

The kinetics of gypsum precipitation, the inhibiting effect of citric acid and its use in the differential precipitation of $\text{Mg}(\text{OH})_2$ from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

PhD Theses

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1. Introduction

The crystallization of solids from supersaturated solutions is a source of numerous complications during a range of industrial processes: undesirable precipitates may clog pipelines, foul membranes, contaminate the target compounds of a process, lower the effectiveness of heat exchange *via* scale formation, *etc.* Calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or gypsum) is one of the most common of such solids, therefore during the last decades, numerous studies were dedicated to the investigation of precipitation kinetics and development of methods potentially suitable for precipitation control and inhibition.

While this work has clear industrial motives, the investigation of these phenomena is also very important from environmental point of view. Desalination processes are used worldwide to obtain potable water from recycled, waste or sea waters. Water conservation is an important issue to sustainably manage the freshwater need of humankind. The recirculation of the different waste waters can help to avoid water scarcity in arid environments. The most used (and cost-efficient) way for desalination is reverse osmosis; however, solids can precipitate from the forming brine clogging the membrane thus slowing or stopping the process completely. Therefore, the inhibition of such reactions is very important. Also this forming brine needs to be dealt with because of its high salinity. By the controlled, separated precipitation of the ionic species from these brines some important, useful materials could be retrieved *e.g.* gypsum (construction industry), magnesium hydroxide (acidic waste treatment) sodium chloride. These processes can lower the amount of waste produced and the fresh water demand.

Another very important issue is the treatment of acidic waste waters, which could exert enormous threat to the environment by their high metal content (could be toxic, carcinogenic) and low pH, if they are not handled properly. Traditionally, these are neutralized by caustic soda or lime precipitating most of the metal ions in hydroxide form and elevating the pH. This results in mixed sludge with many metal hydroxides and gypsum, which has to be stored or disposed. Also, the pH of the final fluid is often too high, and can be harmful to release it into natural waters. By performing the neutralization in multiple steps, the heavy metals can be separated (if possible, even recycled for use) by magnesium-based neutralization (MgO , $\text{Mg}(\text{OH})_2$) in the first step. In the next step using lime, the magnesium can be retrieved and the gypsum by-product can be utilized in the construction industry. This way, less solid and fluid waste forms and has to be disposed, while the cost

of the neutralization process is lowered. This work mainly focuses on the optimization and enhancement of the second step of this neutralization process.

2. Aims

The main goal of our work was to *in situ* separate the precipitation of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and gypsum, to obtain both solids in as pure form as possible. This process can be utilized in the two-step neutralization of various acidic waste waters and also can be useful in desalination processes. To obtain this goal, the precipitation of gypsum and its inhibition was studied.

First, a kinetic model for gypsum precipitation was planned to develop, which is able to describe the nucleation and crystal growth processes in parallel over a wide concentration range. To do this, the precipitation kinetics of gypsum was intended to be studied over the whole, experimentally feasible concentration range, under strict control of the reaction conditions.

In the following step, studying the effects of citric acid on gypsum precipitation was planned, since during the scouting experiments, citric acid proved to be the most promising inhibitor to separate the two precipitation reactions. Investigations on the use of citric acid were planned under near-industrial conditions to test the potentials and limitations of the inhibitor. Furthermore, we intended to learn about the effects of the additive on the kinetics of the reactions and the precipitating solids. Studying analogous reactions in the presence of background electrolyte were also aimed at, to investigate their usefulness in sea water processing.

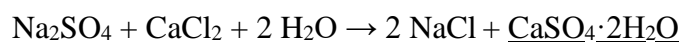
Finally, the optimization of the *in situ* separation of the two parallel precipitation processes was targeted by inhibiting the precipitation of gypsum with citric acid during the $\text{MgSO}_4 + \text{Ca}(\text{OH})_2 + 2 \text{H}_2\text{O} \rightarrow \underline{\text{Mg}(\text{OH})_2} + \underline{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}$ reaction. To mimic industrial conditions, milk of lime, produced from quicklime of natural source, was intended to use as $\text{Ca}(\text{OH})_2$ source. The effects of changing reaction parameters and washing procedures were planned to study with learning about the life cycle of the additive being an economically and environmentally important issue.

3. Experimental

3.1. Experimental procedures

Kinetics of gypsum precipitation

To study the precipitation kinetics of gypsum, the following reaction was carried out:



To initiate the reactions, 50 cm³ solutions containing stoichiometric amounts of the reactants were mixed. The initial reactant concentrations were varied systematically in the 0.04–0.20 M concentration range. The reactions were thermostated at 25°C in every reaction. For good repeatability, the measurements were performed as similarly as possible, always using the same pieces of equipment (vessel, electrodes, stirring rod, stirring speed).

The reactions were followed *in situ* by conductometric and potentiometric measurements using Ca-ISE for the latter. To establish the robustness and reliability of those, ICP-OES measurements were carried out to determine the exact calcium content of the reaction mixture at given times. After the reaction reached its equilibrium, the precipitates were separated by vacuum filtration. The composition of the solids was studied by powder XRD, while the morphologies of the crystals were studied by capturing their SEM images.

The data collected by the conductometric measurements were used to construct a comprehensive kinetic model. The necessary calculations were carried out with the ChemMech program package.

Effects of citric acid on the kinetics of gypsum precipitation

The inhibiting effects of citric acid were also investigated in the stoichiometric reaction of Na₂SO₄ and CaCl₂, using the same pieces of equipment as in the in earlier kinetic measurements. The initial reactant concentration was 0.1 M and the agitation speed was 300 rpm. To determine the effect of pH on the inhibition, the reaction pH was systematically varied between 3.15 and 10 adjusting it with NaOH, and following it during the reactions with a pH electrode. The effects of changing additive concentrations were studied at pH 6.5, optimal for citrate inhibition, increasing the additive concentration systematically until the effect did not change further significantly.

After the completion of the reactions, the solids were separated from the mother liquor, they were kept for further analysis just as the filtrate. The composition of the precipitates

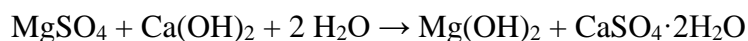
was determined by powder XRD. The morphological changes were studied by capturing SEM images of the precipitated crystals.

To determine the location of citrate after the reactions, UV spectrophotometric measurements were carried out on the diluted samples of the reaction filtrates. To confirm the results, the IR spectra of the solid samples were also recorded.

The inhibiting effect of citric acid was also studied in presence of background electrolyte (higher ionic strength), in 1 M NaCl. For this, the same reaction was carried out in the absence and in the presence of 1.5 mmol citric acid and trisodium citrate. The reactions were followed by potentiometry using Ca-ISE. After the completion of the reactions, the precipitates were examined as described above, by powder XRD and SEM.

Differential precipitation of Mg(OH)₂ from CaSO₄·2H₂O

The *in situ* separation of the Mg(OH)₂ and the CaSO₄·2H₂O precipitates by delaying the latter with citrate was attempted in the following reaction:



As Ca(OH)₂ source, milk of lime prepared from quicklime of natural limestone was used. The precipitation reactions were carried out in a cylindrical glass reactor, the volume of the reaction mixture was always 1 L. The MgSO₄ and the additive was dissolved in distilled water, and the reaction was initiated by the addition of lime milk. The reactions were agitated by a PTFE shaft stirrer with a screw propeller head, at 700 rpm. The reactions were followed *in situ* by conductometric measurements, while monitoring the temperature as well as pH of the mixtures. To back up the results, ICP-OES measurements were carried out on withdrawn samples of the mother liquor.

To optimize the process, the reaction conditions were varied investigating the effects of temperature, initial reactant concentration and additive concentration.

To analyze the precipitating solids, they had to be separated from the mother liquor and from each other. After the separation, two solid and two fluid samples were obtained: Mg(OH)₂, CaSO₄·2H₂O, the washing fluid and the final filtrate.

The separated solids were studied by powder XRD to determine their compositions. SEM was used to look at the morphology of the crystals. SEM-EDX measurement results and elemental maps of the Mg(OH)₂ samples containing gypsum impurities were studied to determine the distribution of the precipitating solids.

To determine the fate of the citrate ions after the completion of both reaction, HPLC measurements were carried out on the fluid and the solid samples (digested in the eluent).

To back up these results, IR spectra of the separated solids, precipitated in the absence and the presence of additive, were also measured.

3.2. Measuring equipment and methods

Variation of the conductivity during the precipitation reactions were followed using a Jenway 027013 conductivity cell connected to a Jenway 3540 pH and conductivity meter. The built-in sensor of the cell was also used to monitor the temperature.

The pH of the solutions was measured with a Sentix 62 pH electrode calibrated to 5 points: pH 2, 4, 7, 10, 11.5.

The potentiometric measurements were carried out with a Metrohm 794 Basic Titrino paired with a Metrohm combined polymer membrane Ca ion-selective electrode.

To perform ICP-OES measurements, samples were withdrawn from the reaction slurries at given times using a syringe. These samples were quickly (approximately 5-10 seconds) filtered through a syringe filter with 0.45 μm pore diameter. The filtrate was diluted hundredfold in 2% nitric acid to avoid any further precipitation. The measurements were carried out using a Thermo Scientific iCAP 7400 ICP-OES DUO spectrometer.

For the powder X-ray diffractometric measurements, a Rigaku MiniFlex II type Röntgen diffractometer was used. The diffractograms of the precipitates were captured in the $2\theta = 4^\circ\text{--}60^\circ$ range with $2^\circ/\text{min}$ scanning speed, using $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation.

The morphologies of the precipitated solids were studied by scanning electron microscopy using a Hitachi S-4700 scanning electron microscope. This instrument was also equipped with a Röntec QX2 spectrometer enabling the elemental mapping of the solids.

UV-Vis spectra of the solutions were measured by an Analytic Jena Specord 210 plus spectrophotometer, using a quartz cuvette.

IR spectra of the solids were measured with two different setups. The spectra initially were measured using BIO-RAD 18 Digilab Division FTS-65 A/896 FT-IR spectrophotometer by DRS technique using KBr for background. Later on, a JASCO FT/IR-4700 spectrophotometer was used for this purpose, the spectrometer was equipped with a ZnSe ATR accessory and a DTGS detector. For one spectrum 256 interferogram was gathered with resolution of 4 cm^{-1} , in the $4000\text{--}650 \text{ cm}^{-1}$ wavenumber range.

HPLC measurements of the fluid and the digested solid samples were carried out on an Agilent 1100 series HPLC using a Grom-Resin ZH type column. The eluent during these measurements was 0.01 M sulfuric acid.

4. New scientific results

T1. A comprehensive kinetic model was developed, which is unique in the sense that it is capable of describing the precipitation kinetics of gypsum from aqueous solution in the whole experimentally feasible concentration range. The model is able to include the nucleation and crystal growth processes of gypsum simultaneously.

The reaction kinetics of the $\text{Na}_2\text{SO}_4 + \text{CaCl}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{NaCl} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ reaction was studied by employing multiple experimental means (conductometry and Ca-ISE) in the 0.04-0.20 M initial concentration range using identical initial reactant concentrations in the individual runs. The limits of the range were chosen to allow the completion of the reaction within reasonable time (lower limit), and the control of system homogeneity and the induction period.

T2. It was proven for the first time that the formation of the $\text{CaSO}_{4(\text{aq})}$ ion-pair had to be taken into consideration for accurately describing the kinetics of the reaction, and that the influence of the wall-effect was negligible under the circumstances applied in this work.

The reaction with 0.06 M initial concentration proceeded very similarly in three different reaction vessels suggesting that the wall-effect did not play major role in the kinetics of the reaction. The experimentally observed conductance values exhibited linear dependence on the ionic concentrations, but the non-zero intercept was rationalized in terms of ion-pair formation. In the kinetic model, the formation of the $\text{CaSO}_{4(\text{aq})}$ neutral ion pair had to be included, and the significant ionic-strength dependence of the molar conductivity of the ionic species had to be taken into account, too.

T3. It was proven that under well-defined conditions, Ca-ISE is suitable for accurately measuring $[\text{Ca}^{2+}]$ during gypsum crystallization. Ca-ISE was employed by us for the first time to directly measure concentration changes of ions during this precipitation process.

It was found that conductometry was suitable for studying gypsum precipitation kinetics in relatively fast reactions in solutions even at relatively high reactant concentrations. The response of the conductometric electrode is very fast, but it cannot be used in the presence of high concentrations of background electrolyte. To circumvent this, an attempt was made

to employ Ca-ISE in slow precipitation reactions with high ionic strengths. The rationale behind this is, that albeit the response time of Ca-ISE is much longer than that of the conductometric one, stable Ca-ISE potential readings require constant and high background electrolyte concentrations. The applicability region of both electrochemical methods were confirmed by ICP-OES measurements.

T4. The inhibiting effects of citric acid on the precipitation of gypsum from highly supersaturated solutions were described at various pH values, and the optimum conditions for maximum inhibition efficiency were established.

The inhibiting effects of citric acid was tested in the stoichiometric reaction of Na_2SO_4 and CaCl_2 with 0.1 M initial concentrations. It was found that under pH 4 the inhibiting efficiency of citric acid rapidly decreased due to the protonation of its carboxylate groups. Above pH 6.5 the inhibiting efficiency displayed saturation curve with increasing citrate concentration. Above 3 mM additive concentration, the precipitation rate was not hindered further significantly with increasing concentration of the additive. The morphological changes of the crystals was also affected by the inhibiting efficiency, instead of the rod- and needle-like crystals, platelets were formed in the presence of citrate ions.

T5. The effects of citric acid on the precipitation of gypsum in systems without added background electrolyte were compared with high-ionic strength systems mimicking sea water. It was established that NaCl increased the inhibiting effect of citrate, but the morphological changes of the precipitating solids were less dramatic in the presence than in the absence of added electrolyte. This implies that chloride ions change the inhibition mechanism of citrate.

The stoichiometric reaction of Na_2SO_4 and CaCl_2 with 0.1 M initial concentration was also performed in the presence of 1 M additional NaCl. The higher ionic strength resulted in bigger solubility of gypsum, therefore the reaction rates were slower, and the inhibition of citric acid and citrate was more efficient resulting in longer induction periods. The changes in the solids had similar tendencies, but the differences were smaller. In the presence of citrate ions at high ionic strength, beside platelets, the majority of the crystals were short, compressed rods.

T6. By inhibiting the gypsum crystallization with citrate ions, the reaction conditions for the *in situ* separation of Mg(OH)₂ and CaSO₄·2H₂O precipitates were optimized for the first time.

In the $\text{MgSO}_4 + \text{Ca(OH)}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ reaction, the precipitation of the two solids were separated in time by inhibiting the precipitation of gypsum with citrate ions. The optimal parameters were 20°C, 0.1 M initial reactant concentration, 1.5 mM citric acid as additive and washing the filtered Mg(OH)₂ with four times the volume of the taken sample using distilled water. It was shown, that with careful planning, the conditions could be changed and adjusted to the specific requirements of the individual reaction sites.

T7. The location of the citrate ions after the completion of the precipitation of both solid phases was determined, and it was shown, that they were split between the Mg(OH)₂ and the final filtrate. With this finding it was demonstrated that the citrate additive was reusable in practical applications.

By HPLC measurements of the digested solid and the fluid samples, a portion of the citrate was found to be bound by the precipitated Mg(OH)₂. It was probably bound to the surface of the solid taking some calcium ions to compensate its charge if needed. Another portion remained in the mother liquor inhibiting the precipitation of gypsum. The IR spectra of the solids precipitated in the absence and the presence of citrate ions confirmed these assumptions.

5. Potential practical uses and relevance in environmental protection

The separation of the precipitation reaction of Mg(OH)₂ and CaSO₄·2H₂O by inhibiting the latter with citrate ions can be utilized in the two-step neutralization of acidic waste waters. As the parameters of the separation are tunable, it can be used in different sites. The method can improve the economic viability of those processes decreasing the environmental risks as well. The separate precipitation of heavy metals decreases the amount of solid waste produced. The solids precipitated in the second step of the neutralization are useful materials in pure form, Mg(OH)₂ could be recycled in the first step of the neutralization, while the gypsum can be used in the construction industry. Citrate is a biodegradable additive, and could be a much better alternative for the inhibition of gypsum in these system than the often

used, non-degradable poly(acrylic acid). Our results show that it can be even recycled, further improving the environmental viability of the process. The results obtained in the high-ionic strength systems suggest that citric acid/citrate can be used as inhibitor of gypsum precipitation in processes involving sea water, such as in desalination.

6. Publications

6.1. Published full papers related to the Theses

[1] **Ziegenheim, Sz.;** Peintler, G.; Pálinkó, I.; Sipos, P.:

The kinetics of the precipitation of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, over a wide range of reactant concentrations

Reaction Kinetics, Mechanisms and Catalysis 131 75-88. (2020)

Impact factor: 1.520₍₂₀₁₉₎

[2] **Ziegenheim, Sz.;** Szabados, M.; Kónya, Z.; Kukovecz, Á.; Pálinkó, I.; Sipos, P.:

Differential precipitation of $\text{Mg}(\text{OH})_2$ from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ using citrate as inhibitor – a promising concept for reagent recovery from MgSO_4 waste streams

Molecules 25 5012. (2020)

Impact factor: 3.267₍₂₀₁₉₎

[3] **Ziegenheim, Sz.;** Szabados, M.; Kónya, Z.; Kukovecz, Á.; Pálinkó, I.; Sipos, P.:

Manipulating the crystallization kinetics and morphology of gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ via addition of citrate at high levels of supersaturation and the effect of high salinity

Polyhedron 204 115253. (2021)

Impact factor: 2.343₍₂₀₁₉₎

[4] **Ziegenheim, Sz.;** Slam, Sz.; Szabados, M.; Sipos, P.; Pálinkó, I.:

Effect of Na-citrate on the precipitation of gypsum from highly supersaturated solutions

Melnik M.; Segl'a P.; Tatarko M. (editor): Progressive Trends in Coordination, Bioinorganic and Applied Inorganic Chemistry ISBN: 978-80-8208-014-1

Bratislava, Slovakia: Slovak Chemical Society (2019) 104-110.

6.2. Other full papers published in refereed journals

[1] **Ziegenheim, Sz.;** Varga, G.; Szabados, M ; Sipos, P ; Pálinkó, I.:
Cu(II)Cr(III)-LDH: synthesis, characterization, intercalation properties and a catalytic application

Chemical Papers/Chemická Zvesti 72 897-902. (2018)

Impact factor: 1.246

[2] Varga, G.; **Ziegenheim, Sz.;** Muráth, Sz.; Csendes, Z.; Kukovecz, Á.; Kónya, Z.; Carlson, S.; Korecz, L.; Varga, E.; Pusztai, P.; Sipos, P.; Pálinkó, I.:

Cu(II)-amino acid–CaAl-layered double hydroxide complexes, recyclable, efficient catalysts in various oxidative transformations

Journal of Molecular Catalysis A: Chemical 423 49-60. (2016)

Impact factor: 4.211

6.3. Other full paper published in conference proceeding

[1] **Ziegenheim, Sz.;** Varga, G.; Sipos, P ; Pálinkó, I.:

Ni-aminosav komplexek interkalálása Ca₂Al-LDH rétegei közé

XXXVIII. KÉMIAI ELŐADÓI NAPOK : Program és előadásösszefoglalók

Szeged, Magyarország: Magyar Kémikusok Egyesülete (MKE) 59-63. (2015)

[2] **Ziegenheim, Sz.;** Sztégura, A.; Pálinkó, I.; Sipos, P.:

Kelátképzők inhibíciós hatása gipsz kristályosodására

XLII. KÉMIAI ELŐADÓI NAPOK - Előadásösszefoglalók

Szeged, Magyarország: Magyar Kémikusok Egyesülete Csongrád Megyei Csoportja 154-160. (2019)

Full papers

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