Appendix D Analysis and geochemical interpretation of inflowing and outflowing solutions in the long-term compaction test

All solutions were analysed with respect to Na, K, Mg, Ca, Cl, and SO4. The charge balance which theoretically should be zero amounts to 0.00 to 0.95 % with respect to moles of charge. Given, that concentrations for six solutes altogether were determined independently, this indicates a good quality of the analyses. Thus, these values were used for the geochemical calculations without further refinement. Analytical compositions in mg/l and mol/kg are given in Table 1-1 and Table 1-2.

The first four solutions were sampled from an experiment run at 30 °C, the second five from an experiment run at 80 °C. The solid rock salt samples as well as the inflowing solutions were kept at the temperatures during the experiments. However, outflowing solutions were allowed to cool down to room temperature. From verbal communication it is known that in some of the samples solid precipitates were observed but no records were taken in which samples they occurred. These precipitates were not brought to solution prior to analysis. In addition, it is unknown, how long the solutions were allowed to evaporate water prior to sampling. Thus, the solution composition given below may not reflect the true composition of solutions.

The solution compositions formed the input for geochemical speciation calculations using PHREEQC, version 3.1.7.9213. The first release from THEREDA (R-01, https://www.thereda.de/de/datenabfrage/ready-to-use-datenbasen?task=downloaddb&format=raw&filename=THEREDA_PIT_PHRC_r01.zip) was used as thermodynamic database. For the experiment it was most important to assess the possibility that the sample of solid rock salt had been altered by dissolution- or precipitation reaction upon contact with the inflowing solution. Thus, the geochemical interpretation is based primarily on the assessment of saturation indices SI, defined as

$$\mathrm{SI}_i = \log\frac{Q_i}{K_i} \tag{2-1}$$

where Q_i s the activity product of species formed by the dissolution reaction of mineral phase i, and K_i is the solubility constant of mineral phase i. $\mathrm{SI}_i = 0$ means that mineral phase i is saturated, $\mathrm{SI}_i < 0$ indicates undersaturation and $\mathrm{SI}_i > 0$ indicates a state of supersaturation.

Table 1-1 Analytical results for solution composition of inflowing and outflowing solutions: mg/l.

Number	Lab. Nr.	TP-Nr.	Remark	Density (DMA 55)	Cl^-	K^+	Ca[tot]	Mg[tot]	Na^+	S[tot]	Sulfat berechnet
				mg/cm3	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
1	**36269**	**1**	**Inflowing solution 15.05.2014**	**1.1992**	**190500**	**63.47**	**762.8**	**34.42**	**125067**	**594**	**1780**
2	36270	1	Outflowing solution I 15.05.2014	1.1435	132000	749.4	1219	241.4	85463	1506	4511
3	36271	1	Outflowing solution II 16.05.2014	1.1949	184000	2346	964.8	734.2	116833	2580	7729
4	36272	1	Outflowing solution III 04.06.2014	1.1344	116000	2823	607.9	907	74263	2745	8225
5	**36273**	**1**	**Inflowing solution 19.11.2014, ~80°C**	**1.2003**	**190000**	**76.83**	**1075**	**47.66**	**122333**	**885.7**	**2654**
6	36274	1	Outflowing solution 0 19.11.2014, ~80°C	1.2051	187000	2588	901.7	863.6	119500	2418	7243
7	36275	1	Outflowing solution I 19.11.2014, ~80°C	1.2057	191500	2852	913.9	971.1	122000	2648	7935
8	36276	1	Outflowing solution II 20.11.2014, ~80°C	1.2062	186500	2896	849.6	1008	119350	2546	7627
9	36277	1	Outflowing solution III 04.12.2014, ~80°C	1.2098	189000	5141	604.2	1775	119000	3864	11577

Table 1-2 Analytical results for solution composition of inflowing and outflowing solutions: mol/kg.

Nummer	**Cl**	**K**	**Ca**	**Mg**	**Na**	**SO4**	**Charge balance**	**Charge balance**
	mol/kg H_2O							error mol_c-%
1	**6.099**	**0.002**	**0.022**	**0.002**	**6.175**	**0.021**	**0.082**	**0.66**
2	4.050	0.021	0.033	0.011	4.044	0.051	0.000	0.00
3	5.882	0.068	0.027	0.034	5.760	0.091	-0.114	-0.95
4	3.512	0.078	0.016	0.040	3.468	0.092	-0.038	-0.52
5	**6.062**	**0.002**	**0.030**	**0.002**	**6.019**	**0.031**	**-0.038**	**-0.31**
6	5.947	0.075	0.025	0.040	5.860	0.085	-0.051	-0.42
7	6.141	0.083	0.026	0.045	6.034	0.094	-0.070	-0.56
8	5.924	0.083	0.024	0.047	5.846	0.089	-0.032	-0.26
9	6.039	0.149	0.017	0.083	5.864	0.137	-0.100	-0.80

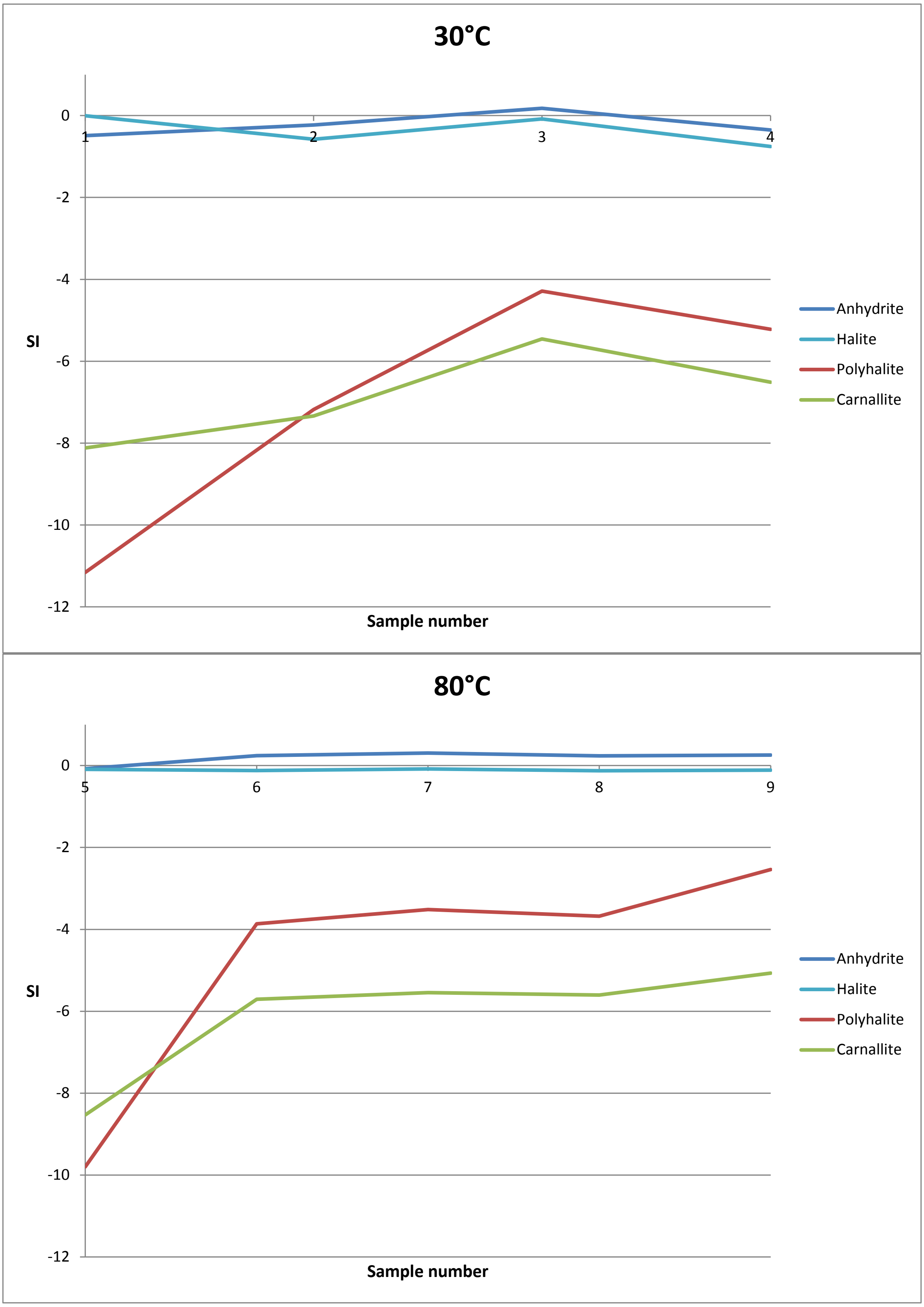

Figure 1-1 Saturation indices of solutions for percolation experiments at 30 °C (top) and 80 °C (bottom). In both cases the first sample on the left marks the inflowing solution

For the further assessment it was assumed that Halite, Anhydrite, Polyhalite and Carnallite constitute the most important mineral phases within the percolated rock salt samples. The calculated saturation indices are given in Figure 1-1.

For the experiment run at 30 °C solution samples 1 to 4 were regarded. Halite and Anhydrite are close to saturation throughout all samples. Saturation indices for Polyhalite and Carnallite increase significantly in samples 2 and 3, while in sample 4 all saturation indices decrease. This delivers the impression that the inflowing solution dissolves Polyhalite within the solid sample, maybe also Carnallite. For the experiment run at 80 °C solution samples 5 to 9 were regarded. Again, Halite and Anhydrite are close to saturation, and Polyhalite and Carnallite saturation increase, leading to a similar conclusion than for the experiment run at 30 °C.

For a qualified assessment about the potential impact which the dissolution of Polyhalite or Carnallite might have had, it would be necessary to know the initial volumetric content of the solid rock salt sample with respect to solid phases in general or Polyhalite and Carnallite in particular. It is estimated that the proportion for Polyhalite expressed in weight percent could be as high as 2 % and for Carnallite about 0.5 %. On the other side Halite with 95 to 97 % and Anhydrite with 0 to 5 % represent the bulk mass of the solid rock salt. For a quantitative estimation of how many solid phases might have dissolved or precipitated it would have been furthermore necessary to know the mass of percolated solution samples.

For the present case it is concluded that the bulk hydraulic properties of the percolated rock salt sample had not suffered significantly from dissolution reactions. However, for future experiments of this kind it is proposed to allow the inflowing solution to equilibrate with a representative subsample of the solid rock salt to be percolated, to perform a thorough analysis of mineral phases within the solid rock salt, and to include precipitated salts in the analyses of the outflowing solutions.