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**Preparation and study of simonkolleite and zinc oxide from  
aqueous precipitation of zinc chloride.**

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## References

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## Abstract

This work deals with the preparation of simonkolleite and zinc oxide from zinc chloride. The main motivation for this work was the preparation of nanoparticles using no surfactant, inexpensive setup and chemicals. A wet precipitation method was chosen for the synthesis, using potassium hydroxide as a precipitation agent for the zinc chloride salt. The precipitation mechanism was studied, as well as the influence of the synthesis parameters on the morphology and nature of the product. Additionally, the addition of butanol to the aqueous suspension was studied, as a stabilizer for simonkolleite suspension. Simonkolleite was synthesized in the shape of nano-platelets, whereas zinc oxide exhibited aggregates of nano and microspheres. Both simonkolleite and zinc oxide had limited dispersion stability in water suspension and showed some sedimentation. Finally, three different potential applications were studied for the products: as an anti-corrosive agent, as a photocatalyst, and as a filler for polymer reinforcement.

## Abstrakt

Tato práce se zabývá přípravou simonkolleitu a oxidu zinečnatého z chloridu zinečnatého. Hlavním cílem bylo připravit nanočástice bez použití surfaktantů s možností využití nenákladného uspořádání zařízení a dostupných chemikálií. Metoda mokrého srážení pomocí hydroxidu sodného jako srážecího činidla byla použita pro syntézu nanočástic z chloridu zinečnatého. Všechny experimenty byly prováděny tak, aby bylo možné studovat mechanismus srážení a vliv parametrů syntézy na morfologii produktů. Dále byl studován vliv přídavku butanolu do vodné suspence simonkolleitu za účelem její stabilizace. Simonkolleit byl syntetizován ve formě nano-destiček, zatímco připravený oxid zinečnatý vykazoval agregáty. Nicméně obě látky, jak simonkolleit, tak oxid zinečnatý, jsou ve vodné suspenzi omezeně stabilní a částečně sedimentují. Na závěr práce byly pro studované produkty zkoumány tři potenciální aplikace – jako antikoroziční činidlo, fotokatalyzátor a plnivo do polymerů.

## Keywords

Zinc oxide, simonkolleite, wet precipitation, composite, zinc chloride

## Klíčová slova

Oxid zinečnatý, simonkolleit, mokré srážení, kompozit, chlorid zinečnatý

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## Introduction

The motivation behind the presented lied in studying easy and cost-efficient ways how to valorise recycled  $\text{ZnCl}_2$ . Especially, the production of nano-particles without the use of any surfactants that could plasticize polymeric systems, and in mild synthesis conditions, while avoiding the use of expensive or sophisticated equipment.

A promising lead was to synthesize ZnO that found numerous applications due to its interesting properties, namely its piezoelectric constant, photoluminescent properties, photocatalytic activity in the UV range, and low toxicity. There are many known ways how to synthesize ZnO, which can be sorted in a few categories: processes where the reactives are in vapor phase, usually requiring high temperatures; processes where the reaction takes place in a solid form, namely mechanochemical process; electrodeposition processes; and other wet precipitations excluding any oxydo-reduction reaction.

Alternatively, it is possible to synthesize simonkolleite, a layered hydroxide salt of zinc, under similar synthesis conditions to ZnO. Simonkolleite has a layered structure and is a potential source for nano sheets, and showed few promising properties as well. Layered hydroxide salts have the general formula  $\text{M}^{2+}(\text{OH})_{2-x} \text{A}^{m-x/m} \cdot n\text{H}_2\text{O}$ , and show good anionic exchange capacity, exfoliation and intercalation of different molecules. Among layered hydroxide salts, simonkolleite and other layered zinc hydroxide salts have been studied because of their interesting catalyst support, drug carrier, UV and visible light absorption, and corrosion inhibition properties.

The main goals of this thesis are to first test two possible synthesis methods for the synthesis of ZnO and/or simonkolleite, both based on a precipitation of salts in aqueous media. The most promising method will be studied more closely to understand the precipitation mechanism, and the influence of different synthesis parameters on the product. Further the effect of n-butanol on simonkolleite and ZnO stabilization in aqueous suspension will be studied, both after and during the synthesis process. Finally, three potential applications will be explored for the synthesized products: ZnO as a photocatalyst, simonkolleite as an anticorrosive agent, and both as fillers for a polymeric matrix.

# 1. Theoretical and literature part

## 1.1 Synthesis methods for ZnO and nano ZnO production

The processes for ZnO synthesis can be classified in the following categories:

- precipitation from reactives in vapor phase, including: pyrometallurgical, chemical vapor deposition (CVD), pyrolysis spray, vapor-liquid-solid (VLS) growth
- reaction from dry form, namely mechanochemical process
- electrodeposition from solutions
- other wet precipitations without any oxido-reduction reaction, including: zinc salt precipitation, sol-gel method, solvothermal and hydrothermal, emulsion reaction confinement.

## 1.2 About layered hydroxide salts and double hydroxide salts

Layered hydroxide salts (LHS) and layered double salts (LDH) also called anionic clays, have a layered structure derived from  $\text{Mg}(\text{OH})_2$ , where  $\text{OH}^-$  are partially replaced by another anion. LDH have the general formula  $[\text{M}^{2+}_{1-x} \text{M}^{3+}_x (\text{OH})_2]^{x+} \text{A}^{m-x/m} \cdot n\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  and  $\text{M}^{3+}$  represent two independent metal cations that can be identical or different. However, less publication about LHS are found, especially concerning their functionalization and intercalation process. LHS have the general formula  $\text{M}^{2+}(\text{OH})^{2-x} \text{A}^{m-x/m} \cdot n\text{H}_2\text{O}$ , and unlike LDH, they contain only one type of metallic cation. The studied LHS, however, showed good anionic exchange capacity, exfoliation and intercalation of different molecules. Among LHS, simonkolleite and other layered zinc hydroxide salts have been studied because of their interesting catalyst support, drug carrier, UV and visible light absorption, and corrosion inhibition properties.

Among LHS, simonkolleite (SK) has the formula  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$  [1] and was first reported in 1985 by Schmetzer et al. [2]. Additionally to the properties described previously, simonkolleite has raised a lot of interest for numerous applications, such as the preparation of photoluminescent aerogels [3], supercapacitors [4–6], polymeric filler, and gas sensors [7].

## **2. Experimental part**

### **2.1 Chemicals**

The chemicals used were ZnCl<sub>2</sub> dried at 105°C, NaOH, and n-butanol all purchased from PENTA, Czech Republic.

The diglycidylether bisphenol A was purchased from Spolchemie under the trade name CHSE530, and the diamino polyether was purchased from Huntsman under the trade name Jeffamine D400. Both reactive were used without any further purification.

### **2.2 Instruments and devices**

#### **2.2.1 XRD of powder crystals**

Practically, the synthesized samples were evaluated by XRD analysis of polycrystalline powders using a diffractometer D8 Advance, monochromatic CuK $\alpha$  radiation and a scintillation detector, Bruker, GB and a diffractometer Rigaku Miniflex 600, at the Joint Laboratory of Solid State Chemistry, University of Pardubice.

#### **2.2.2 Atomic absorption spectrometry**

Atomic absorption spectrometry was used to analyse the absolute atomic content of Zn and Na in the synthesized samples at the Department of Inorganic Technology, University of Pardubice. The apparatus used was a AA 936 from GBC, Australia, equipped with a flame atomizer, fed with a mix of acetylene and air.

#### **2.2.3 Particle size distribution measurement by the laser diffraction method**

The particle size distribution of the samples was analysed using a Mastersizer 2000 from Malvern, at the Department of Inorganic Technology, University of Pardubice. The samples were measured and the results analysed using the Mie theory and using the optical parameters of ZnO to simulate the refraction of the lasers by the particles.

#### **2.2.4 Thermogravimetric analysis**

Thermogravimetry measurements were made on a TGA Q500 from TA, at Toseda s.r.o., Pardubice. Typically, a dozen of milligrams of dried product are loaded in a titanium pan, and the weight loss of the sample is monitored depending on the temperature and time. Typical conditions for this analysis were a heating ramp from room temperature to 600 or 1000 °C, with a constant heating rate of 10 °C/min, under a N<sub>2</sub> flow. Sometimes, an isotherm was applied above 100 °C, to allow the product to be completely dry before proceeding further.

#### **2.2.5 Atomic force microscopy**

The AFM apparatus used was a Dimension icon from Bruker, at Toseda s.r.o., Pardubice. The scans were taken in tapping mode, with the PeakForce quantitative nano-mechanism mode activated.

## **2.2.6 Scanning electron microscopy**

In our case, SEM scans were performed on the dried samples to analyse their morphology on a TM3030 plus electron microscope from Hitachi, at Toseda s.r.o., Pardubice. Dried powder was applied on the target without any grinding or other pre-treatment.

## **2.2.7 Dynamic mechanical analysis**

Dynamic mechanical measurements were performed on a Hybrid Rheometer Discovery apparatus from TA, at Toseda s.r.o., Pardubice. The samples were cut in rectangular strips of variable geometry and were measured under a oscillating torsion mode under a constant heating rate of 2 °C/min.

## **2.3 Procedures**

### **2.3.1 Synthesis of simonkolleite and ZnO**

In a typical experiment, a solution of 0.5 mol/L of NaOH into distilled water was prepared and 50 ml was heated to 45 °C at least 30 min under stirring. Then 30 ml of 0.6 mol/L ZnCl<sub>2</sub> solution into distilled water was injected in the reactor containing NaOH solution. The reaction was carried out at 45 °C for 2 hours under vigorous mechanical stirring and the reactor was sealed.

At the end of the reaction, the precipitate was kept and washed with distilled water, by vacuum filtration over a paper filter. The quality of the washing process was assessed by testing the presence of Cl<sup>-</sup> ions in the filtrate by AgNO<sub>3</sub>. Once clean, the slurry was dried at ambient atmosphere overnight, then gently crushed into fine powder and bottled up.

### **2.3.2 Study of precipitation mechanism of simonkolleite/ZnO**

In a typical experiment, 200 ml of a solution of 0.5 mol/L of NaOH into distilled water was prepared, then heated at 55 °C under magnetic stirring. A second solution of 2.5 mol/L of ZnCl<sub>2</sub> into water was prepared, and was added drop by drop into the NaOH solution under stirring. Once the addition of ZnCl<sub>2</sub> solution was completed, the mixture was kept under stirring at 55 °C for 90 min, after what the samples were filtrated, washed several times with deionized water, dried at room temperature and bottled up.

In a first serie, the total amount of ZnCl<sub>2</sub> added varied from 20 to 400 ml. In another serie, 0.1 mol of NaCl was introduced in the NaOH solution before injection. In a third serie, the reaction was stopped at different stages: right after the addition of 10ml of ZnCl<sub>2</sub>; and 0, 30, 60 and 90 min after the addition of 40 ml of ZnCl<sub>2</sub> solution.

In a third serie of experiments, 26.7 to 80 ml of 0.5 mol/L NaOH solution was injected in 200 ml of a 0.1 mol/L ZnCl<sub>2</sub> solution.

### **2.3.3 Study of influence of n-butanol addition on simonkolleite dispersion**

A serie of experiment was performed, were 7.77 g of KOH was dissolved in 100 ml of deionized water and a variable amount of n-butanol was added, ranging from 0 to 24 g. This solution was stirred and heated at 55 °C until the temperature stabilizes. A second solution of a variable amount of ZnCl<sub>2</sub> ranging from 6.74 to 18.87 g in 20 ml of



deionized water was prepared, then injected at once into the reactor still under stirring. The reaction was allowed to mature for 2 hours at 55 °C under stirring, then it was washed over a paper filter if the precipitate did not go through, or by sedimentation in a centrifuge in the opposite case. Washing by centrifugation can be tedious in the case of large volumes, but is necessary when the particles are too small to be filtered by paper. The suspensions were washed minimally 5 times with deionized water, then dried overnight at ambient air, gently crushed into powder and bottled up.

#### **2.3.4 Synthesis of ZnO from thermal degradation of simonkolleite**

ZnO was produced via calcination of pure simonkolleite at 600 °C in air, during 3h. The samples of simonkolleite were used in powder form without any further preparation, put in a crucible and laid in the oven. The powder layer had a few mm in thickness only, to allow a uniform contact with air to the whole sample.

The photocatalytic activity of the calcinated simonkolleite was measured using methyl orange as an indicator of the degradation activity, measurement of the relative intensity of its absorption peak at 470 nm as an indication of its remaining concentration in the solution was carried out.

In each measurement, 0.5 g of dry powder sample was weighted and added to 0.5 L of a methylene orange solution at 20 mg/L concentration. The suspension was constantly stirred by the means of magnetic agitation and circulated between a reservoir and the reactor with the UV lamp. The whole reaction was carried out at room temperature, and the absorption spectra was measured from 400 to 700 nm with a 1 min interval.

#### **2.4 Preparation of composites**

In a typical composite preparation, 1.32 g of modified simonkolleite particles was dispersed in 50 g of Jeffamine D400 via ultrasonic treatment. The dispersion was carried on until the suspension was visibly uniform. Then 25 g of Jeffamine/Simonkolleite mix was mixed with 36.99 g of CHSE530. The mixture was then outgassed under vacuum to remove bubbles, then casted in a metallic form and cured at 80 °C for 24 h.

Additionally, a neat system was prepared by mixing 25 g of Jeffamine D400 with 37.74 g of CHSE530. The mixture was homogenized by hand, outgassed under vacuum to remove bubbles, then casted in a metallic form and cured at 80 °C for 24 h.

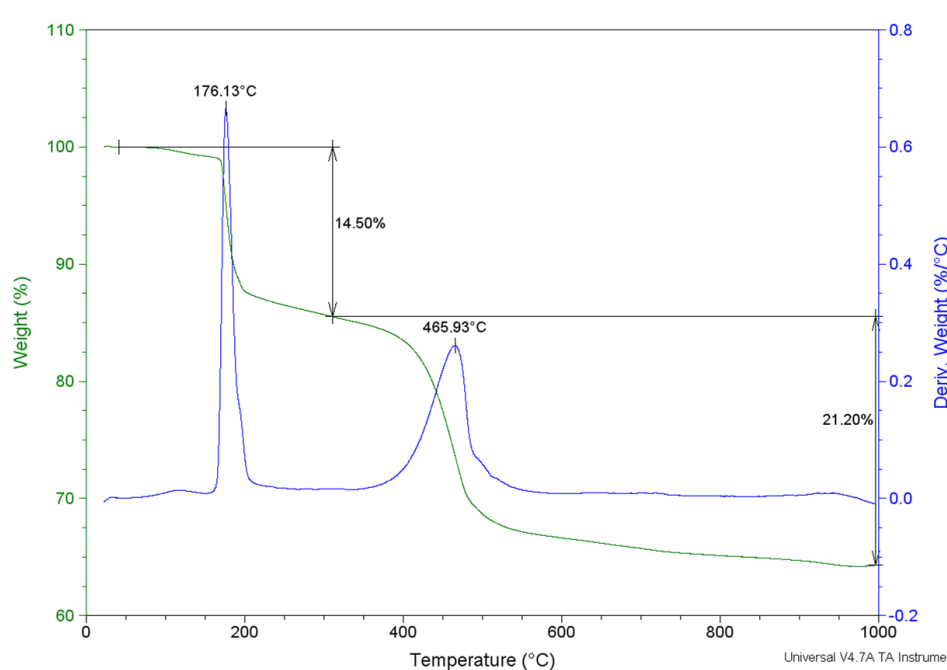
### **3. Results and discussion**

#### **3.1 Precipitation of ZnCl<sub>2</sub> in presence of NaOH**

This synthesis method was inspired from the previous work of Ullah et al. [8]. They present a simple precipitation method, followed by aging of the precipitate.

However, with these experimental conditions, we did not obtain ZnO as expected, but the layered zinc hydroxide compound simonkolleite, which has the theoretical formulae  $Zn_5(OH)_8Cl_2 \cdot H_2O$ . The nature of the product was determined by the combination of several analysis described below.

The XRD analysis showed that the product contains a major phase matching the pattern of simonkolleite. There was no other crystalline phase identified by XRD, but there still might be other amorphous phases present, especially  $\text{Zn}(\text{OH})_2$ . The chemical composition of the sample was further tested, to check if there is any deviation from the simonkolleite theoretical composition (Table 1). The results show traces of  $\text{Na}^+$ , which is probably associated to  $\text{Cl}^-$  to form  $\text{NaCl}$ , accounting for 0.29 % of the total mass. After deduction of the  $\text{NaCl}$  mass, we compared the composition to the stoichiometry of simonkolleite and found that  $\text{Zn}^{2+}$  is in limiting quantity and that there is an excess of  $\text{OH}^-$  and  $\text{Cl}^-$ .



**Figure 1: TGA profile of the sample, displaying two major mass losses**

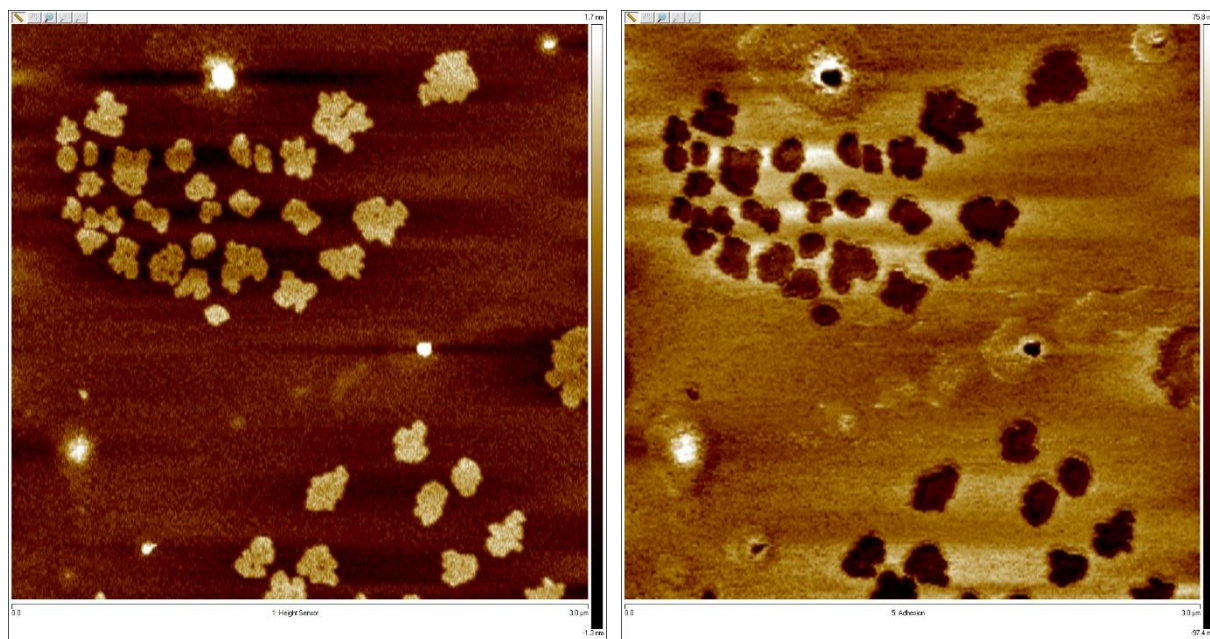
Moreover, the thermogravimetric analysis showed two mass losses at 176 °C and 466 °C (Figure 1), corresponding to the theoretical mass losses of simonkolleite, described more in details in section 3.5 of this thesis. The combination of those three different analysis allow us to conclude that the samples contain pure simonkolleite, except for traces of  $\text{NaCl}$ .

**Table 1: Chemical analysis of the synthesized samples**

<i>Atomic content</i>	<i>% Zn</i>	<i>% OH</i>	<i>% Cl</i>	<i>% H<sub>2</sub>O</i>	<i>% Na</i>
Average	57.8	25.1	13.7	2.2	0.12
Standard deviation	0.86	0.49	0.24	0.98	0.005
$\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$	59,24	24,65	12,85	3,26	0,00

AFM scans of the product reveal some sheets of irregular shape, but of comparable thickness, as illustrated on Figure 2. The observed particles had a diameter

ranging from 50 to 400 nm, and a thickness of 2 to 5 nm. Furthermore, a lot of aggregates were observed by optical microscope.



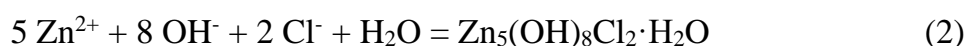
**Figure 2: AFM scans of simonkolleite particles on a mica plate. Topographic map on the left, and adhesion map on the right**

### 3.2 Study of precipitation mechanism of simonkolleite/ZnO

Although in the method described in section 3.1 we obtained pure simonkolleite, we found out that the precipitation of  $\text{ZnCl}_2$  with  $\text{NaOH}$  yielded either simonkolleite or  $\text{ZnO}$  depending on the synthesis conditions. In this section, we describe the influence of the  $\text{OH}:\text{Zn}$  molar ratio, addition method and concentration of  $\text{Cl}^-$  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.

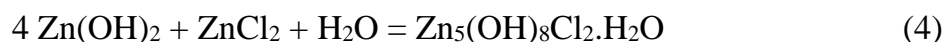
#### 3.2.1 Addition of $\text{ZnCl}_2$

In a first serie of experiments, we added the  $\text{ZnCl}_2$  solution into the  $\text{NaOH}$  solution, starting from high pH and infinite  $\text{OH}:\text{Zn}$  molar ratio. pH curves showed an equivalence point at a  $\text{OH}:\text{Zn}$  molar ratio of 2.1, accompanied with a large pH drop from 12 to 6. Given the reaction mixture, three different mechanisms are considered as presented in equations 1, 2 and 3.

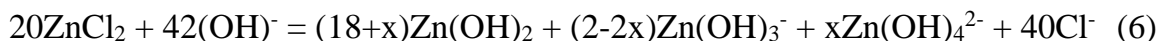


Starting from high pH, the equivalence for both the formation of  $\text{Zn}(\text{OH})_2$  and  $\text{ZnO}$  should occur for  $\text{OH}:\text{Zn}$  molar ratio of 2, and a ratio of 1.6 for the formation of simonkolleite. However, only one equivalence point was observed at 2.1. This means simonkolleite was not formed directly from the dissolved species (Equation 2), but from

the reaction products ( $\text{Zn(OH)}_2$  or  $\text{ZnO}$ ), following a mechanism that does not involve any pH change (Equation 4 and 5).



Moreover, since the equivalence point is at 2.1 instead of 2, it was deduced that there is an equilibrium between  $\text{Zn(OH)}_2$ ,  $\text{Zn(OH)}_3^-$ , and  $\text{Zn(OH)}_4^{2-}$  (Equation 6).



At the same time,  $\text{Zn(OH)}_2$  could also dehydrate into  $\text{ZnO}$ , reversibly or not, during the synthesis (Equation 8).



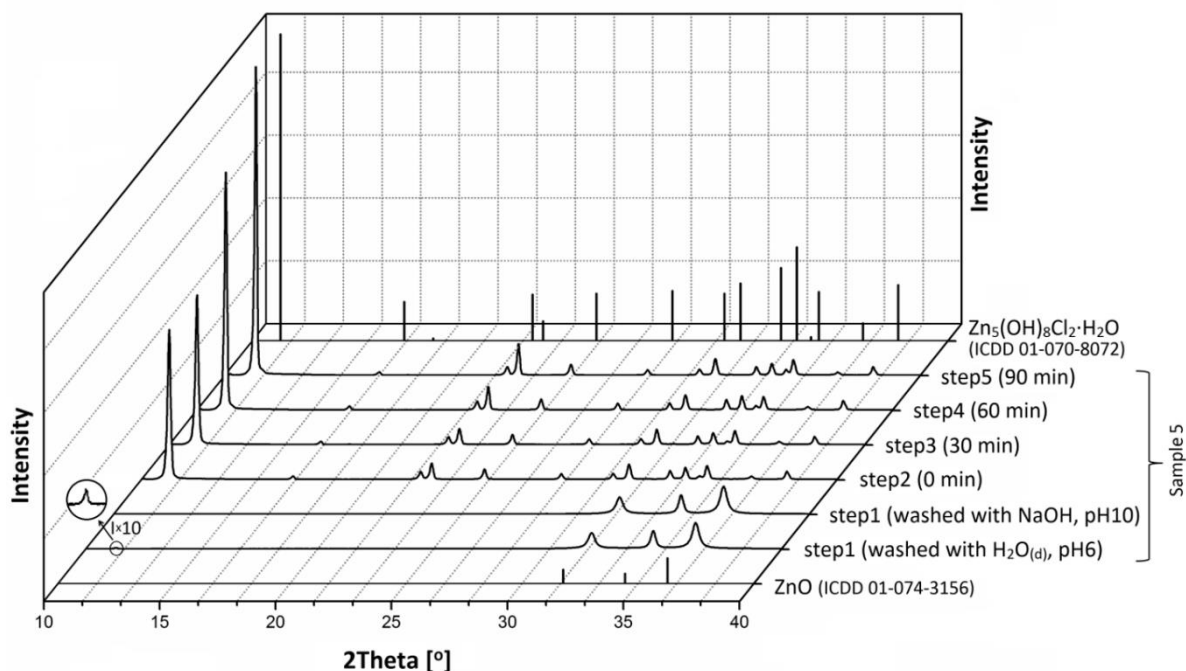
In general, the formation of simonkolleite phase can be described as follows. After addition of the first drop of  $\text{ZnCl}_2$  (0.05 ml) to a highly basic  $\text{NaOH}$  solution, besides the formation of  $\text{ZnO}$  or  $\text{Zn(OH)}_2$ , two soluble zinc hydroxide complexes  $\text{Zn(OH)}_4^{2-}$  and  $\text{Zn(OH)}_3^-$  are also formed.

When continuing to add more  $\text{ZnCl}_2$ , past a  $\text{OH}:\text{Zn}$  molar ratio of 2, simonkolleite started to form without changing the pH from either  $\text{Zn(OH)}_2$  or  $\text{ZnO}$  (Equation 12 and 13). In both cases, the pH continued to decrease very slowly since  $\text{ZnCl}_2$  is acidic.

### 3.2.2 Influence of maturation time

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 ( $\text{Zn(OH)}_2$  or  $\text{ZnO}$ ), a series of additional experiments was performed. To this purpose, the products of 5 different reaction steps were studied:

- step 1: the reaction was stopped after addition of 10 ml of 2.5 mol/L  $\text{ZnCl}_2$  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 ( $\text{NaOH}$  solution with  $\text{pH} = 10$  and distilled  $\text{H}_2\text{O}$  with  $\text{pH} = 6$ );
- step 2: the reaction was stopped before the equivalence after addition of 42 ml of 2.5 mol/L  $\text{ZnCl}_2$  solution), the pH of the suspension was 5.3;
- step 3, 4, 5: the reaction was stopped 30, 60 and 90 min respectively after addition of all the  $\text{ZnCl}_2$  solution;

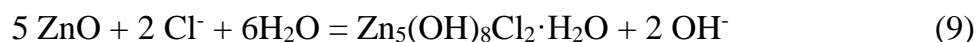


**Figure 3: Results of XRD analysis of sample 5 (OH : Zn = 1) at different reaction stages; diffraction patterns of ZnO and  $Zn_5(OH)_8Cl_2 \cdot H_2O$  (database PDF-2)**

The results of XRD analysis 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 (Figure 3). The content of simonkolleite phase in this sample after washing constituted  $\sim 1.31(2)$  %. As the main product at step1, low crystalline ZnO was detected (crystallite size  $\sim 10$  nm). Although the results of the experiment imply that ZnO was the intermediate product and the formation of simonkolleite took place according to Equation 5, ZnO may also be formed from  $Zn(OH)_2$  during drying stage, rendering detection of  $Zn(OH)_2$  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. After the whole  $ZnCl_2$  solution was added and the pH decreased (steps 2-5), simonkolleite was the only phase observed with XRD analysis pointing out that the kinetic of its formation was very fast. With increasing aging time, the crystallite size gradually increased from 13-15 nm to 50-60 nm.

### 3.2.3 Influence of excess $Cl^-$ ions

Since simonkolleite and  $Zn(OH)_2$  have a similar crystal structure,  $Zn(OH)_2$  could be converted to simonkolleite via partial replacement of  $OH^-$  into  $Cl^-$  following the equation 8. Or, alternatively,  $Zn_5(OH)_8Cl_2 \cdot H_2O$  could also be formed from ZnO according to equation 9.



Concerning our experiment, the concentration of  $Cl^-$  in the system was increased via addition of a NaCl solution. In this experiment, the OH:Zn molar ratio was 1.6, and NaCl was added to have the same amount of  $Cl^-$  as in a mixture with an OH:Zn molar ratio of 2. A mixture 8 % richer in simonkolleite was obtained when adding  $Cl^-$  from

NaCl. However, adding the same amount of  $\text{Cl}^-$  from  $\text{ZnCl}_2$  resulted in pure simonkolleite. It was therefore concluded that adding  $\text{Cl}^-$  favoured a little bit the formation of simonkolleite, but not as significantly as the presence of both  $\text{Zn}^{2+}$  and  $\text{Cl}^-$  ions.

### 3.2.4 Morphology of the samples

When adding  $\text{ZnCl}_2$  into  $\text{NaOH}$ , no noticeable influence of the OH:Zn molar ratio was observed ranging from 0.1 to 1.5. Pure simonkolleite was obtained, having 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 (Figure 4-a, b, c, e). Then for molar ratios from 1.6 to 2 a mixture of  $\text{ZnO}$  and simonkolleite was observed. Simonkolleite kept a hexagonal plates shape, and  $\text{ZnO}$  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 4-e, f).

By adding  $\text{NaOH}$  in  $\text{ZnCl}_2$ , the reaction started at a low pH, and the formation of pure simonkolleite was also observed in the OH:Zn molar ratio range of 0.5-1.5. 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 (Figure 4-b, d).

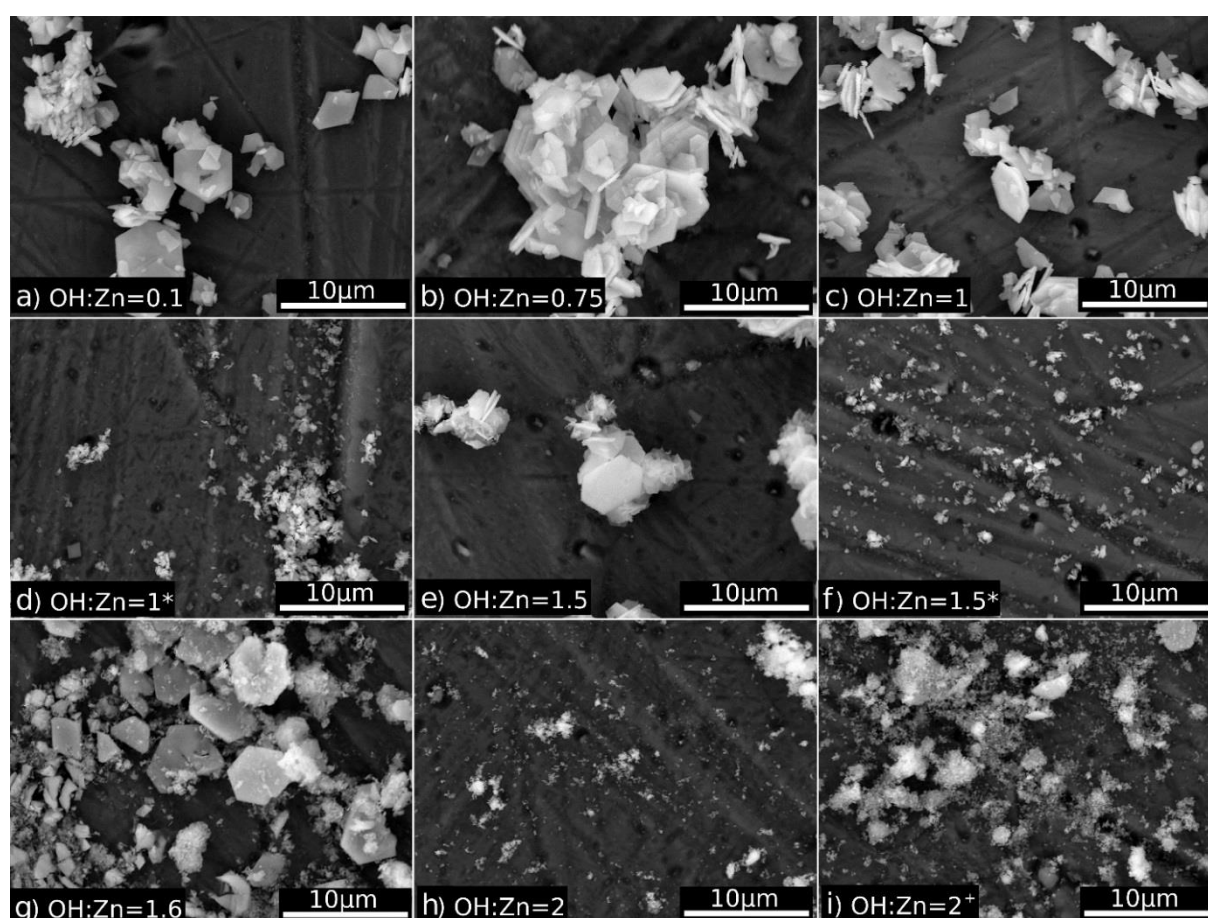


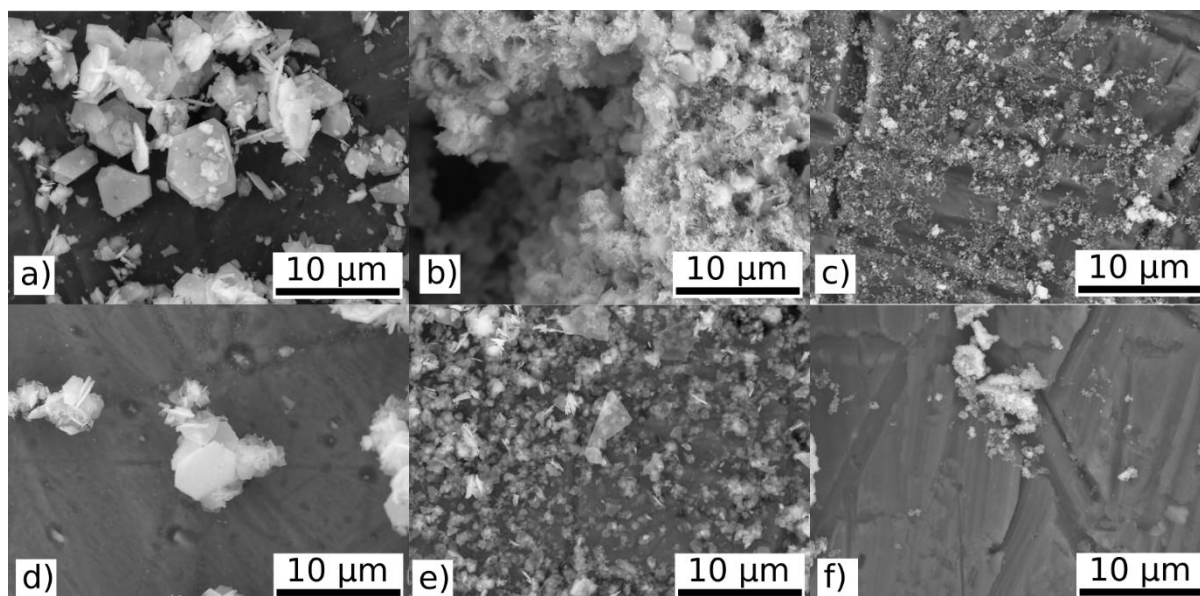
Figure 4: SEM scan of dried samples. a) sample 1, OH:Zn= 0.1;b)sample 4, OH:Zn= 0.75;c) sample 5, OH:Zn= 1; d) sample 14, OH:Zn= 1, reversed addition; e) sample 9, OH:Zn= 1.5; f) sample 15, OH:Zn= 1.5, reversed addition; g) sample 16, OH:Zn= 1.6; h) sample 11, OH:Zn= 2, addition of NaCl

### 3.3 Influence of n-butanol addition

In a serie of experiments, the n-butanol was added in the reaction mixture to observe its influence on the morphology of simonkolleite and ZnO formation, and their suspension stability. The amounts of n-butanol and ZnCl<sub>2</sub> varied to obtain different n-butanol:H<sub>2</sub>O and Zn:OH ratios.

The nature of the products was tested by TGA, and confirmed the addition of n-butanol had no influence on the product nature in the tested range.

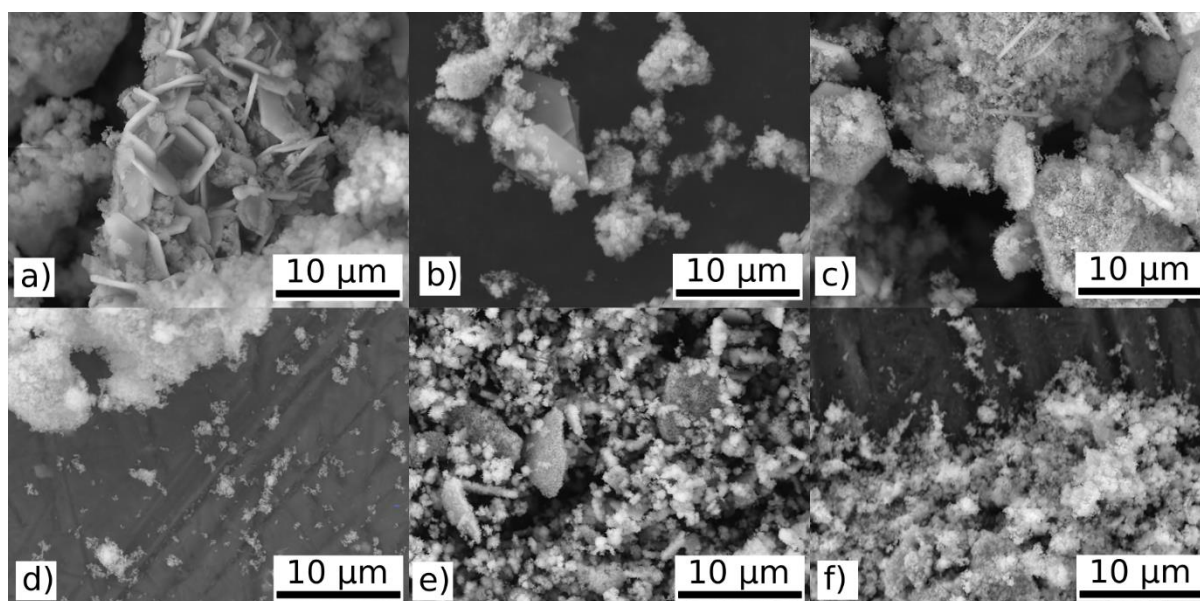
As illustrated in Figure 5, it was observed that an increasing amount of n-butanol will reduce the size of the simonkolleite plates, while the molar ratio Zn:OH has a very mild influence. This reduction of the particles size is not desirable since it reduces the aspect ratio of the plates.



**Figure 5: SEM scans of simonkolleite synthesized in presence of BuOH. a) BuOH:H<sub>2</sub>O = 0, OH:Zn = 1; b) BuOH:H<sub>2</sub>O = 0.1, OH:Zn = 1; c) BuOH:H<sub>2</sub>O = 0.2, OH:Zn = 1; d) BuOH:H<sub>2</sub>O = 0, OH:Zn = 1.4; e) BuOH:H<sub>2</sub>O = 0.1 OH:Zn = 1.4; f) BuOH:H<sub>2</sub>O = 0.2 OH:Zn = 1.4**

In the case where a lower Zn:OH molar ratio was used, the formation of ZnO as a major product was observed (Figure 6). Interestingly, a mixture of two different morphologies was observed: some platelets with a hexagonal shape, and some aggregates of very small primary particles. The size and shape of the primary particles cannot be determined on the SEM scans since their size is lower than the resolution power on apparatus. Additionally, the addition of an increasing amount of n-butanol did not prevent the aggregation of the primary ZnO particles.

The role of n-butanol as a growth inhibitor during the precipitation of ZnO under used experimental conditions was not proved. Moreover, as in the case of simonkolleite, it is not an efficient dispersion stabilizer, as the primary particles in all experiments were visibly strongly aggregated.



**Figure 6: SEM scans of ZnO synthesized in presence of BuOH. a) BuOH:H<sub>2</sub>O = 0, OH:Zn = 2.2; b) BuOH:H<sub>2</sub>O = 0.1, OH:Zn = 2.2; c) BuOH:H<sub>2</sub>O = 0.2, OH:Zn = 2.2; d) BuOH:H<sub>2</sub>O = 0, OH:Zn = 2.8; e) BuOH:H<sub>2</sub>O = 0.1, OH:Zn = 2.8; f) BuOH:H<sub>2</sub>O = 0.2, OH:Zn = 2.8**



### 3.4 Synthesis of ZnO from thermal degradation of simonkolleite

The layered morphology of simonkolleite was lost after thermal degradation into ZnO, as the product consisted of aggregated spherical particles. The aggregates are strongly linked and cannot be properly dispersed even under ultrasonic treatment. Compared to the standard ZnO, the calcinated product has a slightly yellow color, that might be due to defects in the ZnO structure (Figure 7). Possible defects in the structure can be Cl<sup>-</sup> ions or vacancies in the crystal lattice introducing new energy levels.

#### 3.4.1 Photocatalytic activity of the prepared ZnO

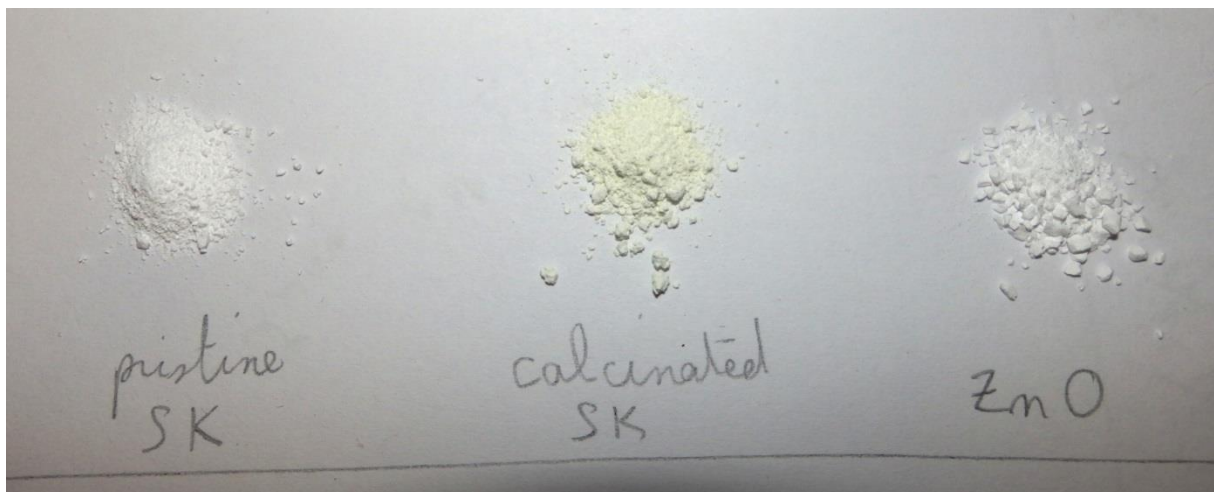


Figure 7: Visual aspect of simonkolleite (left), calcinated simonkolleite (middle), and ZnO (right)

The concentration of methylene orange was assumed to be proportional to the intensity of the absorption peak at 490nm, after subtraction of the baseline. As a result, we obtain curves displaying the relative concentration of methyl orange against reaction time.

To assess the kinetic parameters and compare quantitatively the kinetic of degradation of each sample, the obtain data is fitted to a kinetic model of the following form:

$$\frac{1}{n-1} [x_f^{1-n} - x_i^{1-n}] = B \cdot t \quad (10)$$

Where  $x$  is the intensity of the absorption peak at 490nm,  $n$  is the order of the reaction,  $Ea$  is the activation energy,  $R$ , the gas constant, and  $T$  the absolute temperature of the reaction mixture.  $A$  is a constant including both the pre-exponential kinetic factor and the proportional factor between the methylene orange and the absorption peak intensity.

The remaining kinetic equation contains two unknowns, that can be determined using excel solver by minimizing the sum of squared differences between the measured and calculated reaction time for each measured point. The results are summarized in Table 11.

**Table 11: Comparative kinetic parameters of photodegradation reaction**

Sample	Calcinated SK	Synthesized ZnO	ZnO standard
B	$7.17 \cdot 10^{-2}$	$2.52 \cdot 10^{-2}$	$7.23 \cdot 10^{-1}$
N	1.03	1.00	1.51
R2	0.9997	0.997	0.9997

As a result, the degradation was much slower for our two samples than for the standard ZnO. Since the ZnO catalyst is heterogenous, the kinetic of degradation is directly proportional to the specific surface. The decrease in catalytic activity can therefore be explained by the strong aggregation during the thermal degradation of simonkolleite, which led to a lower specific surface. However, we observe that simonkolleite after calcination has a higher catalytic activity than the directly synthesized ZnO. This might be due to the presence of defects in the crystal, allowing to absorb light at different energy levels, or stabilizing the radicals on the ZnO surface created during the absorption of photons.

However, the results were not promising enough to justify pursuing the research in this direction. To improve the photocatalytic activity further, the particles should be individual to offer a higher specific surface.

### 3.5 Preparation of composites

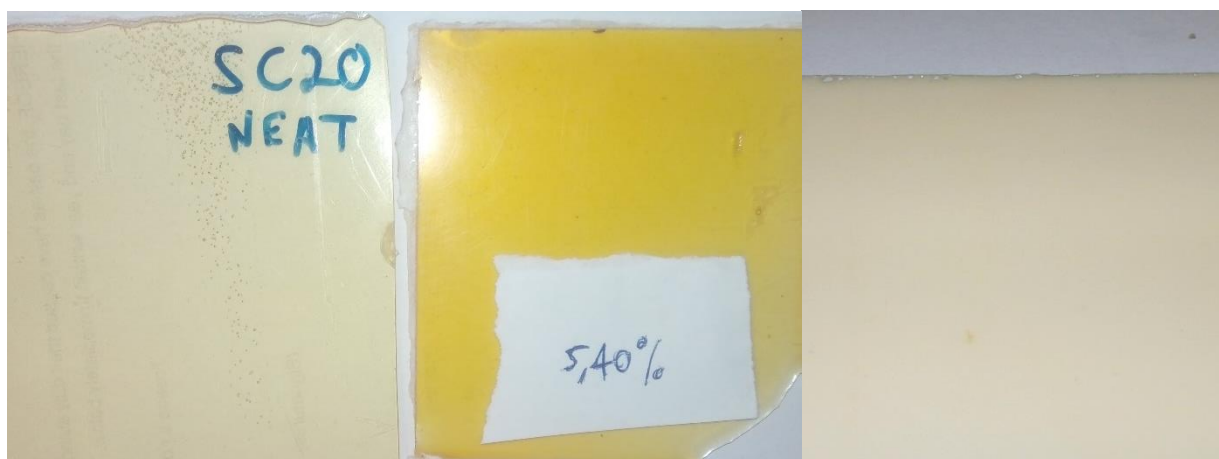
The last of the potential applications for simonkolleite, but also ZnO is the reinforcement of polymers. A diglycidylether of bisphenol A epoxy system was chosen for this study, cross-linked with a diamino polyether hardener.

In a typical composite preparation, the particles are first dried and redispersed in the amine reactive rather than the epoxy because it is more hydrophilic and therefore has a better affinity with both simonkolleite and ZnO. However, sedimentation of the particles in the amine reactive was observed within a few hours to a few days at room temperature.

Two composites were prepared using ZnO particles synthesized according to the method described in section 3.1. The OH:Zn molar ratio was equal to 2.8 and the n-butanol:H<sub>2</sub>O weight ratio was 20%. The resulting composites are opaque and show signs of particles aggregation and partial sedimentation. This shows the bad compatibility of the particles with the polymer and is the sign of aggregation of the particles, leading probably to weakening rather than strengthening of the material. Moreover, larger pieces would probably contain more accentuated sedimentation and therefore inhomogeneous properties along the material. From the SEM scans of both simonkolleite and ZnO it appears that ZnO forms stronger aggregates.

To ensure an optimal interface between the matrix and the nanoparticles, the simonkolleite particles were modified by Toseda to obtain reactive amine groups on the nanoparticle surface. The amount of amine groups per gram of particles was estimated by TGA, by quantifying the amount of simonkolleite, according to the method described in the extended version of this thesis.

The resulting samples are both transparent, although the sample with simonkolleite is slightly coloured. The transparency of the material and its homogenous appearance are both a sign of the adequate dispersion quality of the particles in the polymeric matrix (Figure 8).



**Figure 8: Comparison of the neat system (left), the composite loaded with 5% weight content of modified simonkolleite (middle), and the composite with 5% of unmodified simonkolleite (right)**

DMA analysis show very similar storage modulus in glassy state, very similar glass transition temperature, but an increase of 70% storage modulus in the rubber state for the composite with modified simonkolleite (Table 2). Even at low simonkolleite loading content, a significant increase of the mechanical performances was observed.

**Table 2: DMA results of a composite with modified simonkolleite and a neat system**

	Pristine matrix	Composite with simonkolleite
<b>Storage shear modulus in glassy state</b>	1.11 GPa	1.14 GPa
<b>Glass transition</b>	61 °C	63 °C
<b>Storage shear modulus in rubber state</b>	4.29 MPa	7.30 MPa

The barrier effect of simonkolleite nanoparticles against solvent intake was further investigated with toluene. After three days of soaking, both samples lost their structural integrity. It was found out, that the mass increase is proportional to the square root of the time for both systems. The intake was found to be 28 % slower for the composite system than the neat system. This is to be expected since simonkolleite has a sheet structure and is impervious to toluene. It is also possible that the sheets oriented themselves in a coplanar orientation with the mold walls during pouring of the uncured mixture

The modification of simonkolleite by chemically bounded amine terminated molecules improved the dispersion quality and prevented sedimentation of the particles in the composite. Mechanical performances of the polymer were improved even at low loading of nanoparticles, and the barrier properties of simonkolleite against solvent were demonstrated.

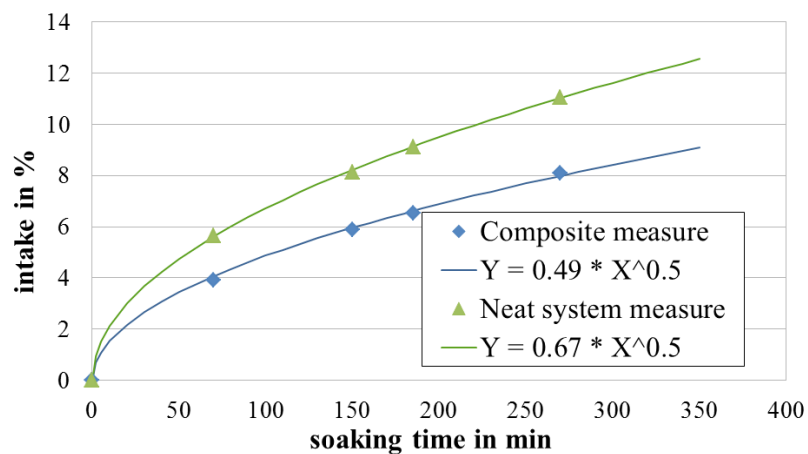


Figure 8: Mass changes of pristine polymer and composite vs. time

## 4. Conclusion

The main goals of this thesis were at first to test two possible synthesis methods for the synthesis of ZnO and/or simonkolleite, both based on a precipitation of salts in aqueous media. Subsequently, the most promising method should be studied with the aim of more closely to understand the precipitation mechanism and to find out the influence of different synthesis parameters on the product. Further aim was to study the effect of n-butanol on simonkolleite and ZnO stabilization in aqueous suspension, both after and during the synthesis process. And finally, three potential applications were chosen to be explored for the synthesized products: ZnO as a photocatalyst, simonkolleite as an anticorrosive agent, and surface modified simonkolleite as a filler for a polymeric matrix.

Two synthesis methods were tested to produce ZnO, following a wet precipitation of ZnCl<sub>2</sub> salt. Both methods consist of precipitating Zn<sup>2+</sup> ions with OH<sup>-</sup>. In the first method, hydrogen peroxide was used as a source of oxygen, but the Zn<sup>2+</sup> ions are also oxidized into Zn<sup>4+</sup>, and yield ZnO<sub>2</sub> rather than ZnO. In the second method, no peroxide was used and OH<sup>-</sup> ions were the main source of oxygen. The second method allows to yield both ZnO and simonkolleite.

The precipitation mechanism was studied and it was concluded that a higher molar ratio of OH:Zn favored the formation of ZnO, while the addition of Cl<sup>-</sup> ions did have a faint influence on the nature of the product. The initial pH had a strong influence on the size of the simonkolleite particles, whereas the OH:Zn molar ratio had no strong effect on the size or shape of the product.

Butanol was found to improve slightly the dispersion stability of simonkolleite into water. It was theorized that the hydrophobic chains reduce their free energy by bonding to the simonkolleite surface and act as a stabilizer. However, since the chains are short and in the absence of electrostatic stabilization, the particles eventually aggregated and sedimented. The effect of butanol on both ZnO and simonkolleite morphology was studied in the concentration range where it stabilized the best simonkolleite dispersions. The effects were very faint, especially for ZnO where it did not prevent aggregation of the nanoparticles.

Further, three potential applications of simonkolleite were studied. The use of simonkolleite for the intercalation of other molecules was theorized, but in the case of the replacement of Cl<sup>-</sup> with PO<sub>4</sub><sup>3-</sup>, the structure of simonkolleite was destabilized, and the layered shape was lost. Furthermore, the thermal conversion of simonkolleite into ZnO was also tested, but a strong aggregation occurred. The final ZnO did not retained the layered shape of the simonkolleite, but showed strong aggregates, which would be impossible to break down to individual particles unless using milling. The photocatalytic activity of the synthesized ZnO was tested, but it was lower than at standard ZnO commercially available. Finally, composites were prepared using surface modified simonkolleite particles. After dispersion of reactive mixture by US the cured samples showed transparency and a shear modulus 70% higher in rubber state.

The major outputs of this work are the understanding of simonkolleite/ZnO formation, and the control over the proportion of simonkolleite and ZnO in the final product by controlling the synthesis conditions. It was shown that simonkolleite has a

potential in polymers for barrier effect, and might also behave well as a fire retardant, but was not tested. Although it does not possess the same properties as ZnO, simonkolleite was the most successful product in term of nano-structure, given the synthesis constraints.

Finally, some potential applications that were not explored in this work further include: fire retardant properties due to the layered structure hindering the diffusion of oxygen in a material during combustion, and the release of water during the thermal decomposition of simonkolleite; and the depollution of water and soil by ion absorption of simonkolleite as a general layered zinc hydroxide.

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