed. With the support of pH profiles, kinetic studies, and thermodynamic equilibrium data, we were able to propose a global synthesis mechanism explaining the influence of those three parameters, and identify the range of conditions in which simonkollite can be formed. Depending on the desired application, we were able to synthesize bigger or smaller layered crystals of simonkollite, in the presence or absence of ZnO.

Keywords: simonkollite, zinc hydroxide chloride, zinc oxide, precipitation, zinc layered hydroxide salt

Introduction

Simonkollite (SK) has the formula $Zn_5(OH)_8Cl_2 \cdot H_2O$ (Hawthorne & Sokolova, 2002) and was first reported in 1985 by Schmetzer et al. (Schmetzer et al., 1985). Simonkollite is part of the layered hydroxide salts (LHS), which structure derives from brucite-like structure, where some of the hydroxide groups are replaced by anions, and molecules of water are intercalated between the layers. The two-dimensional layers of simonkollite are formed of ZnO_6 octahedra interconnected with ZnO_3Cl tetrahedra, which is shown in Fig. 1 (ab plane). Across the c axis, the layers are stacked into the 3d-structure.

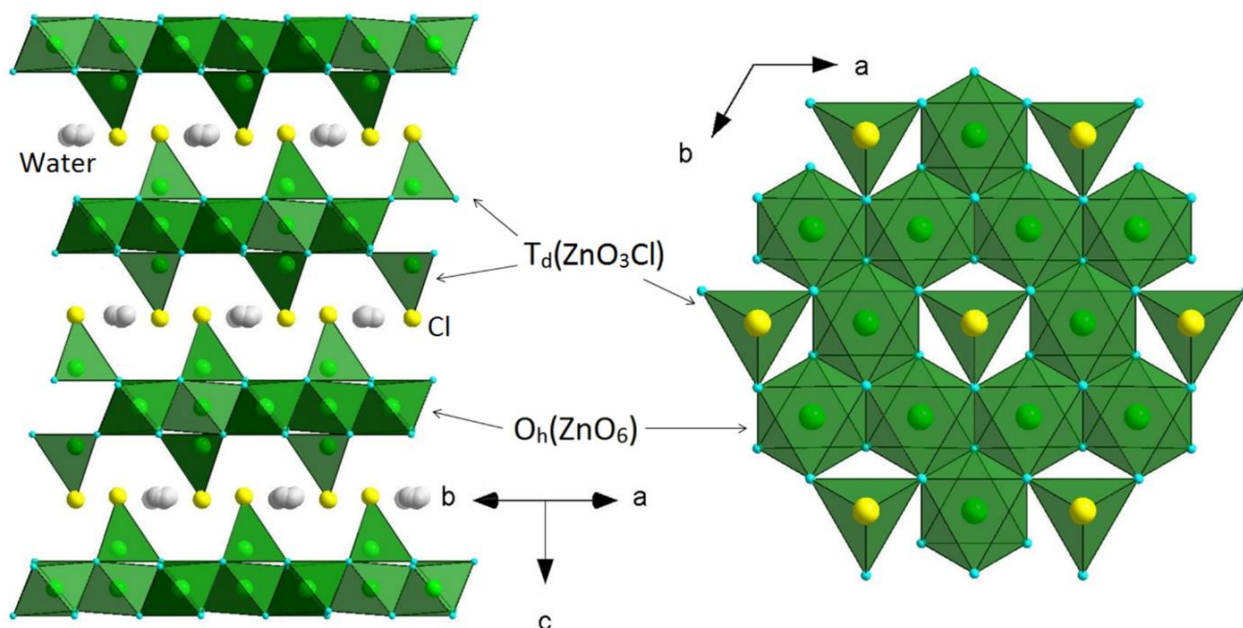


Fig. 1 Arrangement of structural layers of simonkolleite across the axis *c* and two dimensional projection of the layers at plane *ab*. (Hawthorne & Sokolova, 2002)

LHS can be used for many applications : catalysts (Baikousi et al., 2013; Machado et al., 2012; Xu et al., 2011), water pollutant removal (Kozai et al., 2006), separation of isomers (Komarneni et al., 1996; Tagaya et al., 1993, 2000), drug carriers (Rives et al., 2013; Rojas & Giacomelli, 2013), nanofillers (D. Li et al., 2006; Lonkar et al., 2013), UV protection (Cursino et al., 2010), mixed metal oxides precursors (Audebrand et al., 1998; Markov et al., 1990), flame retardants (Camino et al., 2001; Z. Li & Qu, 2003; Wang et al., 2005)... Several studied LHS showed good anionic exchange capacity, exfoliation and intercalation of different molecules (Arizaga et al., 2007). Among LHS, simonkolleite and other zinc layered hydroxide salts have been studied because of their interesting catalyst support (Machado et al., 2012), drug carrier (Rojas & Giacomelli, 2013), UV and visible light absorption (Cursino et al., 2010), photoluminescent aerogels (Zhu et al., 2016), and corrosion inhibition (Boshkov et al., 2005) properties (although simonkolleite is mostly an important corrosion product of zinc in marine environment). They can be used for many applications such as filler for polymeric systems, catalysts support, or super capacitors (Khamlich et al., 2013, 2016; Momodu et al., 2015).

Precipitation of $ZnCl_2$ with $NaOH$ yielded either simonkolleite or ZnO depending on the synthesis conditions. In this paper, we studied the influence of the $OH:Zn$ molar ratio, addition method and concentration of Cl^- anions on the product nature and morphology. Based on the study of the pH curves, kinetic studies and thermodynamic equilibrium values,

we proposed a global formation mechanism to explain the influence of all the synthesis conditions on the product nature and morphology.

Synthesis

A solution of NaOH (P.A., Penta, CZ) in water was prepared with a concentration of 0.5 mol/L. A second solution of ZnCl₂ (P.A., Lachema, CZ) was prepared with a concentration of 2.5 mol/L. In a typical experiment, one solution was heated up at 50°C under magnetic stirring, until the temperature was stable. Then the second solution was added drop by drop in the first one. The pH was monitored during the synthesis to observe the equivalence point and the rate of the reaction. After the addition was completed, the suspension was further stirred at 50°C during 90min, then it was cooled down, filtered on a Buchner setup, washed with distilled water and dried overnight at room temperature. The amount of NaOH solution was always 200 ml, while the amount of ZnCl₂ solution varied. Additionally, in one experiment some amount of NaCl was introduced in the reactor prior to addition, to test the influence of Cl⁻ ions on simonkolleite formation. The synthesis conditions for each prepared sample are presented in Table 1.

Table 1¹. Synthesis conditions of all the samples

<i>Experiment number</i>	1	2	3	4	5 ⁺	6	7	8
<i>Amount of ZnCl₂ solution ml</i>	400	160	80	53.3	40	36.4	33.3	28.6
<i>Solution added</i>	ZnCl ₂	ZnCl ₂	ZnCl ₂	ZnCl ₂	ZnCl ₂	ZnCl ₂	ZnCl ₂	ZnCl ₂
<i>Initial OH:Zn [mol/mol]</i>	0.1	0.25	0.5	0.75	1	1.1	1.2	1.4
<i>Experiment number</i>	9	10	11	12*	13	14	15	
<i>Amount of ZnCl₂ solution ml</i>	26.7	25	20	20	80	40	26.7	
<i>Solution added</i>	ZnCl ₂	ZnCl ₂	ZnCl ₂	ZnCl ₂	NaOH	NaOH	NaOH	
<i>Initial OH:Zn [mol/mol]</i>	1.5	1.6	2	2	0.5	1	1.5	

Measurements

The synthesized samples were evaluated by X-Ray diffraction of powders (XRD) analysis of polycrystalline powders (a diffractometer D8 Advance, monochromatic CuK α radiation and a scintillation detector, Bruker, GB: step scanning over 2 θ range from 10 to 80° with a step size of 0.02° and 3s counting time at each step; a diffractometer Rigaku Miniflex

¹ +Was repeated 5 times and interrupted at different stages

*0.1 mol of NaCl is added to double the amount of Cl⁻ ions in the reactive mixture

600: continuous scanning over 2θ range from 10 to 80° , scanning speed – 5-10 2θ degrees per min). Reference intensity ratio (RIR) method with Rietveld refinement was used to determine the content of simonkolleite and ZnO in the final products. The crystallite size of the powders was calculated on basis of Scherrer and Halder-Wagner methods. For the calculation, only well resolved XRD peaks were used. The values indicate average crystallite size distribution. Selections of only basal peaks provided very close results which can be explained by the wide size distribution/thickness of the SK plates.

Scanning Electron Microscopy (SEM) scans were performed on the dried samples to analyse their morphology. Dried powder was applied on the target without any grinding or other pre-treatment. The observation conditions were an acceleration voltage of 15 kV, and the final image is the combination of both scattered and back-scattered electrons scans (TM3030 plus electron microscope, Hitachi).

Measurements of the specific surface area of dried powders were performed using surface area and pore size analyser (NOVA 1200e, Quantachrome instruments, USA). Surface area was calculated using Multipoint BET adsorption approach. Measurements were performed at -196.15°C in 9mm manifold using N_2 and He as adsorptive and non-adsorptive gases respectively; the samples weight were between 2.4-3.6 g. Seven relative pressure points were measured in the range of 0.03-0.25 P/P0 under the following equilibrium conditions: pressure tolerance 0.1 mmHg, equilibration time 90 sec, equilibration timeout 240 sec. At least four P/P0 points were used to build multi-point BET plot. Prior to the measurement, the samples were degassed using vacuum for 24 h at room temperature.

The pH was monitored during the addition to provide additional information about the precipitation reaction (a pH/conductivity meter InoLab, WTW, Germany).

Results and discussion

The results of XRD RIR analysis are summarised in Tables 2-3. The table also contains general information on the sample morphology. SEM images of the dried samples are presented in Fig. 2.

When adding ZnCl_2 into NaOH, we observed no noticeable influence of the OH:Zn molar ratio ranging from 0.1 to 1.5. (Table2) We obtained pure simonkolleite in the shape of hexagonal platelets of dimensions varying between 1 to $10\mu\text{m}$ in width and 0.1 to $1\mu\text{m}$ in thickness. Lower OH:Zn molar ratio tended to yield thinner plates, with the exception of the molar ratio 1.5 which also yielded thin plates. (Figure2 a-b, c, e) Then for molar ratios from 1.6 to 2 we observed a mixture of ZnO and Simonkolleite. (Table2) Simonkolleite kept a

hexagonal plates shape, and ZnO was either in the form of shapeless small particles on the surface of simonkolleite for the molar ratio 1.6, or in aggregated form for the molar ratio 2. (Figure 2-e, f)

By adding NaOH in ZnCl₂, we started from low pH, and we also observed the formation of pure simonkolleite in the OH:Zn molar ratio range of 0.5-1.5. (Table3) However the morphology was totally different with much smaller plates than for the opposite addition method. Again, for the same addition method, the ratio had very little or no influence on the resulting morphology. (Figure2-b, d)

Table2. Composition and morphology of samples 1 to 12²

<i>Experiment</i>	<i>OH:Zn initial molar ratio [mol/mol]</i>	<i>Phase composition obtained by XRD RIR</i>	<i>Morphology</i>
1	0.1	SK 100 %	Small plates, 3-5 μm*0.1-0.3μm
2	0.25	SK 100 %	Small plates, 1-3μm*0.1-0.3μm
3	0.5	SK 100 %	Small plates, 2-5μm*0.1-0.3μm
4	0.75	SK 100 %	Small plates, 3.5-4.5μm*0.2-0.4μm
5	1	SK 100 %	Small plates, 4-5 μm*0.2-0.4μm
6	1.1	SK 100 %	Small plates, 3-7μm*0.1-0.3μm
7	1.2	SK 100 %	Regular big plates, 10-5μm*0.5-1μm
8	1.4	SK 100 %	Small plates, 4-8 μm*0.1-0.4μm
9	1.5	SK 100 %	Lots of thin plates, lower than 0.1 μm, 3-7 μm wide
10	1.6	SK 75 %	Plates 3-8 μm and some much smaller particles
11	2	SK 28 %	No visible plates, only big shapeless solids covered with very small particles
12 [*]	2	SK 36 %	No visible plates, only big shapeless solids covered with very small particles

² *0.1 mol of NaCl is added to double the amount of Cl⁻ ions in the reactive mixture

Additionally, surface area of the samples varied from $2.9\text{-}5.3\text{m}^2\text{g}^{-1}$. However, no regularity has been observed regarding synthesis conditions and crystal shape or size. At the same time, the measured result depended very much on degassing conditions prior to the measurement. It should be connected with removal of crystalline water and structure collapse under vacuum treatment above room temperature.

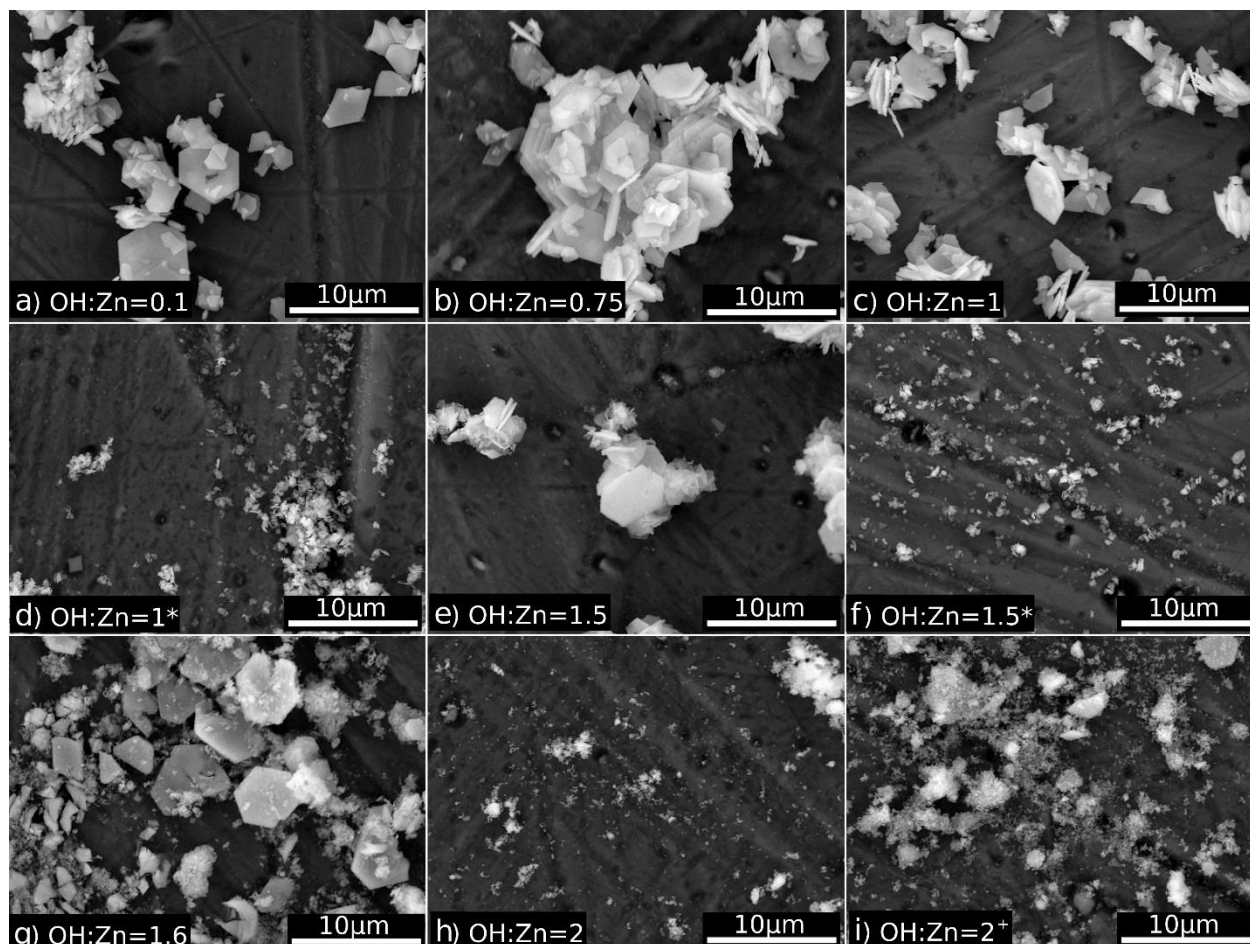


Fig. 2³ SEM scan of dried samples. a) sample 1, OH:Zn= 0.1;b)sample 4, OH:Zn= 0.75;c) sample 5, OH:Zn= 1; d) sample 14, OH:Zn= 1, reversed addition; e) sample 9, OH:Zn= 1.5; f) sample 15, OH:Zn= 1.5, reversed addition; g) sample 16, OH:Zn= 1.6; h) sample 11, OH:Zn= 2; i) sample 12, OH:Zn= 2, double amount of Cl⁻

Table3. Composition and morphology of samples n°13 to n°15

<i>Experiment</i>	<i>OH : Zn [mol/mol]</i>	<i>XRD phase composition</i>	<i>Morphology</i>
13	0.5	SK 100 %	0.5-0.6 µm
14	1	SK 100 %	0.6-0.9 µm
15	1.5	SK 100 %	0.5-0.8 µm

³ *reversed addition order
⁺double amount of Cl⁻ ions

In the next section, the mechanism of the formation of simonkolleite will be discussed depending on the synthesis methodology.

Addition of ZnCl₂

In the series of experiments n°1 to 11, we added the ZnCl₂ solution into the NaOH solution, starting from high pH and infinite OH:Zn molar ratio, and going towards lower values of pH and OH:Zn molar ratio. We observed an immediate precipitation from the first added drop, and the pH is stabilized instantly upon addition of one solution in the other. At the beginning of the addition, the pH decreased very slowly, until the system went through a pH equivalence point at a OH:Zn molar ratio of 2.1, accompanied with a large pH fall from 12 to 6. After the equivalence, the pH continued to decrease very slowly with further addition of ZnCl₂. A typical curve of pH change during synthesis is shown in Fig. 3. based on experiment n°4 conditions (OH:Zn = 0.75). The pH equivalence point of all experiments of the series (n°1-11), and the concentration range were almost identical, because the initial concentration of NaOH as well as concentration of added ZnCl₂ solution were the same. The difference between the experiments consisted only in the amount of added ZnCl₂, which in all cases was above the amount required to reach the equivalence point.

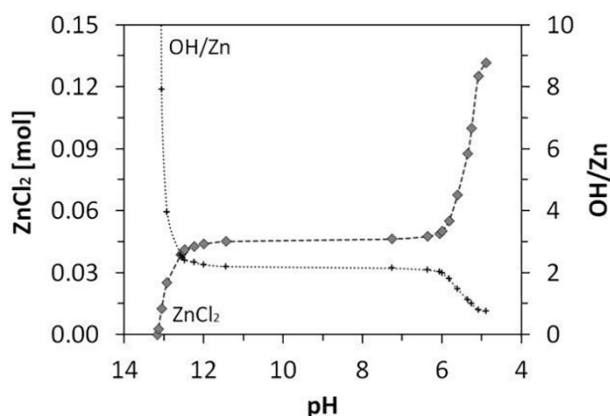


Fig. 3 Effect of added amount of ZnCl₂ and OH:Zn ratio in the matrix solution on its pH, experiment n°4 (OH:Zn=0.75; initial amount of NaOH is 0.1 mol, V = 200ml).

The dependence of the pH on the concentration of ZnCl₂ in the matrix solution for the same experiment (n°4) is presented in Fig. 4. To support our analysis of the processes which take place in the reaction mixtures during addition, we used equilibrium diagrams for Zn²⁺ fractions which are presented in Fig. 4. The diagrams represent the thermodynamically stable Zinc (II) phases (both the solid phases and soluble species) depending on the pH in a ZnCl₂-H₂O system at 25°C (calculated on basis of equilibria and thermodynamic data using Medusa-Hydra chemical equilibrium software). The equilibrium diagrams are presented for 5 different

concentration points marked at the main graph. According to the equilibrium diagrams, both ZnO and Zn(OH)₂ solids are thermodynamically stable at given concentrations over a similar pH range. The pH edge of the stability range of this solid was shifted from 7 to 9 when the ZnCl₂ concentration was increased from 0.00062 to 0.521 mol/L. Simonkolleite solid phase, Zn₅(OH)₈Cl₂·H₂O, becomes stable at a concentration C(ZnCl₂) ≥ 0.007 (10^{-2.15}) mol/L. Concerning the soluble species, zinc hydroxide complexes, Zn(OH)⁺, Zn(OH)₃⁻ and Zn(OH)₄²⁻, are stable only at lower ZnCl₂ concentrations: the first one – at pH range 5-9, while two others – at very basic pH (>12). The Zn²⁺ and other chloride complexes are stable at pH < 7; the H₂O molecules in coordination sphere of Zn²⁺ ion were not specified at the diagrams for simplicity reasons.

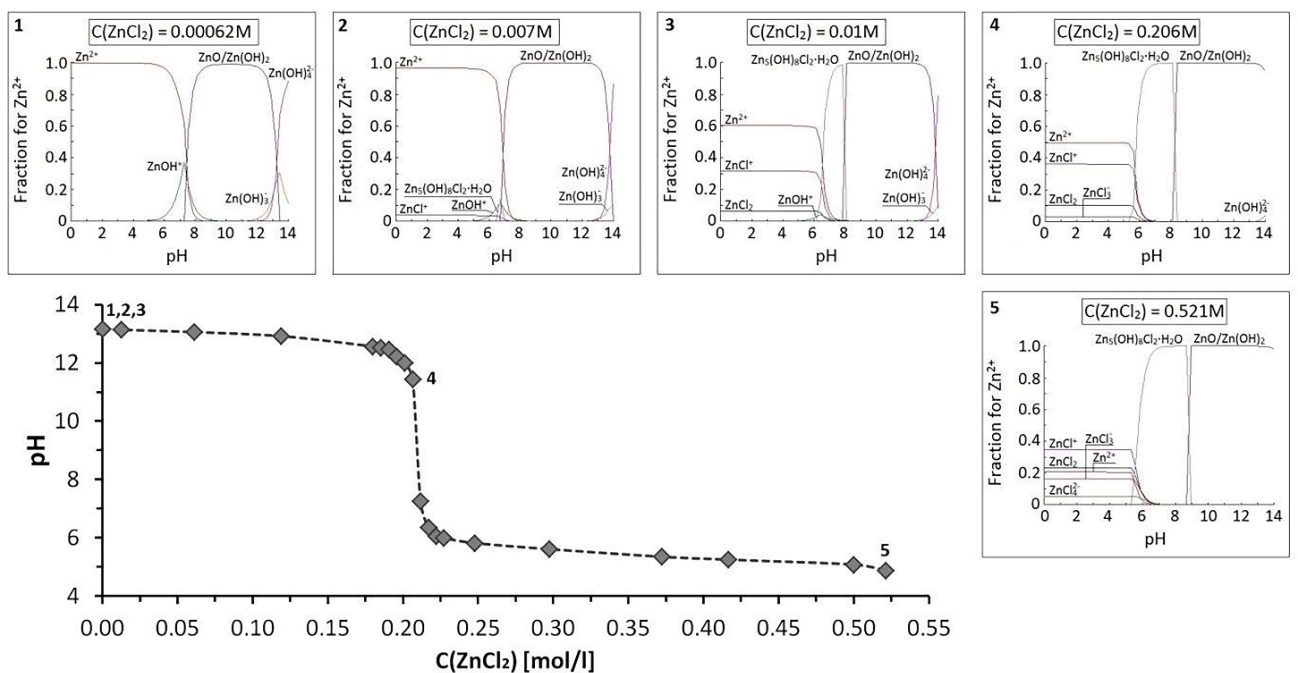
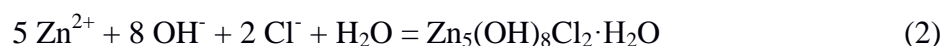


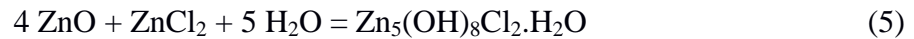
Fig. 4 pH change during synthesis of sample 4 (OH:Zn=0.75) and equilibrium diagrams for Zn²⁺ fraction at 5 different points at 25°C. The main graph represents dependence of pH on concentration of ZnCl₂ in the matrix solution (initial concentration of NaOH solution was 0.494mol/L).

Considering our system, the observed pH decrease during synthesis could be achieved via two different mechanisms: either by consumption of OH⁻ during the formation of the insoluble solid hydroxide/hydroxide chloride or, neutralisation by the H⁺ ions released during the formation of ZnO. The simplified reactions corresponding to these mechanisms are presented below (Scheme 1, 2 and 3).

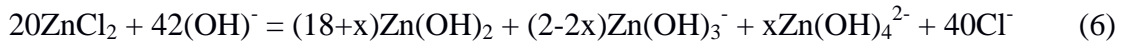




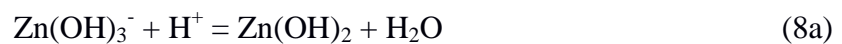
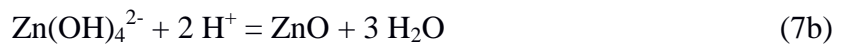
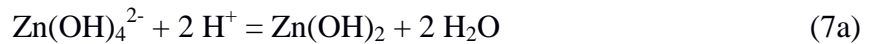
According to the equilibrium diagrams (Fig. 4), starting from high pH, either ZnO or Zn(OH)₂ should have been formed (Scheme 1 and 3), while simonkolleite could have been formed only when the pH is low enough. From the schemes (1) and (3), it is visible that the equivalence for both the formation of Zn(OH)₂ and ZnO should occur for OH:Zn molar ratio = 2. From scheme (2), it is visible that the equivalence for the formation of simonkolleite should occur at a molar ratio OH:Zn = 1.6. However, instead of two equivalence points as should be expected, the pH measurements during the addition showed only one (Fig. 3 and 4) at 2.1. In both mechanisms, no further OH⁻ was consumed for the formation of simonkolleite beyond the first equivalence point. Therefore, the equivalence point that we observed should correspond either to the consumption of OH⁻ for the formation of Zn(OH)₂ (Scheme 1) or to neutralisation during the formation of ZnO (Scheme 3). Moreover, instead of being formed directly from the soluted species (Scheme 2), simonkolleite should be formed from the reaction products (Zn(OH)₂ or ZnO), following a mechanism that does not involve any pH change (Scheme 4 and 5).



In the case of Zn(OH)₂ formation, if only Zn(OH)₂ was formed, we would observe an equivalence point at OH : Zn molar ratio of 2. Since it is at 2.1, we deduced there is an equilibrium between Zn(OH)₂, Zn(OH)₃⁻, and Zn(OH)₄²⁻ (Scheme 6).



It is worth to note that according to the equilibrium diagrams (Fig. 4), Zn(OH)₃⁻, and Zn(OH)₄²⁻ are stable only at high pH, while with pH decrease they should transform into ZnO or Zn(OH)₂ (Scheme 7a, b and 8a, b). At the same time, Zn(OH)₂ could also dehydrate into ZnO during the synthesis (Scheme 9). Therefore, when approaching the equivalence point, the concentration of Zn(OH)₃⁻, and Zn(OH)₄²⁻ should become negligible, while the main phases present in the mixture should be Zn(OH)₂ and/or ZnO.



The second mechanism, which may lead to decrease of pH, is neutralisation in result of the direct formation of ZnO by hydrolysis (Scheme 3). In this case, the formation of H⁺

ions should lead to neutralisation of the solution. According to the reaction (Scheme 3), formation of one ZnO produces two H^+ ions, thus the pH equivalence point should be reached with $OH : Zn = 2$, which is also very close to the observed value ($OH : Zn = 2.1$). The slight difference to the stoichiometry can again be explained by the formation of $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$. The whole mechanism can be represented by the general equation (Scheme 10), where x is comprised between 0 and 1.



In general, according to the equilibrium diagrams and the observed pH change of the solution, the formation of simonkolleite phase can be described as follows. After addition of the first drop of $ZnCl_2$ (0.05ml) to highly basic NaOH solution, besides the formation of ZnO or $Zn(OH)_2$, two soluble zinc hydroxide complexes $Zn(OH)_4^{2-}$ and $Zn(OH)_3^-$ are also formed (point 1, Fig 4). Further increase of $ZnCl_2$ concentration in the solution leads to the formation of only ZnO or $Zn(OH)_2$, which, according to the equilibrium diagram (Fig. 4, point 3, equilibrium diagram 3), are the only thermodynamically stable compounds at this concentration and pH. The formation of ZnO or $Zn(OH)_2$ should lead to neutralisation of the solution. The equivalence point corresponds to pH 9 and is associated with a sharp fall in pH from 12 to 6. The fact, that equivalence point corresponded to pH higher than 7 can be explained with the limited stability of $Zn(OH)_2$ and ZnO at lower pH. In particular, when pH became low enough, the reactions leading to pH increase may take place (Scheme 11 and 12) that prevented further sharp falling of the pH in the system.



In order to prove this suggestion, we have performed another experiment. For a separate sample the $ZnCl_2$ solution was added in the amount a little bit less than required to reach the equivalence point and, thereafter, we started to add a very acidic HCl solution ($C(HCl) = 0.5 \text{ mol/l}$, similar to the initial concentration of NaOH) instead of $ZnCl_2$ solution. The experiment was aimed to reveal how the acid will influence the equilibrium in the system. Although we expected that by addition of HCl the equivalence point will be reached almost immediately and a sharp fall of pH will take place, it did not happen. Instead, the pH remained stable (around 12.2) and it fell only after the addition of 80ml of HCl solution. Thus, in our opinion, the result can be explained by the consumption of H^+ ions via the dissolution of precipitation products ($Zn(OH)_2$ or ZnO) according to the above described reactions (Scheme 10 and 11) that prevented the pH fall.

When continuing to add more ZnCl_2 , past a OH:Zn molar ratio of 2, simonkolleite started to form without changing the pH from either $\text{Zn}(\text{OH})_2$ or ZnO (Scheme 4 and 5). A similar reaction between ZnO and $\text{Zn}(\text{NO}_3)_2$, has already been described in literature (Moezzi et al., 2013), but since we did not know whether ZnCl_2 reacted with dehydrated ZnO or $\text{Zn}(\text{OH})_2$, we could not conclude which of the reactions occurred during our synthesis method. In both cases, the pH continued to decrease very slowly on the account of the addition of ZnCl_2 solution, which is acidic. To ensure that the reaction was accomplished, the mixtures were aged during 90 min under constant stirring. The final conditions that were reached after complete addition of ZnCl_2 solution for experiment n°4 corresponded to equilibrium diagram 5 (Fig. 4). The final pH value for this experiment was below 5 and, according to the equilibrium diagram, only the soluble Zn^{2+} species are thermodynamically stable in ZnCl_2 - H_2O system at this pH pointing out that the solid should gradually dissolve. This was the same situation for other experiments where the OH:Zn molar ratio was below 1 (n°1-5). As follows, it was expected that the yield of simonkolleite phase in these experiments should have in general gradually decreased. However, a decrease in the yield was observed only for the samples n°1 and 2, which was especially low for the sample n°1 with $\text{Zn}/\text{OH} = 0.1$, where the most acidic final pH was reached. It was connected not with sample dissolution, but with partial loss of the solid sample during filtration due to penetration of low crystal size fracture through the filtration paper. Moreover, according to SEM analysis, lower OH : Zn molar ratio also resulted in slightly thinner crystal plates. At the same time, the pH of the system during stirring also almost did not changed. In view of this facts, we came to the conclusion that the system had reached some kind of dynamic equilibrium between the dissolution of simonkolleite crystals and their recrystallization. Also, because the pH in this series of experiments was only slightly lower than the stability range of simonkolleite phase, the process of dissolution could be very slow. This result is quite interesting because via correlation of OH:Zn molar ratio in the system, we could manipulate the equilibrium in the system and slightly influence the thickness of the crystal plates formed.

Influence of maturation time

After 90 min stirring, the samples were filtrated, washed and dried at room temperature. As a result, well crystalline pure phase products of simonkolleite were obtained for $\text{OH} : \text{Zn} \leq 1.5$. In the case where the molar ratio OH:Zn was above 1.5, a mixture of simonkolleite and ZnO phases was obtained. This result indicates that an excess of ZnCl_2 is required for the formation of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ pure phase product that also testifies in favour of our conclusion that the formation of simonkolleite in the studied system takes place

according to the Scheme 4 and 5 and thus requires both Zn^{2+} and Cl^- ions to be present in the solution.

In order to study the kinetic of the formation of simonkolleite in more details as well as to clarify which compound is formed at the intermediate step ($\text{Zn}(\text{OH})_2$ or ZnO), we have performed a series of additional experiments. In particular, the addition of ZnCl_2 solution (experiment n°5, $\text{OH} : \text{Zn} = 1$) was stopped at different stages and the resulting solid was filtrated, washed, dried and studied with XRD analysis. To this purpose, the products of 5 different reaction steps were studied:

step1: the reaction was stopped after addition of 10ml of 2.5M ZnCl_2 solution (reached $\text{OH}:\text{Zn}$ molar ratio at this point was 4, pH of the suspension was close to 13); the solid was washed using 2 different liquids (NaOH solution with pH10 and distilled H_2O with pH 6);

step2: the reaction was stopped immediately after addition of all the ZnCl_2 solution required to reach $\text{OH}:\text{Zn}$ molar ratio 1 (42ml of 2.5 mol/L solution), the pH of the suspension was 5.3;

step3: the reaction was stopped 30min after addition of all the ZnCl_2 solution;

step4: the reaction was stopped 60min after addition of all the ZnCl_2 solution;

step5: the reaction was stopped 90min after addition of all the ZnCl_2 solution.

The results of XRD analysis of the obtained samples are presented in Fig. 5.

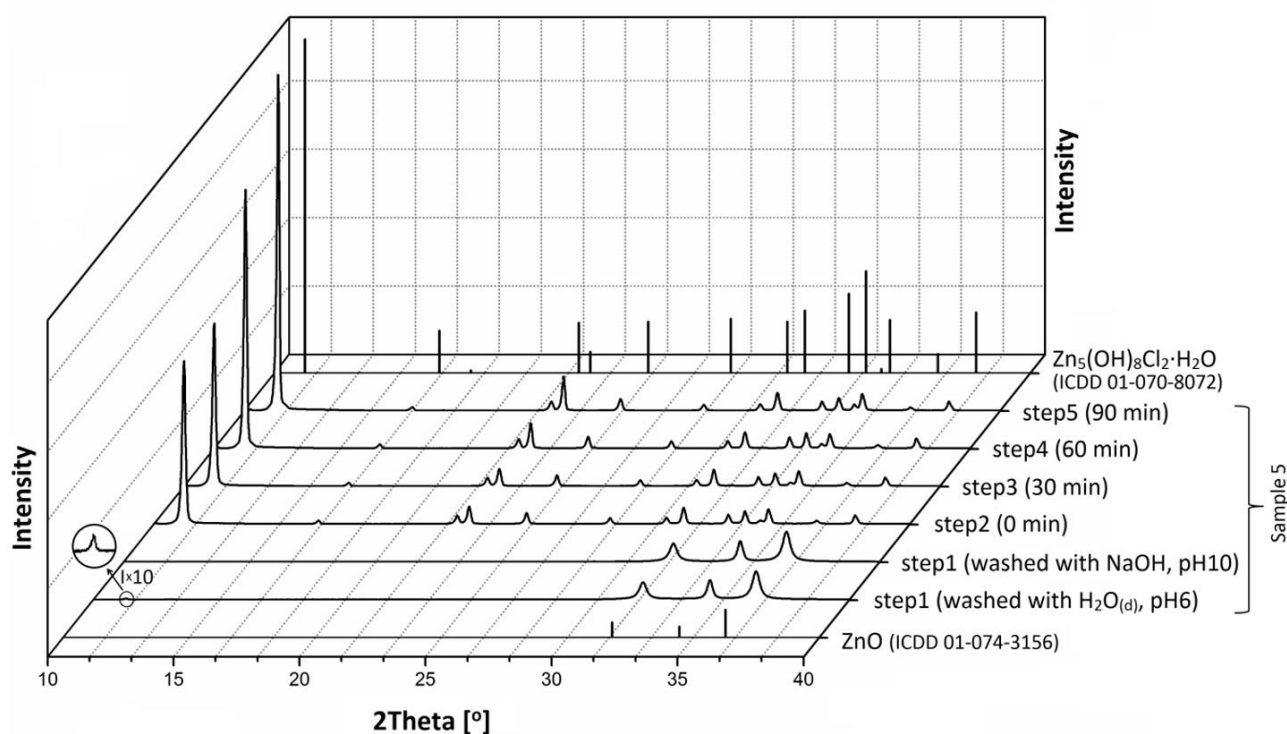
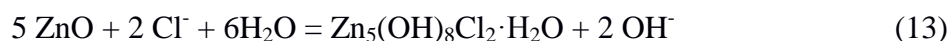


Fig. 5 Results of XRD analysis of sample 5 (OH : Zn = 1) at different reaction stages; diffraction patterns of ZnO and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ (database PDF-2).

The results indicate that even in the case when the equilibrium point was not reached (step1), simonkolleite phase started to form during washing of the sample with slightly acidic water. The content of simonkolleite phase in this sample after washing constituted ~1.31(2)%. As the main product at step1, low crystalline ZnO was detected (crystallite size ~10nm). After the whole ZnCl_2 solution was added and the pH decreased (steps2-5), simonkolleite became immediately the only phase observed with XRD analysis pointing out that the kinetic of its formation was very fast. With continuous stirring, the crystallinity of the samples significantly improved (the crystallite size gradually increased from 13-15nm to 50-60nm). Although the results of the experiment imply that ZnO was the intermediate product and the formation of simonkolleite took place according to Scheme 5, ZnO may also be formed from $\text{Zn}(\text{OH})_2$ during drying stage, rendering detection of $\text{Zn}(\text{OH})_2$ impossible when the conditions are altered. Therefore, definite confirmation that ZnO is the only intermediate product of the studied reaction could be obtained only in result of in situ studies.

Influence of excess Cl⁻ ions

In order to gain more information on the reaction of the formation of simonkolleite, we have also studied the impact of Cl^- ions and their ability to shift the equilibrium towards the formation of simonkolleite phase. In particular, because simonkolleite and $\text{Zn}(\text{OH})_2$ have a similar crystal structure, $\text{Zn}(\text{OH})_2$ could be converted to simonkolleite via partial replacement of OH^- into Cl^- following the Scheme 12. Or, alternatively, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ can be also formed from ZnO according to Scheme 13.



Concerning our experiment, the concentration of Cl^- in the system was increased via addition of a NaCl solution (experiment n°12). In this experiment, we have the same OH:Zn molar ratio as in experiment n°11 (which resulted in the formation of a ZnO and $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ mixture), but the amount of Cl^- is similar to the experiment n°5, which resulted in the formation of pure $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. Since we obtained a mixture 8% richer in simonkolleite than for experiment n°11, we conclude that adding Cl^- favoured a little bit the formation of simonkolleite, but not as significantly as the presence of both Zn^{2+} and Cl^- ions.

Addition of NaOH

In order to find out how the order of the added solution would affect the precipitated product, we have chosen 3 points with OH:Zn molar ratio 0.5, 1 and 1.5. For all these points,

a pure simonkolleite phase was obtained in case of addition of ZnCl_2 into NaOH. Similarly, to the previous case, we observed immediate precipitation during the addition of NaOH solution into ZnCl_2 solution. The initial pH of the solutions was quite acidic (4.23-4.36) and it increased and stabilized instantly upon addition of one solution in the other. However, the character of pH change was totally different than in previous case: with addition of NaOH, the pH increased quite quickly to 4.85-4.92 while above this point it increased much slower. The curves of pH change during synthesis for all 3 experiments (n°13-15) are shown in Fig. 6.

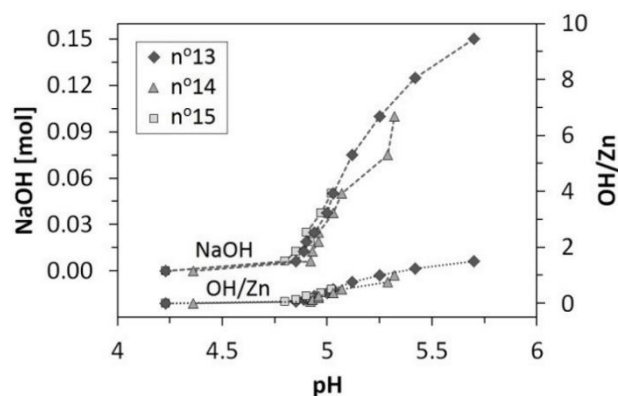


Fig. 6 Effect of the added amount of NaOH and OH:Zn molar ratio in the matrix solution on its pH, experiments n°13-15 (OH:Zn=0.5-1.5; initial amount of ZnCl_2 is 0.1 mol, $V = 200\text{ml}$)).

With the addition of NaOH, the initial concentration of ZnCl_2 in the matrix solution decreased from 0.5 mol/L to 0.385-0.455 mol/L depending on final OH : Zn molar ratio. In such case, the equilibrium diagram for Zn^{2+} fraction should be very similar to those presented in Fig 4, equilibrium diagram 5. Accordingly, simonkolleite phase should have appeared only at a pH above 6. However, in spite that the pH in these experiments was below 6, pure simonkolleite phase was obtained in all cases. With the increase of OH:Zn molar ratio, the product yield also significantly increased. It can be explained with higher final pH where the simonkolleite phase became more thermodynamically stable. For all studied experiments, the resulting powders consisted of very thin and small crystal plates pointing out less favourable conditions for the formation of simonkolleite than in case of addition of ZnCl_2 into NaOH solution.

Those results can be put in parallel with those obtained by Zhu et al. (2016), where they used propylene oxide (PO) as a cation scavenger instead of NaOH, and DMF as a solvent. In this study, they added some water as a source of OH groups, and explained the formation mechanism by the formation of two complexes of Zn^{2+} corresponding to the octahedron and tetrahedron present in the SK structure. Although the reaction mechanism was

different, and the obtained structure was flower-like, they observe that the ratio between PO and Zn^{2+} had a major influence on the results.

Conclusion

As a conclusion, the synthesis mechanism of simonkolleite is favoured at slightly acidic pH, whereas the ZnO formation is being favoured by a higher initial OH:Zn molar ratio.

The study of the pH profile during the addition of ZnCl_2 into NaOH solution at 50°C , showed three things: the system reaches an equilibrium immediately, simonkolleite is formed through the reaction of either ZnO or Zn(OH)_2 intermediate products, and the intermediate product neutralizes HCl. The kinetic study showed that the intermediate product yields a major part of ZnO after drying, and a very small part of simonkolleite when neutralized before drying. Moreover, an increasing stirring time post-addition increases the crystallinity of the product. With the support of thermodynamic equilibrium diagrams, we concluded that ZnO and/or Zn(OH)_2 are the main intermediate products. Since the position of the equivalence is shifted to a OH:Zn molar ratio slightly higher than 2, we deduced that there is also a small part of Zn(OH)_3^- and/or Zn(OH)_4^{2-} present in the intermediate product. Simonkolleite is further formed by the reaction between ZnCl_2 and the intermediate product, with no pH change involved. Despite its structure being close to that of Zn(OH)_2 , simonkolleite is not formed by partial replacement of OH^- by Cl^- anions, but the addition of Cl^- can slightly favour the formation of simonkolleite.

The influence of OH:Zn molar ratio on the morphology of simonkolleite is very faint. We could observe thinner plates formation for lower OH:Zn molar ratios, with the exception of with the exception of the molar ratio 1.5 which also yields thin plates. The thickness of the plates is probably influenced by the final pH, regulated by an equilibrium between dissolution and reprecipitation of simonkolleite in slightly acidic conditions at 50°C .

On the other side, the addition order had a big influence on the morphology. Starting from low pH yielded much smaller plates than the opposite way. This could be due to different precipitation pathways for simonkolleite. Starting from low pH, Zn(OH)_2 would react immediately with the excess of ZnCl_2 , but starting from high pH, Zn(OH)_2 would first dehydrate into ZnO before further reacting with ZnCl_2 . In the latter case, the size and morphology of simonkolleite depends on the one of the intermediate product.

This study allows us to identify the OH:Zn molar ratio range in which simonkolleite can be formed, with or without the presence of ZnO. Furthermore, it is possible to obtain pure

simonkolleite, by having an initial OH:Zn molar ratio lower than 1.5, leading to a final within 6-5. By understanding the formation mechanism of simonkolleite, we can explain and anticipate the influence of the addition order, pH, and concentration of both ZnCl₂ and NaOH on the final product. Depending on the final application it can be interesting to have bigger or thinner plates, with or without the presence of a small amount of ZnO. Thinner plates can be particularly interesting for adsorption of ions; larger aspect ratios are interesting for barrier effects and fire-retardant properties; and the presence of a small amount of ZnO can be interesting for photocatalytic properties.

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References

- Arizaga, G. G. C., Satyanarayana, K. G., & Wypych, F. (2007). Layered hydroxide salts: Synthesis, properties and potential applications. *Solid State Ionics*, 178(15–18), 1143–1162. <https://doi.org/10.1016/j.ssi.2007.04.016>
- Audebrand, N., Auffredic, J. ., & Louer, D. (1998). X-ray-diffraction study of the early stages of the growth of nanoscale zinc-oxide crystallites obtained from thermal-decomposition of 4 precursors - general concepts on precursor-dependent microstructural properties. *Chem. Mater.*, 2450:2461.
- Baikousi, M., Stamatis, A., Louloudi, M., & Karakassides, M. A. (2013). Thiamine pyrophosphate intercalation in layered double hydroxides (LDHs): An active bio-hybrid catalyst for pyruvate decarboxylation. *Applied Clay Science*, 75–76, 126–133. <https://doi.org/10.1016/j.clay.2013.02.006>
- Boshkov, N., Petrov, K., Vitkova, S., & Raichevsky, G. (2005). Galvanic alloys Zn-Mn - Composition of the corrosion products and their protective ability in sulfate containing medium. *Surface and Coatings Technology*, 194(2–3), 276–282. <https://doi.org/10.1016/j.surfcoat.2004.09.016>
- Camino, G., Maffezzoli, A., Braglia, M., De Lazzaro, M., & Zammarano, M. (2001). Effect of hydroxides and hydroxycarbonate structure on fire retardant effectiveness and mechanical properties in ethylene-vinyl acetate copolymer. *Polym. Degrad. Stab.*, 457:464.
- Cursino, A. C. T., Gardolinski, J. E. F. C., & Wypych, F. (2010). Intercalation of anionic organic ultraviolet ray absorbers into layered zinc hydroxide nitrate. *J Colloid Interface Science*, 347(1), 49–55. <https://doi.org/10.1016/j.jcis.2010.03.007> [rS0021-9797(10)00275-4 [pii]]
- Hawthorne, F. C., & Sokolova, E. (2002). Simonkolleite, Zn₅ (OH)₈ Cl₂ (H₂O), a decorated

- interrupted-sheet structure of the form $[M\Phi_2]_4$. *Canadian Mineralogist*, 40(3), 939–946. <https://doi.org/10.3749/gscanmin.40.3.939>
- Khamlich, S., Bello, A., Fabiane, M., Ngom, B. D., & Manyala, N. (2013). Hydrothermal synthesis of simonkolleite microplatelets on nickel foam-graphene for electrochemical supercapacitors. *Journal of Solid State Electrochemistry*, 17(11), 2879–2886. <https://doi.org/10.1007/s10008-013-2206-0>
- Khamlich, S., Mokrani, T., Dhlamini, M. S., Mothudi, B. M., & Maaza, M. (2016). Microwave-assisted synthesis of simonkolleite nanoplatelets on nickel foam–graphene with enhanced surface area for high-performance supercapacitors. *Journal of Colloid and Interface Science*, 461, 154–161. <https://doi.org/10.1016/j.jcis.2015.09.033>
- Komarneni, S., Menon, V. C., Li, Q. H., Roy, R., & Ainger, F. (1996). Microwave-Hydrothermal Processing of BiFeO₃ and CsAl₂PO₆. *Journal of the American Ceramic Society*, 79(5), 1409–12. <https://doi.org/10.1111/j.1151-2916.1996.tb08605.x>
- Kozai, N., Mitamura, H., Fukuyama, H., Esaka, F., & Komarneni, S. (2006). Synthesis and characterization of nickel-copper hydroxide acetate, NiCu(OH)_{3.1}(OCOCH₃)_{0.9} · 0.9H₂O. *Microporous and Mesoporous Materials*, 89(1–3), 123–131. <https://doi.org/10.1016/j.micromeso.2005.10.015>
- Li, D., Tuo, Z., Evans, D. G., & Duan, X. (2006). Preparation of 5-benzotriazolyl-4-hydroxy-3-sec-butylbenzenesulfonate anion-intercalated layered double hydroxide and its photostabilizing effect on polypropylene. *Journal of Solid State Chemistry*, 179(10), 3114–3120. <https://doi.org/10.1016/j.jssc.2006.06.006>
- Li, Z., & Qu, B. (2003). Flammability characterization and synergistic effects of expandable graphite with magnesium hydroxide in halogen-free flame-retardant EVA blends. *Polymer Degradation and Stability*, 81(3), 401–408. [https://doi.org/10.1016/S0141-3910\(03\)00123-X](https://doi.org/10.1016/S0141-3910(03)00123-X)
- Lonkar, S. P., Kutlu, B., Leuteritz, A., & Heinrich, G. (2013). Nanohybrids of phenolic antioxidant intercalated into MgAl-layered double hydroxide clay. *Applied Clay Science*, 71, 8–14. <https://doi.org/10.1016/j.clay.2012.10.009>
- Machado, G. S., Wypych, F., & Nakagaki, S. (2012). Anionic iron(III) porphyrins immobilized on zinc hydroxide chloride as catalysts for heterogeneous oxidation reactions. *Applied Catalysis A: General*, 413–414, 94–102. <https://doi.org/10.1016/j.apcata.2011.10.046>
- Markov, L., Ioncheva, R., Marinov, M., & Ivanov, K. (1990). Synthesis and thermal decomposition of Cu(II)-Zn(II) hydroxide nitrate mixed crystals. *Mater. Chem. Phys.*, 493:504.
- Moezzi, A., Cortie, M., & McDonagh, A. M. (2013). Formation of Zinc Hydroxide Nitrate by H⁺-Catalyzed Dissolution-Precipitation. *European Journal of Inorganic Chemistry*, 2013(8), 1326–1335. <https://doi.org/10.1002/ejic.201201244>
- Momodou, D. Y., Barzegar, F., Bello, A., Dangbegnon, J., Masikhwa, T., Madito, J., & Manyala, N. (2015). Simonkolleite-graphene foam composites and their superior electrochemical performance. *Electrochimica Acta*, 151, 591–598. <https://doi.org/10.1016/j.electacta.2014.11.015>
- Rives, V., Del Arco, M., & Martín, C. (2013). Layered double hydroxides as drug carriers and for controlled release of non-steroidal antiinflammatory drugs (NSAIDs): A review. *Journal of Controlled Release*, 169(1–2), 28–39.

<https://doi.org/10.1016/j.jconrel.2013.03.034>

- Rojas, R., & Giacomelli, C. E. (2013). Effect of structure and bonding on the interfacial properties and the reactivity of layered double hydroxides and Zn hydroxide salts. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 419, 166–173. <https://doi.org/10.1016/j.colsurfa.2012.12.002>
- Schmetzer, K., Schnorrer-Köhler, G., & Medenbach, O. (1985). Wülfingite, ϵ -Zn(OH)₂, and simonkolleite, Zn₅(OH)₈Cl₂•H₂O, two new minerals from Richelsdorf, Hesse, F.R.G. *Neues Jahrb. Mineral., Monatsh.*, 145:154.
- Tagaya, H., Sasaki, N., Morioka, H., & Kadokawa, H. (1993). Preferential intercalation of isomers of naphthalenecarboxylate ions into the interlayer of layered double hydroxides. *Chem. Mater.*, 1431:1433.
- Tagaya, H., Sasaki, N., Morioka, H., & Kadokawa, J. (2000). Preparation of New Inorganic—Organic Layered Compounds, Hydroxy Double Salts, and Preferential Intercalation of Organic Carboxylic Acids into Them. *Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals*, 341(2), 413–418. <https://doi.org/10.1080/10587250008026174>
- Wang, Z., Han, E., & Ke, W. (2005). Influence of nano-LDHs on char formation and fire-resistant properties of flame-retardant coating. *Progress in Organic Coatings*, 53(1), 29–37. <https://doi.org/10.1016/j.porgcoat.2005.01.004>
- Xu, Z. P., Zhang, J., Adebajo, M. O., Zhang, H., & Zhou, C. (2011). Catalytic applications of layered double hydroxides and derivatives. *Applied Clay Science*. <https://doi.org/10.1016/j.clay.2011.02.007>
- Zhu, Y., Zhang, X., Lan, Z., Li, H., Zhang, X., & Li, Q. (2016). Hydrogen bonding directed assembly of simonkolleite aerogel by a sol–gel approach. *Materials & Design*, 93, 503–508. <https://doi.org/10.1016/j.matdes.2016.01.002>