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SUPPLEMENTARY INFORMATION FOR DEPOSITION

CRYSTALLISATION OF COPPER SULPHATE PENTAHYDRATE FROM AQUEOUS SOLUTION IN ABSENCE AND PRESENCE OF SODIUM CHLORIDE

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Abstract

Additional and more detailed materials are provided including:

S1. Crystallisation and dissolution temperatures of the $CuSO_4$ + H_2O and $CuSO_4$ + NaCl + H_2O systems at different cooling rates.

S2. Solid-state characterisation using thermal analysis (TGA/DSC) and chemical analysis.

S3. Solubilities and activity coefficients for $CuSO_4$ solutions in both H_2O and brine as a function of solute concentration and at five different temperatures.

S4. Sequence of in-situ images of copper sulphate pentahydrate single crystals growing in both H_2O and brine at different supersaturations.

S5. Modelled fits to the experimental growth rate data using the Power law, B&S and BCF growth models for both the {1-10} and {1-1-1} faces for copper sulphate pentahydrate as grown in H_2O and brine.

S1. Crystallisation and dissolution temperatures of the $CuSO_4 + H_2O$ and $CuSO_4 + NaCl + H_2O$ systems at different cooling rates

Figure S1, show the results of T_{cryst} and T_{diss} as a function of cooling rate for 29.52 wt % copper sulphate solutions in two different media: H_2O and 2.4 wt % NaCl in H_2O.

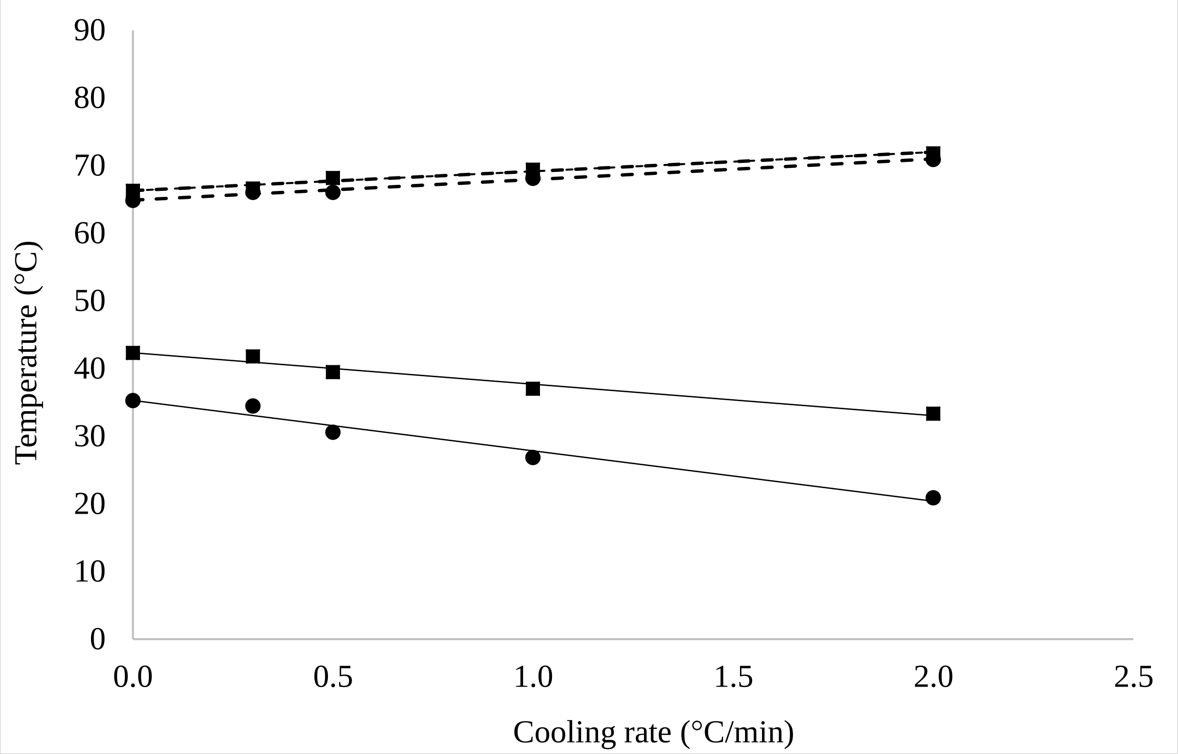

Figure S1. Plot of the crystallisation (-) and dissolution (---) temperatures for 29.52 wt % $CuSO_4$ solutions in different media: (●) H_2O and (■) 2.4 wt % NaCl, as a function of solution cooling rate.

The MSZW is a characteristic property of the crystallisations systems which describes the amount of necessary undercooling to achieve the initiation of spontaneous nucleation. Accordingly, Figure S1 shows not un-expectantly [30-32], that for both systems the observed metastable zone width is wider as the cooling rate increases, while for solutions with 2.4 wt % NaCl, the metastable zone width is significantly narrower than in H_2O media, which is attributed to the influence of the higher salt concentration of the solutions, in terms of promoting the on-set of nucleation. These results suggest that the limit of the metastability is influenced by both the copper sulphate solubility and the NaCl content.

Similar results were observed by Hernández et al. [11] and Justel et al. [12], where the solubility of copper sulphate pentahydrate in acidic seawater was observed to be slightly lower than its solubility in freshwater, reflecting the presence of different salts in the seawater, mainly sodium chloride.

S2. Solid-state characterisation using thermal analysis (TGA/DSC) and chemical analysis

S2.1 Experimental procedure

Copper sulphate crystals as obtained from aqueous solutions and brine at a cooling rate of 1°C/min were filtered, dried, and analysed by thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) to determine their composition, melting points, and to validate if the crystals grown in different media correspond to copper sulphate pentahydrate.

Thermal assays were conducted with a Mettler Toledo Thermogravimeter TGA/DSC1, STARe System. The crucibles used in the TGA/DSC instrument are made of platinum and were hermetically sealed. The test was conducted in a flowing inert nitrogen atmosphere (50 ml/min) and at a heating rate of 10 °C/min. The equipment was calibrated with indium with a sample mass of 10 mg. The temperature used in the experiment ranged from 25 to 300 °C.

In addition to this, chemical analysis of copper sulphate crystals obtained in brine at 1 °C/min was performed to determine the chemical composition of the sample and the concentration range of variation corresponding to the main impurities. Cu^{2+} and SO_4^{2-} concentrations were determined by oxidation-reduction volumetric and gravimetric method with drying of residue, respectively, and Na^+ and Cl^- were determined by Atomic and Molecular absorption spectrophotometry, respectively.

S2.2. Results

Figure S2 was performed to validate if the crystals obtained from brine corresponded to copper sulphate pentahydrate, as well as to compare the temperatures at which the most loss of water of crystallisation occurs for crystals obtained in different media.

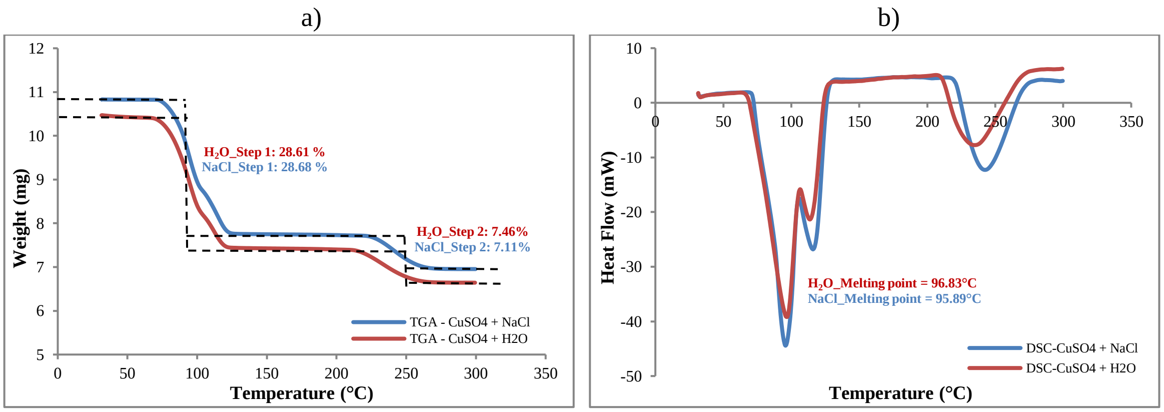

Figure S2. a) TGA and b) DSC curves for copper sulphate pentahydrate crystals obtained at 1 °C/min in H_2O and brine.

Figure S2.a shows that when copper sulphate pentahydrate is heated (from 25 to 300 °C), it loses its water of crystallisation in two steps at different temperatures, obtaining a total dehydration of 36.07 and 35.79% for crystals obtained in H_2O and brine, respectively, where the water loss is 28.61 and 28.68%, respectively, in the first step, corresponding to the loss of four water molecules, and 7.46 and 7.11%, respectively, in the second step, corresponding to the loss of one water molecule. These results allowed us to validate the composition of crystals obtained in both media, confirming that they correspond to copper sulphate pentahydrate.

Differential scanning calorimetry (DSC) analysis from Figure S2.b shows that the temperature at which the most loss of water of crystallisation occurs is at 96.83 and 95.89 °C, for the crystals grown in H_2O and brine, respectively. This similarity allows us to corroborate that crystals of copper sulphate pentahydrate obtained in H_2O at high cooling rates with a needle-like shape, do not correspond to a different polymorph or hydrated state of copper sulphate.

Additionally, the purity of the crystals obtained at 1 °C/min in brine is given in Table S1.

Table S1. Chemical Analysis of $CuSO_4 \cdot 5H_2O$ crystals obtained at 1 °C/min in brine.

Sample	% Cu^{2+}	% SO_4^{2-}	% Na^+	% Cl^-
$CuSO_4 \cdot 5H_2O$	25.41	39.50	0.0819	0.1228

It was demonstrated that 2.4 wt % of sodium chloride is not influencing the crystal structure of copper sulphate pentahydrate, where a purity of 99.8 wt % of $CuSO_4 \cdot 5H_2O$, and a NaCl percentage of 0.2 wt % were obtained. Allowing us to conclude that the change in the shape of crystals at high cooling rates, and the size increment when sodium chloride is present in the solution, is not due to the incorporation of NaCl in the crystal structure.

S3. Solubilities and activity coefficients for $CuSO_4$ solutions in both H_2O and brine as a function of solute concentration and at five different temperature

Little information is available in the literature regarding the effect of seawater as a recrystallisation solvent upon the resultant physical chemical processes of the crystals. Hernández et al. [11] provided experimental data of solubilities and physical properties (density, refractive index, ionic conductivity, and viscosity) of $CuSO_4$ in seawater at various temperatures and at pH 2. Justel et al. [12], studied the influence of seawater on the solid-liquid equilibrium and physical properties (density and viscosity) in copper sulphate solutions at four different temperatures and ten different sulphuric acid concentrations. Then, Justel et al. [13] determined solubilities and the water activities of copper sulphate in seawater at different temperatures. These authors then used this information to represent the solid-liquid equilibrium of copper sulphate-sulphuric acid-seawater system by means of a methodology that uses the Pitzer and the Born model [15, 16] to quantify the relative impact of copper sulphate and sulphuric acid effect, respectively on the phase diagram. Additionally, the amounts of copper sulphate precipitated as a function of the sulphuric acid concentration were predicted. In these studies, the sodium chloride concentration present in seawater was 2.4 wt %, and the experimental data were correlated obtaining relevant information for the design of copper sulphate pentahydrate plants, using seawater as a solvent and the addition of sulphuric acid as the crystallisation initiator.

S3.1 Experimental procedure

Linke and Seidell [33] reported solubility data of copper sulphate in freshwater at different temperatures. In the present work, experimental solubility data of copper sulphate with 2.4 wt % of sodium chloride at different temperatures (from 293.15 to 333.15 K) were determined. The methodology used for the determination of the solubility has been reported previously [12, 13].

In addition, in order to assess the importance of the chemical interactions, the activity coefficients of the copper sulphate solutions have been evaluated. An activity coefficient is a factor used in thermodynamics to account for deviations from ideal behaviour in a mixture of chemical substances [34].

In the present work, the activity coefficients of copper sulphate $\gamma_{\pm}$ were determined by the Pitzer model [35] where for 2-2 electrolytes (as copper sulphate), the mean activity ionic coefficients are given by the following expressions:

$$\ln \gamma_{\pm} = 4f^{\gamma} + mB^{\gamma} + m^2 C^{\gamma} \tag{1}$$

where:

$$f^{\gamma} = -A_{\emptyset}\left[I^{1/2}/\left(1 + bI^{1/2}\right) + 2/b \ln\left(1 + bI^{1/2}\right)\right] \tag{2}$$

$$B^{\gamma} = 2\beta^{(0)} + \left(2\beta^{(1)}/\alpha_1^2 I\right)\left[1 - \left(1 + \alpha_1 I^{1/2} - 1/2\,\alpha_1^2 I\right) exp^{-\alpha_1 I^{1/2}}\right] + \left(2\beta^{(2)}/\alpha_2^2 I\right)\left[1 - \left(1 + \alpha_2 I^{1/2} - 1/2\,\alpha_2^2 I\right) exp^{-\alpha_2 I^{1/2}}\right] \tag{3}$$

$$C^{\gamma} = 3/2\, C^{\emptyset} \tag{4}$$

In these equations, A_ϕ corresponds to the Debye-Hückel term [36], and m and I correspond to the molality and ionic strength, respectively. The symbols $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^\emptyset$ are copper sulphate specific parameters, and the parameters α_1 , α_2, and b are constants with values of 1.4, 12, and 1.2 $Kg^{1/2} \cdot mol^{-1/2}$, respectively, for copper sulphate [35].

In the present work, the values of the $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and $C^\emptyset$ for $CuSO_4$ solutions in H_2O and brine from 293.15 to 333.15 K have been taken from the work of Justel et al. [13, 14]; in the case of the brine solutions, parameter values for copper sulphate in seawater were considered [13]. All the parameters used are shown in the data summarised in Table S2.

Table S2. Binary Pitzer parameters for copper sulphate solutions in H_2O and seawater media.

	$CuSO_4$ + H_2O system [14]				$CuSO_4$ + Seawater system [13]			
T(K)	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\emptyset$	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^\emptyset$
293.15	0.231	2.511	-48.347	0.009	0.571	2.978	0	-0.070
303.15	0.237	2.543	-48.313	0.000	0.579	2.988	0	-0.074
313.15	0.243	2.575	-48.281	-0.008	0.587	2.998	0	-0.079
323.15	0.248	2.605	-48.250	-0.015	0.595	3.008	0	-0.083
333.15	0.254	2.634	-48.219	-0.023	0.602	3.017	0	-0.087

S3.2 Results

Table S3 shows the solubility data for copper sulphate in freshwater at different temperatures reported by Linke and Seidell [33] together with the experimental solubility and density data for the same in brine at five different temperatures (from 293.15 to 333.15 K) determined in the present work.

Table S3. Experimental solubility and density data of copper sulphate in brine at different temperatures. *, refers to the solubility values of copper sulphate in freshwater from literature [33].

T (K)	ρ (g/cm^3)	SD (%)	$CuSO_4$ (mol/Kg H_2O)	SD (%)	* $CuSO_4$ (mol/kg H_2O) [33]
293.15	1.21183	0.00004	1.2826	0.0042	1.2833
303.15	1.23393	0.00001	1.5139	0.0072	1.5196
313.15	1.26730	0.00001	1.7728	0.0081	1.7909
323.15	1.30610	0.00004	2.0988	0.0104	2.1074
333.15	1.34663	0.00005	2.4690	0.0107	2.4729

The data clearly show that for both systems the solubility increases with temperature and that the solubility of copper sulphate in brine was slightly lower than in pure aqueous solutions in good agreement with previous work [11, 12].

Additionally, Figures S3.a and S3.b show the activity coefficients (γ) for $CuSO_4$ solutions in H_2O and brine, respectively, in the temperature range from 293.15 to 333.15 K at copper sulphate concentrations up to the saturation (values from Table S3).

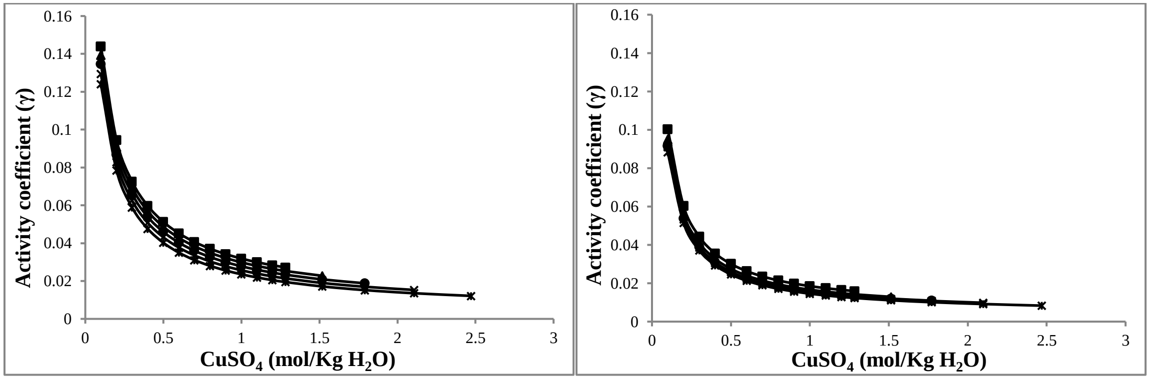
a) b)

Figure S3. Activity coefficients of $CuSO_4$ in a) H_2O and b) brine solutions at different salt concentrations: ■, 293.15 K; ▲, 303.15 K; ●, 313.15 K; ×, 323.15 K; ✳, 333.15 K.

All the curves (from 293.15 to 333.15 K) for both systems, show a similar profile of variation of the activity coefficient (γ) with both the concentration and temperature, where it was found that γ decreased with increasing concentration, and decreased with increasing temperature. Bockris and Reddy [37], and Morales [38] have both pointed out that ion-ion interactions in ionic solutions, give rise to a decrease in the activity coefficients with increasing ionic concentration. On the other hand, an increase in the activity coefficients shows a prevalence of ion-solvent interactions, since at high concentrations the short-range interactions increase in the system. This means that as the concentration of the electrolyte increases, the amount of the effective solvent decreases, and the amount of water molecules capable of dissolving the added ions decreases [38]. The data shows that for both systems $CuSO_4$ at low molalities shows a predominance of ion-solvent interactions over ion-ion interactions. However, as the concentration increases, an increase of the ion-ion interactions was observed.

Examination of the activity coefficients reveals higher activities as a function of temperature values (from 293.15 to 333.15 K), in pure aqueous media compared to brine. This indicates that the ion-solvent interactions within the aqueous solutions are stronger than those within the brine. These results agree with those from Table S3, where it was shown that the solubility of copper sulphate in aqueous media was higher than in brine, which is due to the stronger interactions with the solvent.

Additionally, Figure S4 shows a comparison of the activity coefficients for $CuSO_4$ solutions in H_2O and brine, in the temperature range from 293.15 to 333.15 K at copper sulphate concentrations up to the saturation. These values were determined using the Pitzer binary parameters in H_2O and seawater, respectively, obtained from the works of Justel et al. [13, 14].

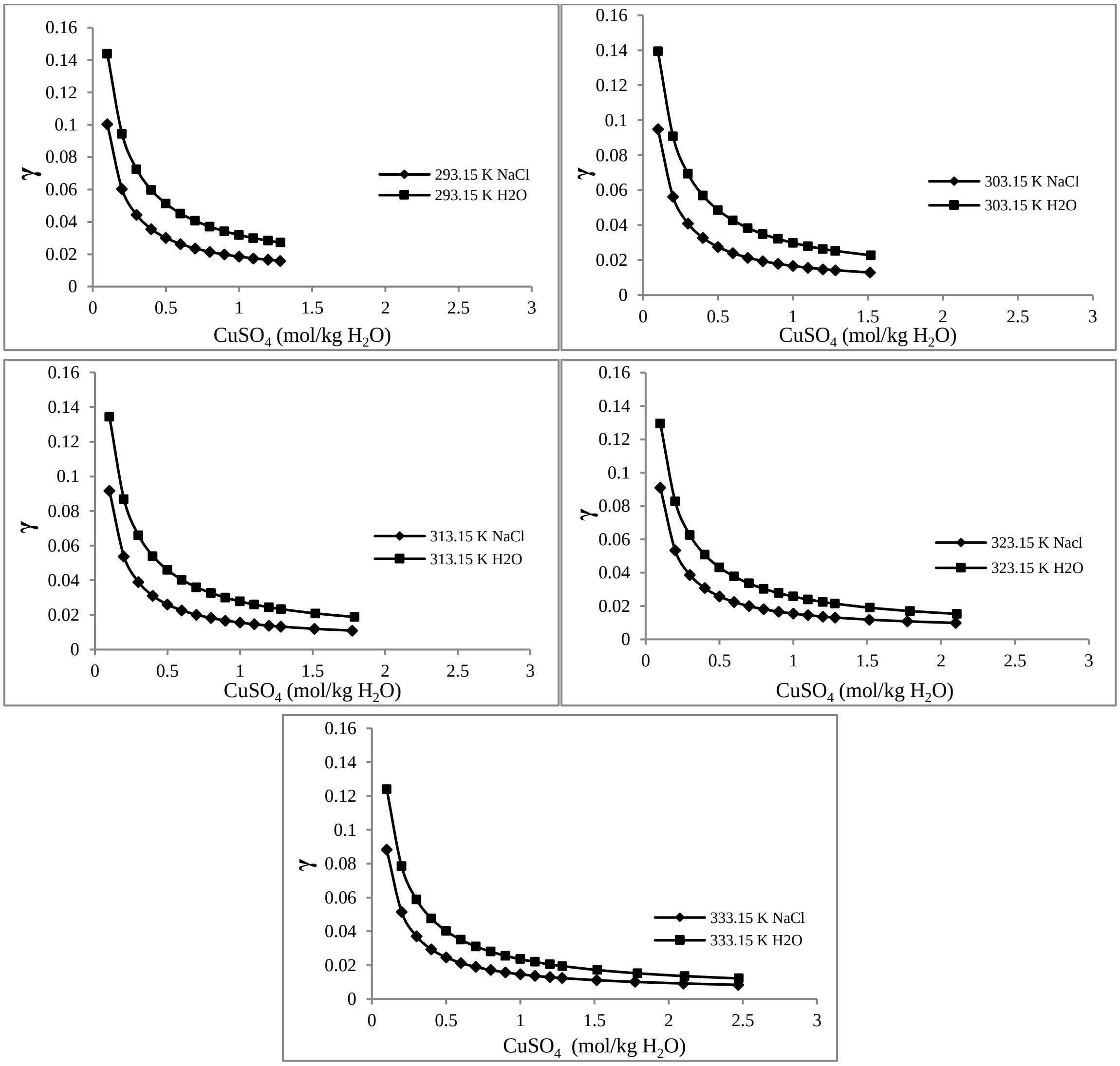

Figure S4. Activity coefficients comparison between $CuSO_4$ solutions in (■) H_2O and (♦) brine as a function of the concentration at five different temperatures (293.15, 303.15, 313.15, 323.15, and 333.15 K).

S4. Sequence of in-situ images of copper sulphate pentahydrate single crystals growing in both H_2O and brine at different supersaturations

a) Copper sulphate pentahydrate crystals grown in H_2O.

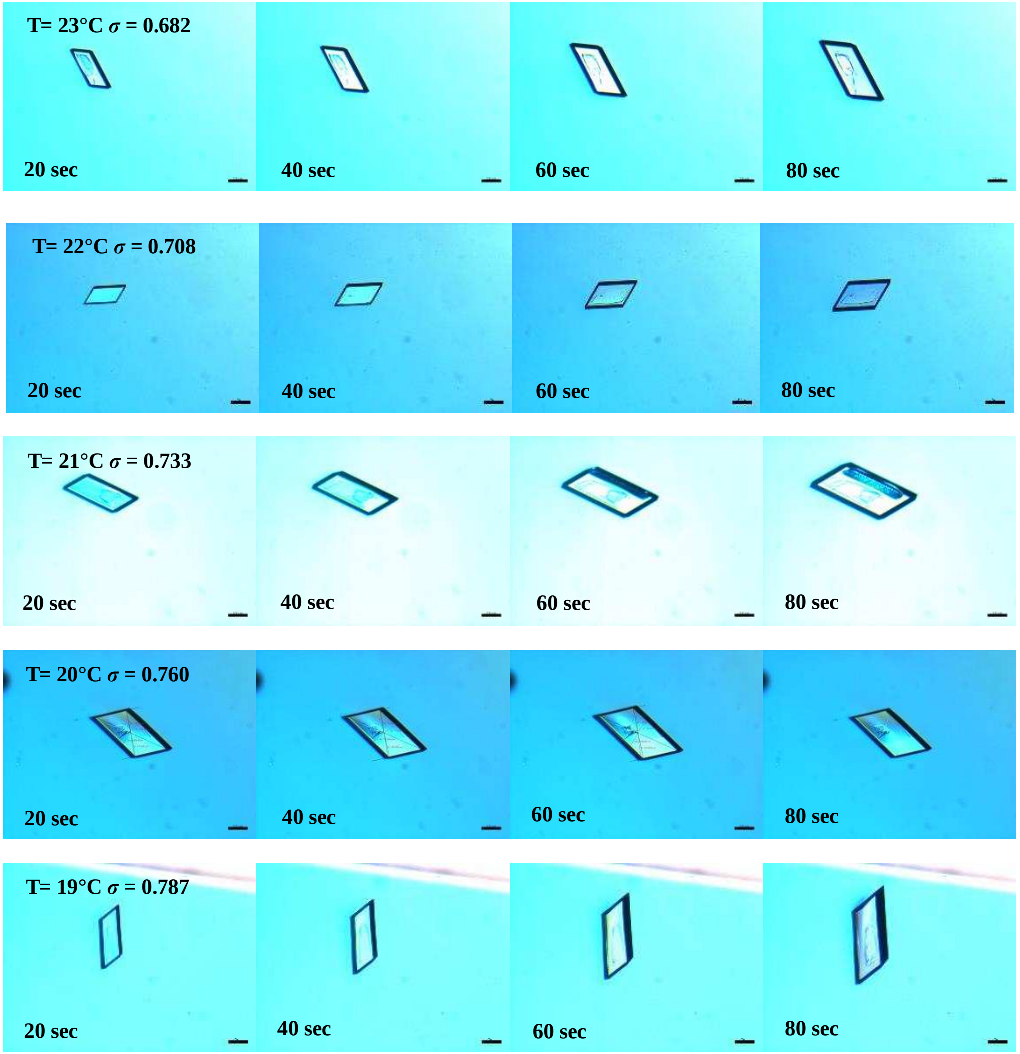

Figure S5. Series of optical micrographs of copper sulphate crystals grown in H_2O in the supersaturation range from $\sigma = 0.682$ to $\sigma = 0.787$ at the 0.5 ml scale size showing the growth of the crystals and their morphology as a function of elapsed time and supersaturation. Black line in the picture represents the scale bar of 100 µm.

b) Copper sulphate pentahydrate crystals grown in 2.4 wt % NaCl media.

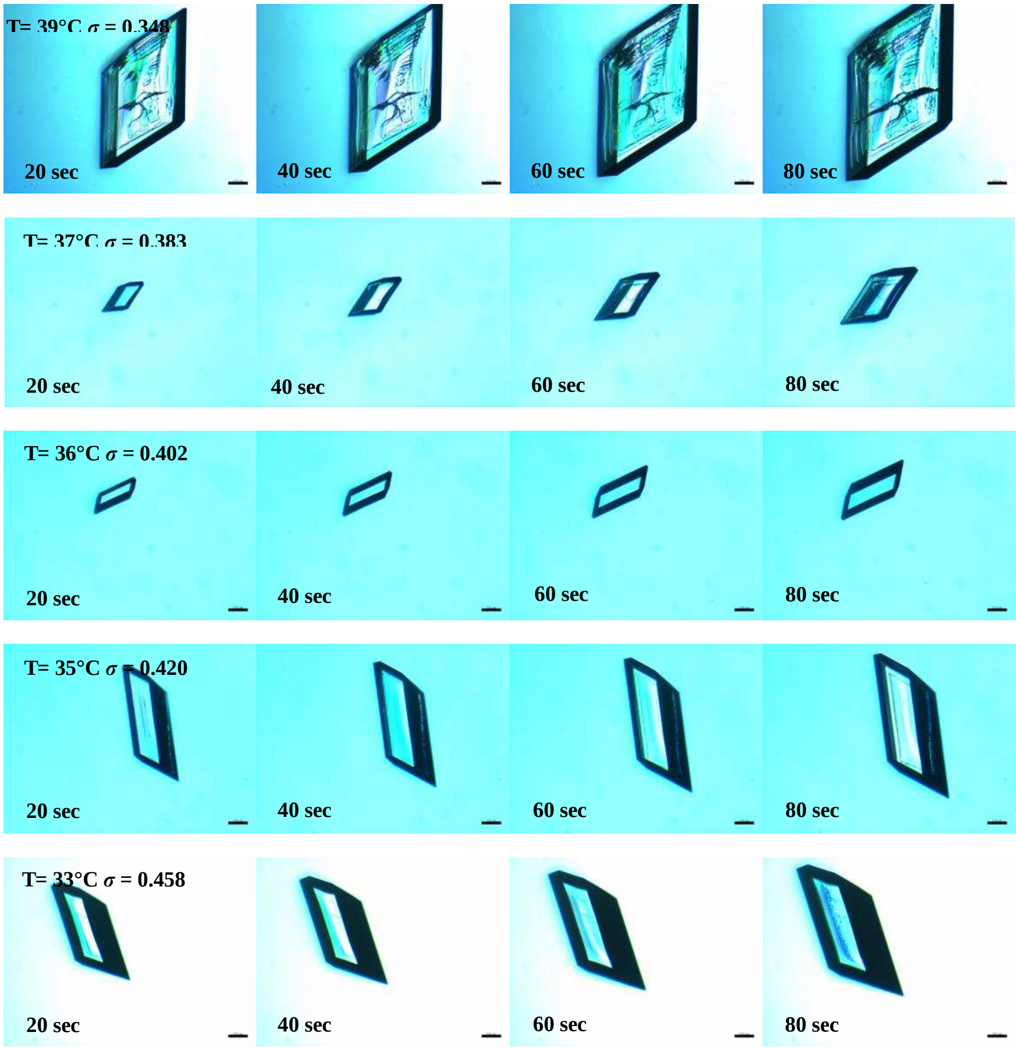

Figure S6. Series of optical micrographs of copper sulphate crystals grown in brine in the supersaturation range from σ = 0.348 to σ = 0.458 at the 0.5 ml scale size showing the growth of the crystals and their morphology as a function of elapsed time and supersaturation. Black line in the picture represents the scale bar of 100 µm.

S5. Modelled fits to the experimental growth rate data using the Power law, B&S and BCF growth models for both the {1-10} and {1-1-1} faces for copper sulphate pentahydrate as grown in H_2O and brine

Figures S7.a and S7.b show the best fits of the growth models for both the {1-10} and {1-1-1} faces for copper sulphate pentahydrate in H_2O and brine, respectively. Additionally, all relevant parameters obtained through this analysis are presented in Table S4. For comparative assessment, all fitting lines were drawn and the corresponding modelled parameters were also given.

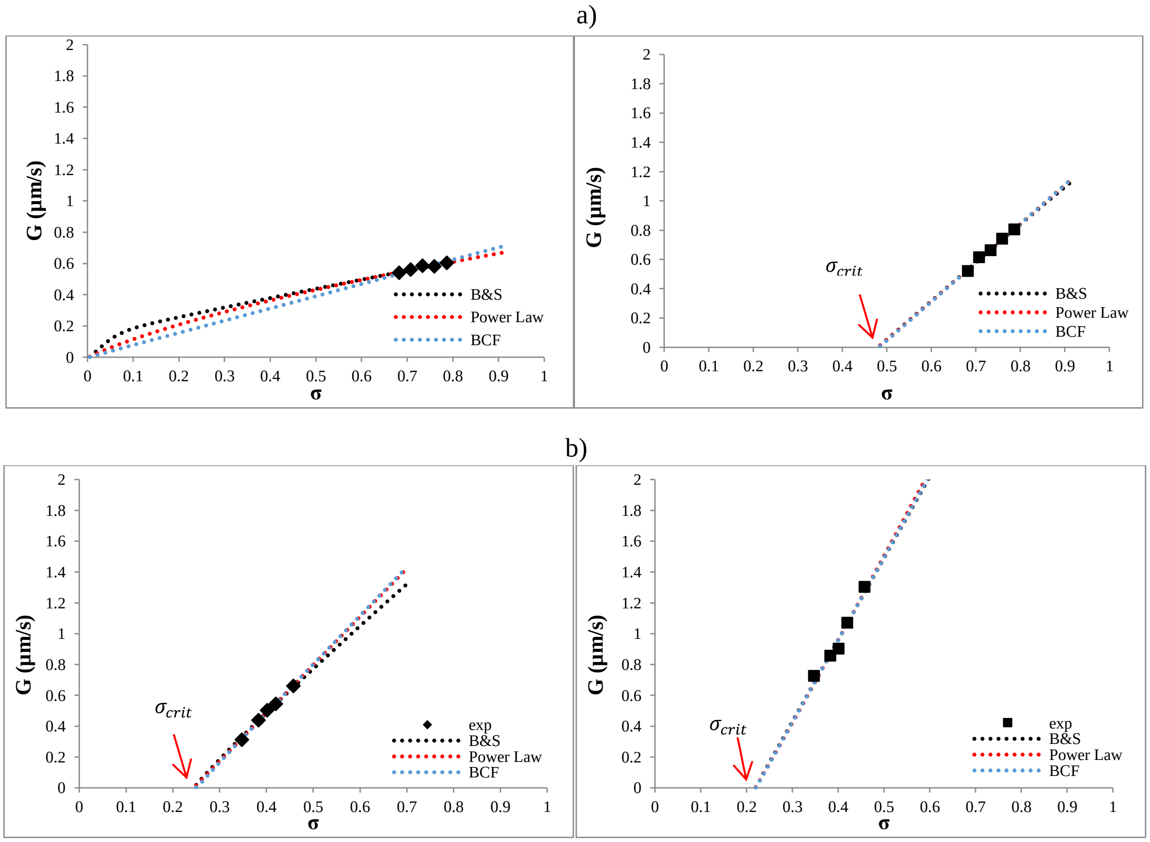

Figure S7. $G(\sigma)$ experimental data of copper sulphate pentahydrate grown in a) H_2O and b) brine fitted to the Power law, B&S and BCF models. Left (♦) refers to the {1-10} and right (■) to the {1-1-1} faces respectively.

Table S4. Crystal growth kinetics parameters obtained from the fit of the Power Law, B&S and BCF models to the experimental $G(\sigma)$ data.

		$CuSO_4 + H_2O$		$CuSO_4 + NaCl + H_2O$	
	Range σ studied	0.682 to 0.787		0.348 to 0.458	
Fitting model	Range of $\Delta C = (C - C_e)$ studied	760.8 to 819.1		500.1 to 600.9	
Power law Equation (2)	Faces	{1-10}	{1-1-1}	{1-10}	{1-1-1}
	$\frac{1}{k'_{MT}}$	6.40E+11	3.31E+11	4.74E+10	4.75E+10
	$k_{MT}\left(\frac{m}{s}\right)$	1.75E-11	3.38E-11	1.83E-10	1.82E-10
	$k_G\left(\frac{m}{s}\right)$	1.33E+00	2.29E+01	3.66E-12	7.48E-12
	$\frac{1}{k_G(\sigma - \sigma_{crit})^{r-1}}$	6.34E-01	4.92E-02	2.72E+11	1.41E+11
	σ_{crit}	0.003	0.480	0.245	0.219
	r	0.45	1.09	0.9983	1.0331
	R^2	90%	99%	99%	96%
B&S Equation (3)	$\frac{1}{k'_{MT}}$	3.81E+11	3.80E+11	1.88E+11	1.89E+11
	$k_{MT}\left(\frac{m}{s}\right)$	2.93E-11	2.94E-11	4.60E-11	4.59E-11
	$k_G\left(\frac{m}{s}\right)$	8.47E-01	1.39E+00	5.60E-12	6.24E-12
	$\frac{1}{k_G(\sigma - \sigma_{crit})^{-1/6}\exp\left(\frac{A_1}{\sigma - \sigma_{crit}}\right)}$	8.91E-01	1.10E-04	1.58E+11	3.78E+06
	σ_{crit}	0.004	0.480	0.245	0.219
	A_1	0.1671	2.1737	0.0002	5.4302
	R^2	90%	99%	99%	96%
BCF Equation (4)	$\frac{1}{k'_{MT}}$	3.70E+11	3.75E+11	1.86E+11	1.87E+11
	$k_{MT}\left(\frac{m}{s}\right)$	3.03E-11	2.98E-11	4.65E-11	4.63E-11
	$k_G\left(\frac{m}{s}\right)$	6.21E+01	7.68E+02	2.27E-10	2.70E-09
	$\frac{1}{k_G(\sigma - \sigma_{crit})tanh\left(\frac{A_2}{(\sigma - \sigma_{crit})}\right)}$	9.11E-01	5.13E-03	1.32E+11	7.19E+08
	σ_{crit}	0.000	0.480	0.245	0.219
	A_2	0.020	9.507	0.034	47.660
	R^2	77%	99%	99.5%	96%
Rate limiting step		Diffusion of growth units within the bulk of the solution		Diffusion of growth units within the bulk of the solution	

References

The reference numbering in the supplementary information coincides with the references in the paper.