

Supplementary information: How can pH drop while adding NaOH? Formation and transformation of $\text{Mn}_4(\text{OH})_6\text{SO}_4$

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1 Dissolution of the solids

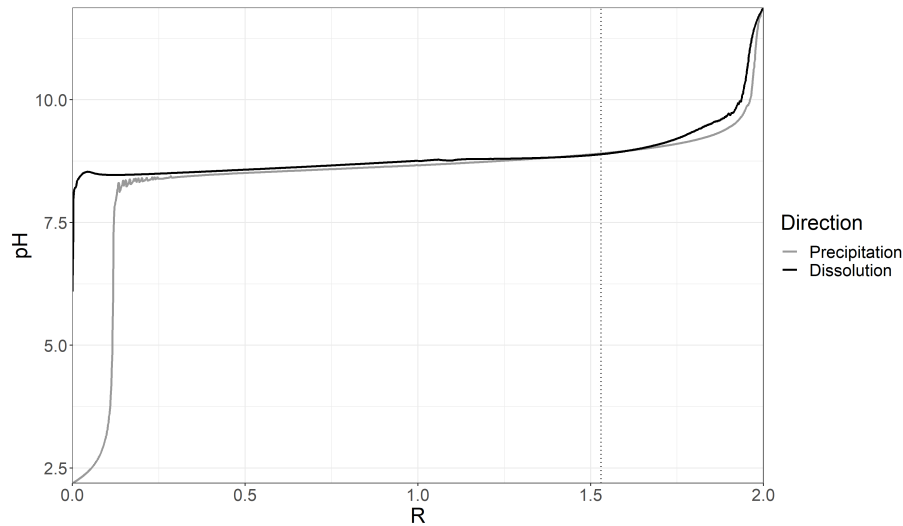


Figure S1: Titration (black) of MnCl_2 (0.4 mol.L^{-1}) solution by NaOH and pH recorded during dissolution using HCl (grey)

Once precipitated using NaOH, the solids using MnCl_2 or MnSO_4 were dissolved using HCl solution (1 mol.L^{-1}). The R ratio is now calculated with:

$$R = 2 - \frac{n(\text{HCl})}{n(\text{Mn}^{2+})} \quad (1)$$

to match with the ratio of OH^- during the precipitation.

Despite the nitrogen flow, some oxidation of the $\text{Mn}(\text{OH})_2$ solid can be inferred in both cases with some black particles observed in the liquids. This explains why the pH drops during dissolution before reaching the $R = 0$ value, as the oxidised manganese does not dissolve in the solution.

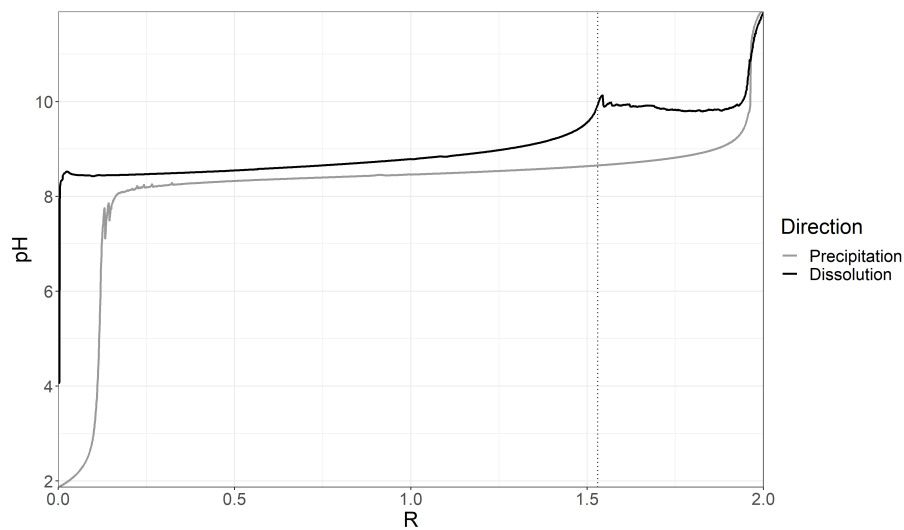


Figure S2: Titration (black) of MnSO_4 (0.4 mol.L^{-1}) solution by NaOH and pH recorded during dissolution using HCl (grey)

2 Drying process of the $R = 1.5$ solid

XRD patterns of the solid obtained from MnSO_4 solution at $R = 1.5$ dried with nitrogen is more complex than the one of the wet sample: along with the unknown pattern attributed to the new $\text{Mn}_4(\text{OH})_6\text{SO}_4$ solid, additional peaks attributed to $\text{Mn}_9(\text{OH})_{14}(\text{SO}_4)_2$ and to Na_2SO_4 appear.

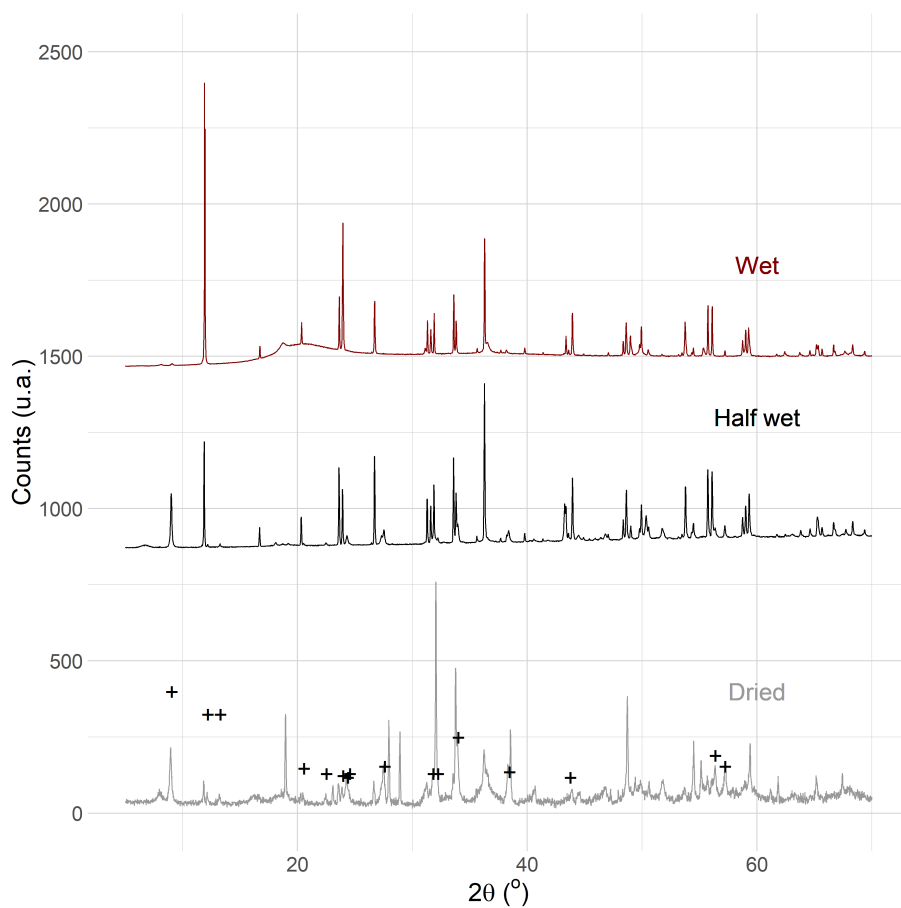


Figure S3: XRD patterns of the solids from the MnSO_4 solution for $R = 1.5$ in various condition: "wet" (top) is taken after synthesis, covered with glycerol (which explains the bump around $2\theta = 20^\circ$). "Half wet" (middle) is taken under nitrogen flow with a RH above 90%. "Dried" (bottom) sample is obtained under pure nitrogen flow. Cross depict the position and intensities reported for $\text{Mn}_9(\text{OH})_{14}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ (JCPDS file 00-018-0788).

N	2θ [obs]	H	K	L	2θ [calc]	obs-calc	Int.[calc]	d[obs]	d[calc]
1	11.912	0	0	2	11.895	0.0171	100.0	7.4237	7.4343
2	16.713	1	0	2	16.718	-0.0050	3.3	5.3003	5.2987
3	20.345	1	1	0	20.346	-0.0011	9.6	4.3616	4.3614
4	23.626	1	1	2	23.632	-0.0054	15.4	3.7627	3.7618
5	23.937	0	0	4	23.920	0.0175	35.8	3.7145	3.7171
6	26.702	1	0	4	26.707	-0.0055	15.3	3.3359	3.3352
7	31.301	2	1	0	31.303	-0.0028	9.9	2.8554	2.8552
8	31.595	1	1	4	31.600	-0.0054	7.2	2.8295	2.8290
9	31.888	2	1	1	31.890	-0.0023	11.8	2.8042	2.8040
10	33.593	2	1	2	33.596	-0.0034	17.2	2.6656	2.6654
11	33.801	2	0	4	33.806	-0.0050	9.3	2.6497	2.6493
12	35.630	3	0	0	35.626	0.0036	1.2	2.5178	2.5180
13	36.279	2	1	3	36.282	-0.0032	32.5	2.4742	2.4740
14	37.685	3	0	2	37.687	-0.0014	0.9	2.3850	2.3849
15	38.183	1	0	6	38.191	-0.0082	0.9	2.3551	2.3546
16	39.772	2	1	4	39.777	-0.0048	1.7	2.2646	2.2643
17	43.366	3	0	4	43.369	-0.0029	5.3	2.0849	2.0847
18	43.592	3	1	1	43.591	0.0015	1.3	2.0746	2.0746
19	43.924	2	1	5	43.927	-0.0027	12.2	2.0597	2.0596
20	47.051	3	1	3	47.052	-0.0005	0.9	1.9298	1.9298
21	48.351	2	2	4	48.351	-0.0009	4.1	1.8809	1.8809
22	48.607	2	1	6	48.610	-0.0028	9.4	1.8716	1.8715
23	48.986	0	0	8	48.970	0.0158	4.9	1.8580	1.8586
24	49.768	4	0	2	49.775	-0.0069	3.3	1.8306	1.8304
25	49.926	3	1	4	49.927	-0.0014	7.7	1.8252	1.8252
26	50.528	1	0	8	50.531	-0.0038	1.5	1.8049	1.8048
27	51.723	3	0	6	51.714	0.0092	0.4	1.7659	1.7662
28	53.172	3	2	1	53.165	0.0061	0.0	1.7212	1.7214
29	53.442	3	1	5	53.455	-0.0132	2.0	1.7131	1.7127
30	53.742	2	1	7	53.744	-0.0016	9.4	1.7043	1.7042
31	54.314	3	2	2	54.310	0.0040	0.9	1.6877	1.6878
32	54.454	4	0	4	54.453	0.0017	2.3	1.6836	1.6837
33	55.720	4	1	0	55.717	0.0027	14.8	1.6484	1.6484
34	56.093	4	1	1	56.088	0.0043	14.6	1.6383	1.6384
35	57.197	4	1	2	57.193	0.0042	1.5	1.6092	1.6094
36	58.742	3	2	4	58.736	0.0067	4.3	1.5705	1.5707
37	59.005	4	1	3	59.005	0.0004	7.1	1.5642	1.5642
38	59.277	2	1	8	59.278	-0.0004	7.3	1.5576	1.5576
39	62.402	0	0	10	62.406	-0.0038	1.1	1.4869	1.4869

Table S1: Hexagonal lattice indexation of the diffractogram of the wet solid obtained from the titration of the MnSO_4 solution at $R = 1.5$

N	2θ [obs]	H	K	L	2θ [calc]	obs-calc	Int.[calc]	d[obs]	d[calc]
1	11.912	0	0	2	11.895	0.0171	100.0	7.4236	7.4343
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4	23.626	1	1	2	23.632	-0.0054	15.4	3.7627	3.7618
5	23.938	0	0	4	23.920	0.0175	35.8	3.7145	3.7171
6	26.702	1	0	4	26.707	-0.0054	15.3	3.3359	3.3352
7	31.301	2	1	0	31.303	-0.0028	9.9	2.8554	2.8552
8	31.595	1	1	4	31.600	-0.0054	7.2	2.8295	2.8290
9	31.888	2	1	1	31.891	-0.0023	11.8	2.8042	2.8040
10	33.593	2	1	2	33.596	-0.0034	17.2	2.6656	2.6654
11	33.801	2	0	4	33.806	-0.0050	9.3	2.6497	2.6493
12	35.630	3	0	0	35.626	0.0036	1.2	2.5178	2.5180
13	36.279	2	1	3	36.282	-0.0032	32.5	2.4742	2.4740
14	37.686	3	0	2	37.687	-0.0014	0.9	2.3850	2.3849
15	38.183	1	0	6	38.191	-0.0082	0.9	2.3551	2.3546
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27	51.723	3	0	6	51.714	0.0092	0.4	1.7659	1.7662
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30	53.742	2	1	7	53.744	-0.0017	9.4	1.7043	1.7042
31	54.314	3	2	2	54.310	0.0040	0.9	1.6877	1.6878
32	54.454	4	0	4	54.453	0.0017	2.3	1.6836	1.6837
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34	56.093	4	1	1	56.088	0.0043	14.6	1.6383	1.6384
35	57.197	4	1	2	57.193	0.0042	1.5	1.6092	1.6094
36	58.742	3	2	4	58.736	0.0067	4.3	1.5705	1.5707
37	59.005	4	1	3	59.005	0.0004	7.1	1.5642	1.5642
38	59.277	2	1	8	59.278	-0.0004	7.3	1.5576	1.5576
39	62.402	0	0	10	62.406	-0.0039	1.1	1.4869	1.4869

Table S2: Trigonal lattice indexation of the diffractogram of the wet solid obtained from the titration of the MnSO_4 solution at $R = 1.5$

3 Characterization of the solids for various R

3.1 Infrared spectroscopy

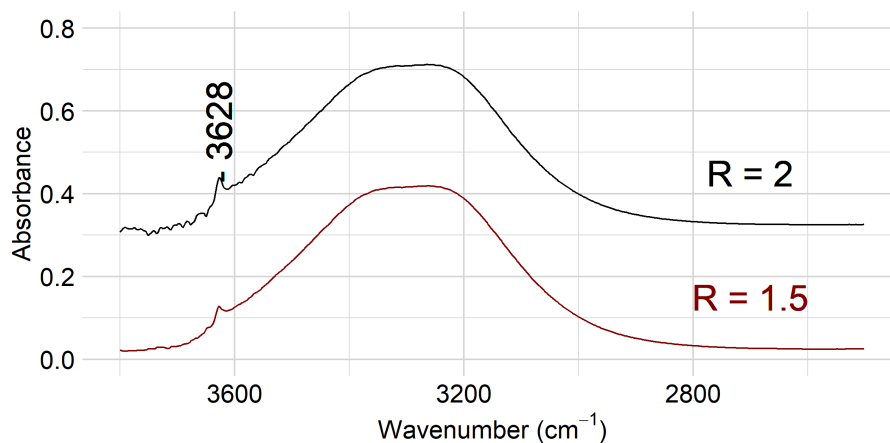


Figure S4: ATR Infrared absorption spectra recorded on the wet solids obtained from MnSO_4 for $R = 1.5$ and $R = 2$ in the range of OH stretching

Figure S4 shows a large absorption between 3000 and 3600 cm^{-1} attributed to water in addition to a small peak at 3628 cm^{-1} attributed to O-H stretching of $\text{Mn}(\text{OH})_2$ in a wet environment. This peak is observed for the $R = 2$ sample but also on the $R = 1.5$ sample, as some peaks attributed to pyrochroite

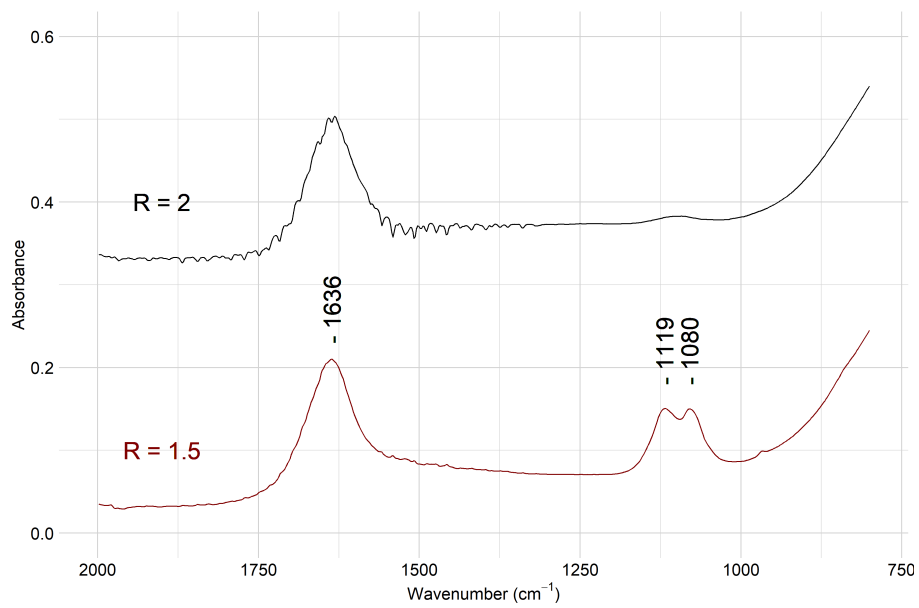


Figure S5: MidIR ATR absorption spectra recorded on the solids obtained from MnSO₄ solution for R = 1.5 and R = 2

3.2 Raman spectroscopy

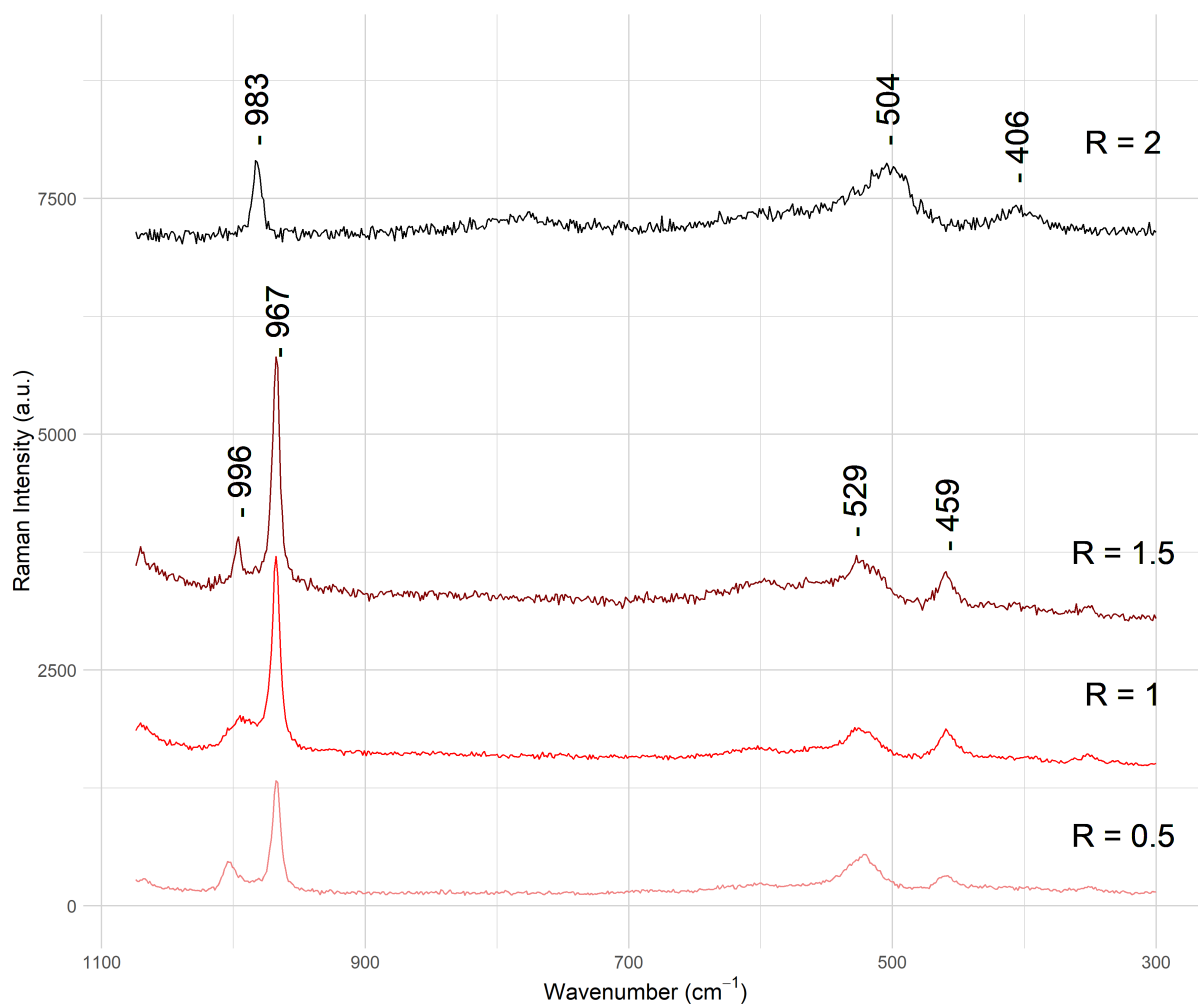


Figure S6: Raman spectra recorded on the solids obtained from MnSO_4 solution for R from 0.5 to 2



Figure S7: MnSO_4 solution after NaOH addition ($R = 1.5$)

4 Color of the solids

The suspension obtained for titration of MnSO_4 solution with NaOH remains white on all the R range from 0 to 2 (see Figure S7).