molecules

Electronic supporting information

Differential precipitation of $Mg(OH)_2$ from $CaSO_4{\cdot}2H_2O$ using citrate as inhibitor – a promising concept for reagent recovery from $MgSO_4$ waste streams

Szilveszter Ziegenheim [1,4], Márton Szabados [2,4], Zoltán Kónya [3,5], Ákos Kukovecz [3], István Pálinkó [2,4] and Pál Sipos [1,4,*]

[1] Department of Inorganic and Analytical Chemistry, University of Szeged; Dóm tér 7., Szeged, H-6720 Hungary
[2] Department of Organic Chemistry, University of Szeged; Dóm tér 8., Szeged, H-6720 Hungary
[3] Department of Applied and Environmental Chemistry, University of Szeged; Rerrich Béla tér 1., Szeged, H-6720 Hungary
[4] Material and Solution Structure Research Group, Institute of Chemistry, University of Szeged, Aradi vértanúk tere 1, Szeged, H-6720 Hungary
[5] MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich B. tér 1, Szeged, H-6720 Hungary
* Correspondence: sipos@chem.u-szeged.hu; Tel.: (optional) +36-62-54-4045 (F.L.)

Appendix A

During our scouting experiments a number of additives were tested in systems containing no Mg^{2+} in the reaction of $Na_2SO_4 + CaCl_2 + 2\ H_2O \rightarrow 2\ NaCl + \underline{CaSO_4{\cdot}2H_2O}$ with 0.2 M initial reactant concentrations at pH ≈ 7. The amount of additives used was calculated considering economical motives, and their effectiveness was compared with the half reaction time which was determined as described in chapter 2.1 of the main article. The results are summarized in Table S1.

Table S1. The effect of additives on gypsum precipitation in the reaction of $Na_2SO_4 + CaCl_2 + 2\ H_2O \rightarrow 2\ NaCl + \underline{CaSO_4{\cdot}2H_2O}$ with 0.2 M initial reactant concentrations

Additive	**Applied additive concentration (mmol/L)**	**Half-reaction time - i (min)**	**Standard error of i (min)**	**Remark**
without additive	-	0.75	0.018	
trisodium-citrate(dihydrate)	3.0	**7.61**	0.16	
Na-gluconate	4.0	0.87	0.016	
sucrose	1.5	0.72	0.013	
glycerol	12.0	0.64	0.012	
ethylene-glycol	18.0	0.80	0.017	
polyethylene glycol (PEG 400)	1.4	0.68	0.013	
Na-polyacrylate (MW *ca.* 1200)	3.0	-	-	Exceptionally long reaction time
K-Na-tartarate	2.0	0.98	0.014	
SDS	1.0	1.20	0.017	Foaming
diethylenetriamine penta(methylene phosphonic acid) Na salt, DTPMP	1.2	-	-	No changes in conductivity for six hours, seemingly colloid formed

In these reactions the carboxylate salts were used to achieve near neutral pH. While sodium citrate showed moderate effect, sodium polyacrylate and DTPMP seemed to work remarkably well, increasing the induction period up to six hours. Therefore, these three additives were tested in the target reaction of $MgSO_4 + Ca(OH)_2 + 2\ H_2O \rightarrow \underline{Mg(OH)_2} + \underline{CaSO_4{\cdot}2H_2O}$ with 0.2 M initial reactant concentration, using milk of lime as $Ca(OH)_2$ source. The results were compared similarly as before, and are shown on Table S2.

The effectiveness of both sodium polyacrylate and DTPMP dropped drastically, under these conditions they were less effective than sodium citrate, which lost only part of its effect in this system. This can be explained according to our results found later. Probably the polyacrylate and DTPMP were also coordinating to the surface of the precipitating $Mg(OH)_2$, however this coordination was much stronger than the coordination of citrate, and there was not enough additive left in the mother liquor to effectively inhibit the precipitation of gypsum.

The results suggested that citrate could be effectively used as an inhibitor of gypsum precipitation even in the presence of $Mg(OH)_2$, therefore it was studied in more detail.

Table S2. The effect of some additives on gypsum precipitation in the reaction of $MgSO_4 + Ca(OH)_2 + 2\ H_2O \rightarrow \underline{Mg(OH)_2} + \underline{CaSO_4{\cdot}2H_2O}$ with 0.2 M initial reactant concentrations

Additive	Applied concentration (mmol/L)	Half-reaction time - i (min)	Standard error of i (min)
without additive	-	1.2	0.007
trisodium-citrate(dihydrate)	3.0	3.89	0.020
Na-polyacrylate (MW *ca.* 1200)	3.0	2.50	0.014
diethylenetriamine penta(methylene phosphonic acid) Na-salt DTPMP	1.2	1.84	0.011

Appendix B

With strict control over the reaction conditions, the repeatability of the reactions was found to be satisfactory, however, as the initial temperature of the reaction mixture was not controlled in our reactions, temperature changes in the environment yielded the most significant differences in the kinetics of the reactions. On Figure S1 the variation of conductivity is presented during three parallel reactions of $MgSO_4 + Ca(OH)_2 + 2\ H_2O \rightarrow \underline{Mg(OH)_2} + \underline{CaSO_4{\cdot}2H_2O}$, where the initial temperature of the reaction mixture was 22.0 ± 0.5°C °C

The initial phase of all three reactions are similar, the induction period variation is about 0.5 minutes while the (presumably more accurate) half-reaction time varies within 0.3 minutes between the parallel runs.

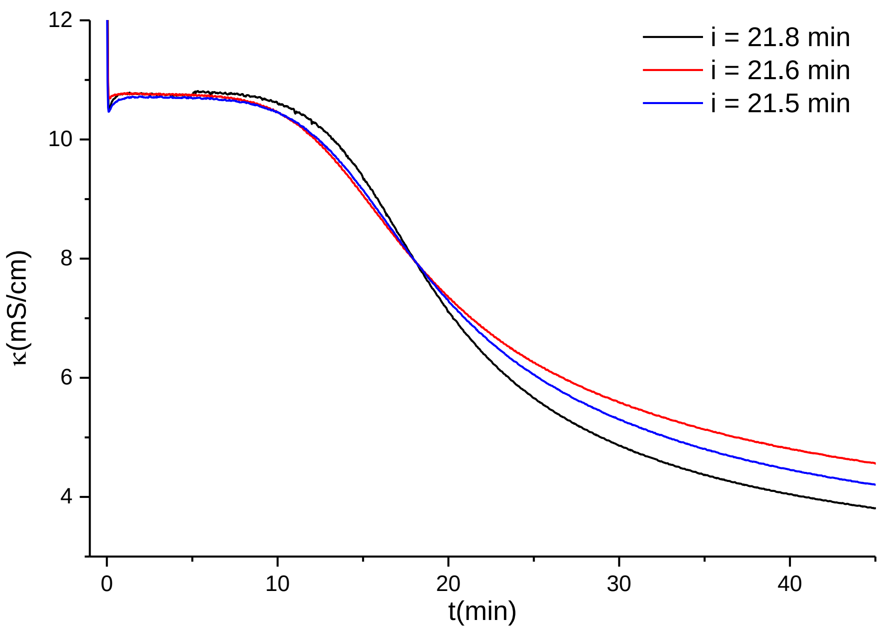

Figure S1. Variation of conductivity during three parallel reactions of $MgSO_4 + Ca(OH)_2 + 2\ H_2O \rightarrow \underline{Mg(OH)_2} + \underline{CaSO_4{\cdot}2H_2O}$ with 0.1 initial reactant concentration and in presence of 1.5 mM citric acid, at 22 °C.