Electronic Supplementary Information - Oxidation-induced alkaline precipitation: the effect of H_2O_2 on the size of CuO and FeOOH nanoparticles

1. Aim of the study

The aim of the study is to demonstrate the effect of the oxidation of metal ions by H_2O_2 on the size of precipitates (so called oxidation-induced precipitation).

2. Experimental setup and method

The experimental setup used a Watson-Marlow 323 peristaltic pump, 3 90 cm Watson Marlow 1.6/3.2 mm Marprene 902 tubes and a Y-junction Hibiki Y-1 3mm. The Y-junction was connected to the ends of each tube. The two tubes connected to the upper legs of the Y-junction were each put into a peristaltic pump head at around the 75 cm mark. One of the inlets went into the NaOH solution, the other inlet into the metal chloride solution. The outlet went into a beaker with a WTW 340i pH meter (WTW - pH elektrode Sentix 61 sensor) calibrated with a two point calibration (pH4 and pH7).

Both the metal chloride solution and the NaOH solution were pumped by equal rate of 100 mL min^{-1} through the Y-junction into the beaker. Depending on the composition of the influents, the effluent was colourless with differently coloured precipitates.

3. Electrolyte synthesis

Four different metal chloride electrolytes, as well as four different NaOH electrolytes, were prepared for the study. The end composition of each of the metal chloride electrolytes was 10 mM metal chloride 0.5 M NaCl at pH 1. This was accomplished by diluting 50 mL of a 50 mM metal chloride 2.5 M NaCl 0.5 M HCl stock solution to 250 mL with demineralized water.

The stock solutions were all made similarly. In a 500 mL volumetric flask, 72.5 g of NaCl was dissolved in 400 mL demineralized water. To this NaCl solution, 25 mL of 10 M HCl (made from 37% HCl Arcos Organics) was added. A certain amount of metal chloride powder was added to this solution, either:

- 4.127 g of $CuCl_2{\cdot}2H_2O$ (Merck)
- 2.475 g of CuCl (Arcos Organics)
- 6.758 g of $FeCl_3{\cdot}6H_2O$ (Chem-Lab)
- 4.970 g of $FeCl_2{\cdot}4H_2O$ (Arcos Organics)

When fully dissolved, the solution was diluted with demineralized water to the 500 mL mark.

The NaOH electrolytes were prepared to match the concentration and the valence of the metal ions in the metal chloride solutions. The necessary amount of OH^- to precipitate all of the metal ions as hydroxides was taken as the starting value ($n\ C_{\text{metal chloride}}$). Because the metal chloride solutions were pH 1, an additional 0.1 M NaOH is necessary to overcome the water equilibrium. The end pH of the solution after mixing was chosen to be pH 12, therefore an additional 0.02 M NaOH (in 250 mL to become 0.01 M in 500 mL) was necessary. In the case of $FeCl_2$ and CuCl, 10 mM H_2O_2 in the form of 0.283 mL of 30% H_2O_2 (Sigma-Aldrich), an excess of 100%, was added to the 250 mL NaOH solution just before mixing (to avoid H_2O_2 decomposition at high pH). The composition of the NaOH solutions was:

- For mixing with $CuCl_2$ solution: 0.14 M (2 x 0.01 M + 0.1 M + 0.02 M) NaOH
- For mixing with CuCl solution: 0.13 M (1 x 0.01 M + 0.1 M + 0.02 M) NaOH + 10 mM H_2O_2

- For mixing with $FeCl_3$ solution: 0.15 M (3 x 0.01 M + 0.1 M + 0.02 M) NaOH
- For mixing with $FeCl_2$ solution: 0.14 M (2 x 0.01 M + 0.1 M + 0.02 M) NaOH + 10 mM H_2O_2

4. Calculating supersaturation

At the Y-junction the metal chloride solution and the NaOH solution are mixed. Just before the precipitation reaction takes place, the metal ion concentration and the hydroxyl ion concentration can be calculated for the total effluent volume. Using the solubility products of the assumed precursors ($Cu(OH)_2$ and $Fe(OH)_3$), a theoretical value for the supersaturation can be calculated. The metal ion concentration is equal to the metal ion concentration of the influent divided by 2. The hydroxyl ion concentration is calculated similarly in the case of $CuCl_2$ and $FeCl_3$ but subtracting the amount of NaOH to neutralize the acidic pH and overcome the water equilibrium. For the cases of CuCl and $FeCl_2$, where H_2O_2 is added, the theoretical calculation should also consider the hydroxyl ions produced from the oxidation reaction between the metal ion and hydrogen peroxide (maximally 1 time the metal concentration; because each metal ion is assumed to oxidize to only one unit of valence higher). For $CuCl_2$, CuCl, $FeCl_3$ and $FeCl_2$ the metal ion concentration is 0.005 M and the OH^- concentrations are respectively:

- For $CuCl_2$ solution: (0.14 M – 0.1 M)/2 = 0.02 M
- For CuCl solution: (0.13 M – 0.1 M + 0.01 M)/2 = 0.02 M
- For $FeCl_3$ solution: (0.15 M – 0.1 M)/2 = 0.025 M
- For $FeCl_2$ solution: (0.14 M – 0.1 M + 0.01 M)/2 = 0.025 M

As observable, the OH^- concentration for the copper cases are equal as well as the OH-concentrations for the iron cases. The end OH^- concentration in the iron cases is 0.005 M more than the copper case. This is expected, because the same end pH is desired but for each Fe^{3+} ion, 1 more OH^--ion needs to react with it compared to the Cu^{2+}-ion, and the metal concentration after mixing is 0.005 M.

With the formula for supersaturation $S = [M][OH]^n/K_{sp,M(OH)n}$, the theoretical supersaturation values can be calculated as shown in following table:

Table S 1: Calculations of the supersaturation values at pH 12

Case	Precursor precipitate	K_{sp}	Theoretical value for initial S(upersaturation)
$CuCl_2$ and CuCl	$Cu(OH)_2$ or $Cu_2(OH)_3Cl$	$2.20\ 10^{-20}$ (*1) or $2.34\ 10^{-35}$ (*2)	$S = \frac{[M][OH]^n}{K_{sp\ M(OH)_n}} = \frac{[Cu][OH]^2}{K_{sp\ Cu(OH)_2}} = \frac{[5\ 10^{-3}][2\ 10^{-2}]^2}{2.20\ \ 10^{-20}} = 9.1\ \ 10^{13}$ $S = \frac{[Cu]^2[OH]^3[Cl]}{K_{sp\ Cu_2(OH)_3Cl}} = \frac{[5\ 10^{-3}]^2[2\ 10^{-2}]^3[6.05\ 10^{-1}]}{2.34\ \ 10^{-35}} = 5.17\ 10^{24}$
$FeCl_3$ and $FeCl_2$	$Fe(OH)_3$	$2.79\ 10^{-39}$ (*1)	$S = \frac{[Fe][OH]^3}{K_{sp\ Fe(OH)_3}} = \frac{[5\ 10^{-3}][2.5\ 10^{-2}]^3}{2.79\ \ 10^{-39}} = 2.8\ \ 10^{31}$

(*1) source: Patnaik P. Handbook of inorganic chemicals. New York: McGraw-Hill; 2003.

(*2) source: Ball JW, Nordstrom DK. User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters;1991.

5. Post-treatment of the precipitates

For each of the samples, the post-treatment was equal. 250 mL of the effluent was kept for storage and possible later use. The other 250 mL was centrifuged with a Jouan CR422 in 6 centrifuge tubes of 50 mL capacity for 10 min at 3000 RPM. The supernatant of the tubes was removed and the remaining precipitate was washed with demineralized water and using a vortex IKA VF2. The resulting solution was diluted to 50 mL into 1 50 mL tube. This tube was centrifuged for 10 min 14000 RPM in a Sorvall LYNX 6000 Superspeed Centrifuge (rotor for 12 50 mL tubes), the supernantant removed and subsequently washed in 50 mL demineralized water. These steps were repeated once more, but adding only 20 mL demineralized water instead of 50 mL.

From this 20 mL, 1 mL was used for dilutions for the single particle ICP-MS measurements. 9 mL was used for dilutions of the DLS measurements. The other 10 mL was dried in a Heidolph Rotavapor Hei-VAP Precision at 70°C and a vacuum of 70 mbar for dry analysis.

6. Characterization with DLS

From the 10 mL solution, 0.1 mL was diluted to 1 mL and put into a cuvette (67.754, Sarsted, polystyrene, 4 optical sides) for DLS characterization. DLS characterization was done with a Malvern - Zetasizer NANO ZSP. Every sample was measured in triplets. Every measurement gave a lognormal distribution of the precipitate sizes. The average and standard deviation of the average z-diameter were taken as the values for publication.

7. sp ICP-MS

The samples obtained after the post-treatment explained in the previous section were first 100-fold diluted with 18MΩ ultra-pure water from a Milli-Q system (Millipore, USA). Prior to analysis, the nanoparticle (NP) suspensions were sonicated using a sonicator, ultrasonic processor (Qsonica LLC, USA) equipped with a microtip 1/16” working in pulse mode and with a maximum amplitude of 40% during 10 minutes in order to avoid NP agglomeration. After sonication, different sample dilutions were prepared using ultra-pure water, followed by a gently stirred.

All measurements were carried out using a high resolution sector-field ICP-MS (HR-SF-ICP-MS) instrument (Nu AttoM ES, Nu Instruments, UK) equipped with a conventional sample introduction system comprising a glass concentric nebulizer mounted onto a baffled quartz cyclonic spray chamber. The instrument was operated in single particle (SP) mode with a dwell time of 50 µs. To overcome spectral overlap, pseudo-medium resolution mode was selected for the monitoring of ^{56}Fe, while low resolution was used in the case of ^{65}Cu (see Table S2). To calibrate the transport efficiency (TE), gold nanoparticles (AuNPs), stabilized in a citrate buffer, of known diameter and ionic standards solutions of Au were used. Additionally, the analyte sensitivity was also measured by using Cu and Fe ionic standard solutions. Appropriate dilutions factors for each of the samples were selected in order to obtain good statistics without compromising the occurrence of double events (Poisson statistics).

Data treatment was performed using the Nu Quant software (Nu Instruments, UK). This software can automatically differentiate the signal spikes corresponding to individual NPs and the continuous background. In this way, particle sizes can be obtained using the calculation’s editor built into the software and based on different algorithms (Shaw P., Donard A., J. Anal. At. Spectrom. 2016, 31, 1234). Additional information required for data treatment, such as shape, chemical composition and density of the particles, is shown in Table S2. In all cases, spherical shape was assumed, and thus, the particle spherical equivalent diameter is reported.

Table S 2: Information related to the SP-ICP-MS measurements

Sample solution	**Particle composition**	**Elemental mass (g mol^{-1})**	**Molecular mass (g mol^{-1})**	**Density (g cm^3)***	**Isotope measured**	**Resolution mode**	**Dilution factor**
$CuCl_2$	CuO	63.55	79.454	6.31	^{65}Cu	Low	2x10^6
CuCl + H_2O_2	CuO	63.55	79.454	6.31	^{65}Cu	Low	2x10^7
$FeCl_3$	FeOOH	55.85	88.852	4.26	^{56}Fe	Pseudo-medium	2x10^8
$FeCl_2$ + H_2O_2	FeOOH	55.85	88.852	4.26	^{56}Fe	Pseudo-medium	2x10^8

* source: Lide DR. CRC Handbook of Chemistry and Physics. 90th (Internet Version 2010) ed.

8. XRD measurements

XRD measurements were carried out with a Bruker D2 phaser (Cu source ($K_{\alpha,avg}$ = 1.54184, line focus, LynxEye detector)). The 2θ angles were chosen between 15° and 70° and a rotation of 15°/s.

9. SEM

The SEM pictures were taken with a FEI Nova Nanosem 450 using an immersion and beam deceleration of 2 kV with a concentric backscatter detector (CBS detector) in backscattered mode at 200000x magnification with a landing energy of 5 kV.

Figure ESI1 corresponds to figure 6 of the main text, but also includes, as insets, digital magnifications for figure 6c and 6d, aiming at demonstrating separate nanoparticles of FeOOH.

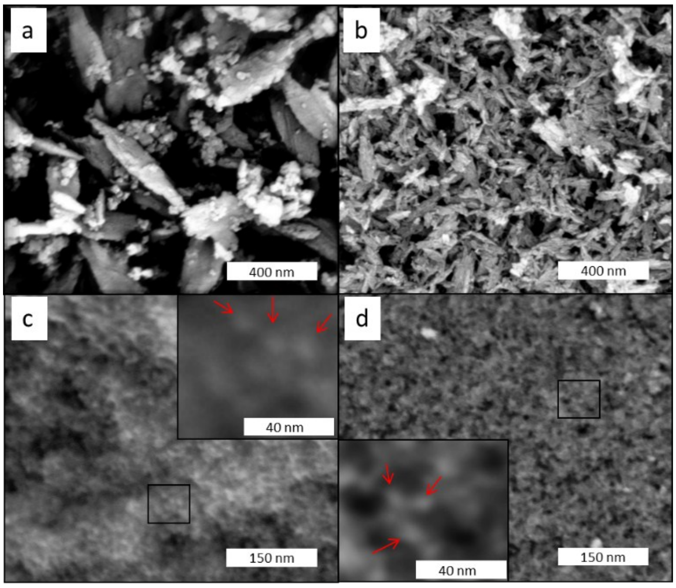

Figure ESI 1. SEM images of the dried precipitates. $CuCl_2$ without H_2O_2 (a) and CuCl with H_2O_2 (b) and $FeCl_3$ without H_2O_2 (c) and $FeCl_2$ with H_2O_2 (d). Inserts in (c) and (d) are digital magnifications that aim to demonstrate separate nanoparticles. Arrows indicate separate nanoparticles.