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# Mineral Precipitations and Hydrochemical Evolution of Brines in Graduation Towers

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**Abstract**

The purpose of this study is to examine hydrochemical changes of saline groundwater and precipitation of mineral phases during evaporative graduation processes. Therefore, concentrated brines and mineral precipitates were sampled at four graduation towers with differing evaporation approaches. Solid phase compositions were qualitatively and quantitatively analysed. Hydrochemistry changes of dissolved ion concentrations during successive evaporation was assessed by comparing natural with concentrated brines. PHREEQC was used to simulate sequence and quantity of mineral precipitates. Finally, a prognosis for expected precipitations of a newly built graduation tower was made using PHREEQC modelling.

The identified mineral phases included calcite, aragonite, gypsum and halite in varying proportions. Concentrations of all investigated ions (except bicarbonate) increase, eventually leading to supersaturation and sequential precipitation of evaporite minerals. Modelled saturation indices show that calcite is the first and halite is one of the last precipitating phases

24    at all sites. Further calculated precipitates include the carbonates dolomite, siderite and

25    strontianite; manganese oxide and hematite; and the sulphates baryte, celestine and gypsum

26    which precipitate depending on local hydrogeochemistry and graduation conditions. Calculated

27    precipitation quantities reach a maximum of 48.6 g/L of applied natural brine at an evaporation

28    grade of 90%. After 25 years, the total expected mass of precipitates at the new graduation

29    tower is about 34.4 t for a graduation process up to a salt content of 19%, and about 356 t for a

30    permanent evaporation grade of 90%.

31

32    **Article Highlights**

33    • Except for bicarbonate, concentrations of all ions increase to different degrees.

34    • Mineral precipitations are composed of calcite, aragonite, gypsum and halite.

35    • Modelled precipitation sequence: carbonates, sulphates, chlorides.

36    • Modelled precipitation amounts: max. 48.6 g/L for natural brine at 90% evaporation.

37    • 25 y precipitation forecast for new graduation tower: max. 356 t at 90% evaporation.

38

39    **Keywords**: graduation tower, saline groundwater, concentrated brine, Münsterland

40    Cretaceous Basin, Germany, evaporite mineralogy

41

42    **1   Introduction**

43    The saline groundwater of the Münsterland Cretaceous Basin, which has been pumped and used

44    for several centuries, is concentrated in some health resorts by graduation towers, i.e.,

45    evaporation (Himstedt et al. 1907; Käß and Käß 2008). This leads to a hydrochemical change

46    in the natural brine and to the precipitation of various mineral phases on the brushwood used as

47    precipitation surface. These precipitates are also called thornstone. In the past, graduation

48    towers were mainly used for salt production. Nowadays, they are mostly used for constitutional

49    open-air inhalation because the increasing concentration of brine by graduation creates a

50    seaside-like climate in its surroundings. Graduation towers are present in several health resorts

51    in Germany, but also in Poland and Austria (GLA NRW 1995; Käß and Käß 2008; GD NRW

52    2016; Kalwasińska et al. 2018). Outside the Münsterland Cretaceous Basin, brines in graduation

53    towers are used for balneological purposes at several locations mainly in central and western

54    Germany, e.g., the edges of the Taunus and Spessart mountain ranges, Hesse (Schäffer and Sass

55    2016; Schäffer et al. 2018). Chruszcz-Lipska et al. (2021) statistically assessed 248 medicinally

56    certified natural waters (partly used in graduation towers) in Polish health resorts and discussed

57    the problem of partly elevated boron concentrations. Halaj (2015) analysed the geothermal

58    potential of waters used in some recreational centres in Poland. Until today, graduation towers

59    represent an important contribution to public health. This is underlined by the new construction

60    of the graduation tower in Bad Sassendorf at the edge of the Münsterland Cretaceous Basin

61    (Bredensteiner 2020), which was completed in 2019.

62    Several investigations have been carried out for the two health resorts Ciechocinek and

63    Inowroclaw in Poland, where aerosols are produced by graduation towers (Nienartowicz et al.

64    2011; Krzyaniak-Sitarz 2012; Burkowska-But et al. 2014; Kalwasińska et al. 2018). These

65    studies dealt with the influence of aerosols on the microbiological air quality, the microbial

66    composition of the concentrated brine and the influence on the soils and flora in the area of the

67    graduation towers. Among other things, they show that aerosols have a positive influence on

68    air quality and can also influence soil composition. A correlation was established between the

69    aerosols of the graduation towers in health resorts and a reduced microbiological contamination

70    in the air. The diversity and number of archaeal and bacterial communities increase due to the

71    graduation process in the brine (Nienartowicz et al. 2011; Krzyaniak-Sitarz 2012; Burkowska-

72    But et al. 2014; Kalwasińska et al. 2018). Graduation towers and their surroundings can also

73  host a rich variety of bryophytes and halophytes due to heterogeneous substrates and a stable

74  gradient of salinity in the landscape (Gugnacka-Fiedor 2011).

75  The thornstone that forms from mineral precipitation on the brushwood must be removed if a

76  graduation tower is operated for a long period of time. Otherwise, the functionality will be

77  impaired and the graduation tower may even collapse. This restoration is time-consuming and

78  expensive, as the encrusted brushwood bundles have to be removed and replaced by new ones.

79  So far, no more effective or cheaper method for removing the precipitates has been developed,

80  although research has already been done on a chemical process for removing thornstone

81  (Forbert 2017).

82  There are currently only few investigations on the composition of mineral precipitates

83  (thornstone) at graduation towers in Germany: a study of gypsum crystals forming at the

84  graduation tower in Bad Kösen in eastern Germany (Engelhardt 2015), and some older

85  references such as Roth (1879). To the authors´ best knowledge, there is no published research

86  available on the evolution and quantity of mineral precipitates in graduation towers, which gave

87  rise to the present study.

88  Since the precipitation of the mineral phases at the graduation towers results from concentration

89  increase in the brines due to evaporation of water, the composition of the solid phases together

90  with the hydrochemical change of the natural brines during a graduation process was examined

91  in this work. Besides, the sequence and the amount of the precipitated minerals for the different

92  evaporation steps were determined. The sequence is expected to be the same as for evaporation

93  of seawater (Herrmann et al. 1973). Furthermore, a prognosis was made for the expected

94  amount of mineral precipitation during the next 25 years for a newly built graduation tower in

95  the spa town Bad Sassendorf.

96

97  **2  Study Area**

98  The four investigated sites are located in different parts of the Münsterland Cretaceous Basin

99  (Fig. 1). This is an asymmetrical syncline structure, which consists of a thick Cretaceous

100  sedimentary succession above the Variscan basement (GLA NRW 1995; AD-HOC-AG

101  Hydrogeologie 2016).

102  Hydrogeologically, the Münsterland Cretaceous Basin can be regarded as a more or less closed

103  groundwater basin in the northwestern part of Germany. This can be subdivided into three parts:

104  the shallow pore aquifer is separated from the lower karst aquifer by the almost impermeable

105  marly Emscher Formation (GLA NRW 1995; AD-HOC-AG Hydrogeologie 2016). The shallow

106  pore aquifer is an isolated sand and gravel layer formed above the Emscher formation. This

107  aquifer consists of Santonian sand layers and sands and gravels of the Quaternary. The

108  underlying Emscher formation was formed from Coniacian to Lower Campanian. There is a

109  local hydraulic connection between the upper and lower aquifer only in the peripheral area of

110  the Münsterland Cretaceous Basin because of the absent Emscher formation. The lower aquifer

111  consists of limestone and marlstone, and was formed in the period from Cenomanian to Lower

112  Coniacian. It crops out along the edges of the Cretaceous Basin. In this area, meteoric water

113  infiltrates through local karst formations to form karst groundwater. It emerges from springs

114  along the Emscher formation boundary (GLA NRW 1995; AD-HOC-AG Hydrogeologie 2016).

115  The deep parts of the Cretaceous Basin are filled with saline water, which emerges at its

116  perimeter. This saline water is diluted by mixing with infiltrated meteoric water (GLA NRW

117  1995; Käß and Käß 2008; AD-HOC-AG Hydrogeologie 2016; Wisotzky et al. 2018).

118
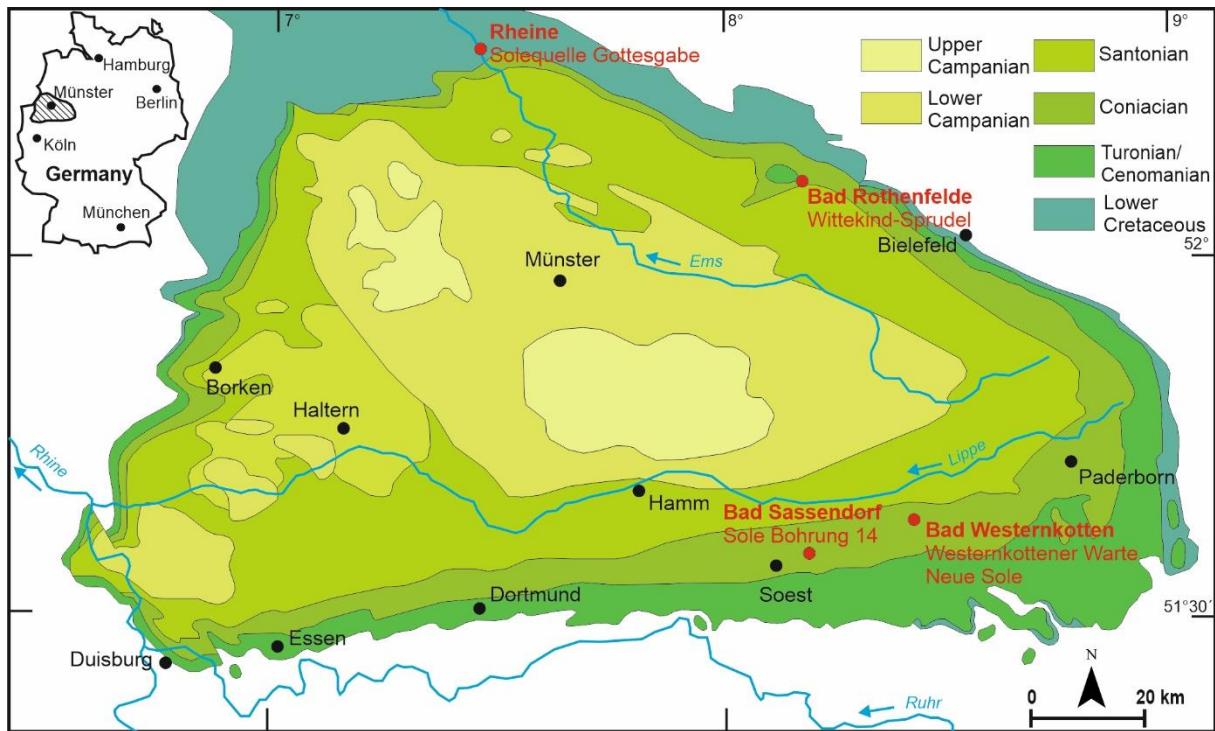


**Fig. 1** Location of the study area in Germany (upper left corner) and geological map of the Münsterland Cretaceous Basin with the studied sites and the names of the extracted and used brines on site in graduation towers (red) (modified after Banning et al. 2013)

The origin of the brine of the Münsterland Cretaceous Basin could not yet be clearly identified. It is assumed to result from several processes such as water-rock interaction, migration and mixing of waters of different origin during the geological development (Grobe and Machel 2002).

On the basis of water analyses for the used natural brines (cf. Fig. 1) and the study of Grobe and Machel (2002), it can be seen that all brines have a higher total dissolved solids content than seawater. Nevertheless, these contents vary considerably depending on the location. Rheine has the lowest value with approximately 38500 mg/L and the natural brine used in graduation tower 1 at Bad Westernkotten site has the highest value with almost 82000 mg/L.

133 The share of $Na^+$ and $Cl^-$ in the total ion concentration is over 90% in each natural brine. Other

134 ions are $Ca^{2+}$, $Mg^{2+}$ and $HCO_3^-$. The concentration of $HCO_3^-$ in Bad Rothenfelde is substantially

135 higher than at the other locations. $SO_4^{2-}$ is found in all brines with the exception of Rheine and

136 shows the highest concentration with a value of 1930 mg/L for the Bad Rothenfelde site.

137 Furthermore, the brines have a high content of free dissolved $CO_2$: 2470 mg/L in the natural

138 brine of Bad Rothenfelde and 1190 mg/L in Bad Sassendorf. The natural brines in Bad

139 Westernkotten have a $CO_2$ concentration of 1225 mg/L.

140 A high content of free dissolved $CO_2$ is typical for the brines from the Münsterland Cretaceous

141 Basin (GLA NRW 1995).

142

143 **3 Materials and Methods**

144 **3.1 Sampling and Analyses**

145 A total of 19 solid phases and 6 concentrated brines were sampled to investigate the

146 precipitation and brines in the graduation towers (Table 1).

147

148 Table 1: Sampled solid phases and concentrated brines for the Bad Rothenfelde, Rheine and

149 Bad Westernkotten sites (✓ sample was taken or ✗ sample was not taken)

|  | Bad Rothenfelde | | | Rheine | Bad Westernkotten | |
|---|---|---|---|---|---|---|
|  | Section 1 | Section 2 | Section 3 |  | Graduation tower 1 | Graduation tower 2 |
| Concentrated brine | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Solid phase white beige reddish | ✓ ✓ ✓ | ✓ ✓ ✓ | ✓ ✓ ✗ | ✓ ✓ ✗ | ✓ ✓ ✓ | ✓ ✓ ✓ |

| greenish | ✘ | ✓ | ✓ | ✘ | ✓ | ✘ |

150

151 Physico-chemical parameters (pH, electrical conductivity, redox potential, temperature,

152 dissolved oxygen) and organoleptic characterization were carried out on site during sampling.

153 The measurement of pH, electrical conductivity and temperature were carried out using a WTW

154 340i handheld pH/Cond Meter. A WTW 340i with a Ag/AgCl probe was used to measure

155 oxidation-reduction potential (ORP, subsequently converted to standard hydrogen electrode

156 (SHE) corrected Eh and pe for PHREEQC modelling), and a WTW Oxi197 was used to

157 measure dissolved oxygen concentrations. Samples for cation and anion analyses were

158 subjected to 0.45 μm filtration on site. Concentrated $HNO_3$ was added to the samples for cation

159 analysis as a stabilising agent. The samples were stored dark and cool until laboratory analysis.

160 Samples were taken from both graduation towers at the Bad Westernkotten site and from the

161 western part of the graduation tower at the location Rheine. In Bad Rothenfelde, brines and

162 solid phases were sampled for each of the three sections of the new graduation tower.

163 The precipitated mineral phases show vertically running colour zones along the brushwood

164 walls (Fig. 2), which served as selection criteria for sampling (Table 1 and Table 2). The

165 coloured zones indicate that the already crystallised phases serve as crystal nucleus upon

166 contact with the supersaturated solution. This nucleation contact leads to overcoming kinetic

167 inhibition, and thus, to precipitation of the corresponding phase (Reznik et al. 2009; Scholz and

168 Kahlert 2018). The concentrated brines were sampled in the lower part of the brushwood walls.

169 Photos of the sampled precipitates were taken on site. These are shown in Fig. 2 for selected

170 solid phases of the graduation tower in Bad Rothenfelde.

171 The sampled precipitates from the graduation towers were pulverised after drying in an agate

172 mortar and analysed by powder X-ray diffraction using PANalytical Empyrean instrumentation.

173 The computer program Match! Version 3.8.3.151 (Putz 2019) with the database COD inorganic

174  compounds only was used for the qualitative evaluation of the diffractograms. The program

175  compares the diffraction pattern of the analysed sample with the reference patterns in the

176  database, whereby the peak intensities and positions are considered. The quantitative analysis

177  was carried out by Rietveld refinement with the program FullProf Version 7.20 implemented

178  in Match! (Putz 2019). The detection limit for X-ray diffraction analysis is different for each

179  mineral and depends, among other things, on the crystal structure and crystallinity. The

180  approximate detection limit is 0.5% to 5% for a total rock analysis of sedimentary rocks

181  (Petschick 2002). Concentrations of anions and cations of the concentrated brines were

182  determined by ion chromatography. For cation analysis, the Dionex DX-500 and for anion

183  analysis, the Dionex ICS-1000 Ion Chromatography System were used. As the ion

184  concentrations were above the load limits of the columns, samples were previously diluted in a

185  ratio of 1:200 to 1:10000. Bicarbonate concentrations were determined by titration with 0.1 M

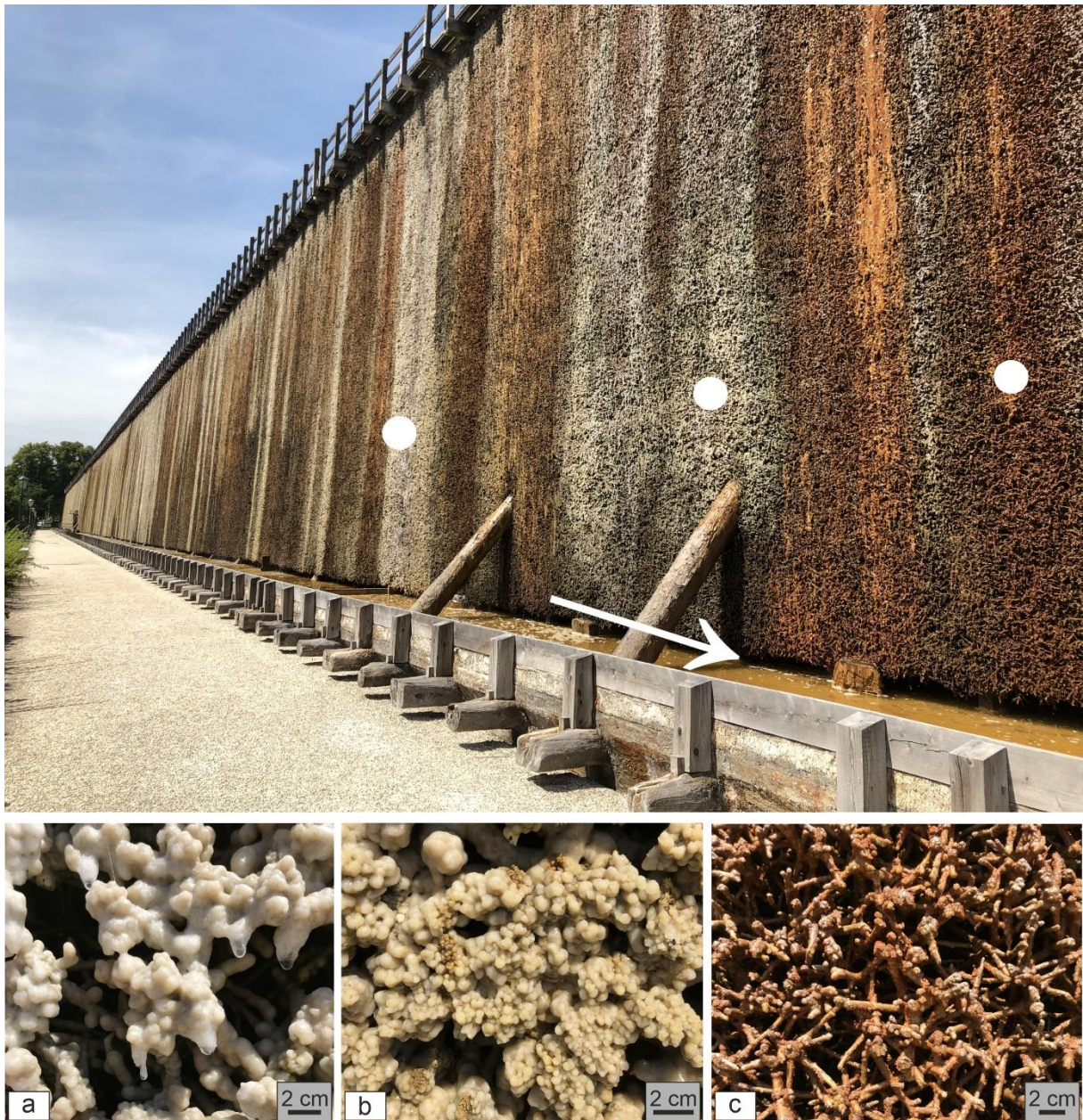186  HCl in the laboratory, directly upon returning from the field.

187

188   **Fig. 2** Top: sampling points for the concentrated brine (white arrow) and for the solid phases

189   (white points). Bottom: (a) white, (b) beige and (c) reddish precipitates of the new graduation

190   tower in Bad Rothenfelde (length 412 m (Käß and Käß 2008) and height 10 m (Elsner 2016)).

191

192   **3.2 Hydrogeochemical Modelling with PHREEQC**

193   The hydrogeochemical computer program PHREEQC Interactive Version 3.5.0.14000

194   (Parkhurst and Appelo 2013) with the database pitzer.dat (a database for the specific-ion-

195    interaction model of Pitzer (Pitzer 1973) as implemented in PHRQPITZ (Plummer et al. 1988)

196    was used to model the processes occurring during a graduation process. Hydrochemical data of

197    the natural brines were applied for the modelling. Bicarbonate concentrations were put in as

198    alkalinity. The pH from the water analysis of Bad Sassendorf was slightly increased from 5.79

199    to 5.98 for modelling to adjust the concentration of dissolved carbon dioxide and bicarbonate

200    to the values of the analyses. As the extent of analysis was not the same for all sites, the Eh

201    value from Bad Sassendorf was used for the unquantified redox conditions of the locations Bad

202    Westernkotten and Rheine. The respective ORP/Eh values were converted to pe and added to

203    the input file. When modelling with the Pitzer database implemented in PHREEQC, pe of the

204    initial solution was used for each modelling step. In contrast to that, when modelling with

205    phreeqc.dat, the pe value entered in the initial solution is overwritten with a new pe for each

206    evaporation step. Therefore, an assumption for pe was made for the modelling with pitzer.dat

207    based on the pe values modelled with the standard PHREEQC database. Because the ionic

208    strength was either already greater than 1 mol/L in the natural brine or reached this value after

209    the first evaporation steps, the Pitzer database was used for modelling (Parkhurst and Appelo

210    2013). The mineral phases and ions, which are not included in the Pitzer database, have been

211    added through the supplement of thermodynamic information from the database wateq4f.dat (a

212    database file derived from WATEQ4F, Ball and Nordstrom 1991). The graduation process was

213    simulated by stepwise evaporation of water using the keyword REACTION. Contact with the

214    atmosphere was simulated by equilibrating with atmospheric oxygen and carbon dioxide

215    (keyword EQUILIBRIUM_PHASES). The mineral phases selected for batch reaction

216    modelling (keyword EQUILIBRIUM_PHASES) were chosen based on the dissolved ions

217    found in the natural brines of the respective location, and allowed to precipitate. These were

218    modelled according to the evaporation sequence of seawater as mineral phases of carbonates,

219    sulphates and halite (Herrmann et al. 1973). Furthermore, the precipitation of the minerals

220    indicated in the literature for thornstone (Roth 1879) was modelled. Amounts of precipitating

221  minerals were read from the output file for the respective evaporation step. The evaporation

222  step of 90% was chosen because halite was detected in the precipitates of the graduation towers

223  and precipitates at this evaporation grade at all locations. Additionally, the evaporation step was

224  selected for a salt content of 18%-19%. In the past, brine was considered as "suitable for

225  boiling" starting from 18%, and was therefore at least concentrated to this salt content (Schulze-

226  Seeger 1988). The salt content was calculated from the modelled sodium content and the

227  modelled density of an evaporation step.

228  In order to convert the total mass of mineral precipitates to kg/d, the amount of natural brine

229  evaporating per day is required. This is based on a daily evaporation of 25000 L of natural brine

230  for hot days for a graduation tower in Bad Dürkheim, SW Germany, with a length of 330 m

231  and a height of 18 m (Pfenning 2014). Out of this, assumptions were made for the investigated

232  graduation towers considering their dimensions: for the graduation tower at the site Rheine

233  (length approx. 35 m (Käß and Käß 2008) and height approx. 7.50 m (Stockmann and

234  Stockmann 1998)), an evaporation of 1105 L/d; for Bad Rothenfelde (length 412 m (Käß and

235  Käß 2008) and height 10 m (Elsner 2016)), an evaporation of 17340 L/d; for Bad Westernkotten

236  graduation tower 1 (length 120 m and height 12.5 m (Käß and Käß 2008)), an evaporation of

237  6313 L/d; and for graduation tower 2 (length 58 m and height 13 m (Käß and Käß 2008)), an

238  evaporation of 3173 L/d.

239  An evaporation of 3072 L/d is assumed for the modelling of the new graduation tower in Bad

240  Sassendorf (length 73 m and height 10 m (Bredensteiner 2020)). In addition, the total amount

241  of mineral precipitation per year and for 25 years is calculated at this location. Since the

242  quantities of the precipitating mineral phases for the forecast are extrapolated to 25 years, the

243  modelling for an annual average temperature of 11 °C (Führer 2020) was carried out for the

244  Bad Sassendorf site.

245

## 4 Results and Discussion

### 4.1 Composition of the Mineral Precipitation

Table 2 shows results of powder X-ray diffraction and the composition of sampled precipitated mineral phases. Solid samples from Rheine consist of the minerals halite and calcite. Precipitates from the locations Bad Westernkotten and Bad Rothenfelde contain the minerals halite, calcite, gypsum and aragonite.

By classifying results according to the colouration of the sampled solid phases (Table 2), it can be seen that the white samples do not contain calcite or aragonite at any site. They are composed of gypsum and halite. No gypsum was found in the reddish samples. These show high calcite contents instead. Consequently, there is a correlation between the increasing intensity of the reddish colour and increasing calcite content. The reddish or brownish colouration of the mineral calcite may be due to the inclusion of organic matter (Martínez-Pillado et al. 2020) or Fe(III) phases (cf. 4.3).

A comparison of the results for the three sections of the graduation tower in Bad Rothenfelde shows that at least one sample for section 1, 2 and 3 contains halite. The amount of gypsum in the samples increases from section 1 to 3. Only one sample of the first section consists of gypsum (100 wt.%). For the second and third section, gypsum is present in 3 samples for each section. The gypsum content in the samples of section 2 is 65 wt.%, 100 wt.% and 32 wt.%, and of section 3, 65 wt.%, 100 wt.% and 100 wt.%. The carbonates calcite and aragonite are detected for sections 1 and 2, but they are not present in the samples of section 3. This trend corresponds to the evaporation sequence of seawater. The carbonates of lower solubility precipitate before the sulphates as evaporation increases. Finally, the highly soluble chlorides precipitate (Herrmann et al. 1973).

270 **Table 2** Results of powder X-ray diffraction (in % by weight) for the white, beige, reddish and

271 greenish samples of the locations Rheine (R), Bad Westernkotten graduation tower 1 (G1) and

272 2 (G2) and Bad Rothenfelde section 1 (S1), section 2 (S2) and section 3 (S3)

| Sample | Identified mineral phases (% by weight) | | | |
|---|---|---|---|---|
| | **Halite** | **Calcite** | **Gypsum** | **Aragonite** |
| **White** | | | | |
| Rheine | 100 | - | - | - |
| Bad Westernkotten G1 | 87.0 | - | 13.0 | - |
| Bad Westernkotten G2 | 48.8 | - | 51.2 | - |
| Bad Rothenfelde S1 | - | - | 100 | - |
| Bad Rothenfelde S2 | 35.5 | - | 64.5 | - |
| Bad Rothenfelde S3 | 34.7 | - | 65.3 | - |
| **Beige** | | | | |
| Rheine | 18.0 | 82.0 | - | - |
| Bad Westernkotten G1 | 3.9 | - | 96.1 | - |
| Bad Westernkotten G2 | 10.9 | 84.9 | 4.2 | - |
| Bad Rothenfelde S1 | 2.8 | 39.4 | - | 57.8 |
| Bad Rothenfelde S2 | - | - | 100 | - |
| Bad Rothenfelde S3 | - | - | 100 | - |
| **Reddish** | | | | |
| Bad Westernkotten G1 | 8.6 | 73.3 | - | 18.1 |
| Bad Westernkotten G2 | 4.3 | 95.7 | - | - |
| Bad Rothenfelde S1 | 12.7 | 72.1 | - | 15.2 |
| Bad Rothenfelde S2 | 5.7 | 80.2 | - | 14.1 |
| **Greenish** | | | | |
| Bad Westernkotten G1 | 33.4 | 66.6 | - | - |
| Bad Rothenfelde S2 | 8.4 | 46.8 | 32.1 | 12.7 |
| Bad Rothenfelde S3 | - | - | 100 | - |

273

274 **4.2 Composition and Evolution of the Concentrated Brine**

275    The pH values of the sampled concentrated brines were between 7.3 and 7.9. Electrical

276    conductivities for 25 °C showed values of approximately 110 to 251 mS/cm, thus, they are in

277    the typical range (over 100 mS/cm) for brines (Wisotzky et al. 2018). The redox milieu can be

278    described as oxidizing for all samples (Wisotzky et al. 2018).

279    A comparison between the concentrations of the constituents of the natural brines and the

280    composition of the concentrated brines shows concentration increases for almost all ions. Only

281    the content of the anion bicarbonate is higher in the natural brine than in the concentrated brine.

282    This is illustrated for selected ions in Fig. 3. The rise in concentration results from the

283    evaporation of water during the graduation process. The difference in increase or possibly even

284    decrease of the ion concentration indicates precipitation of these ions as mineral phases. In the

285    case of bicarbonate, it must also be considered that the increased content of free dissolved

286    carbon dioxide in the natural brine (cf. 2) lead to degassing of $CO_2$ upon contact with the

287    atmosphere. This results in a shift of the carbonate balance and precipitation of carbonates.

288    The differences in concentration changes are reflected by the factors in Table 3. For this

289    purpose, the respective ion concentrations in the concentrated brine were divided by the ion

290    concentrations in the natural brine. Potassium shows the greatest concentration increase for all

291    sites, and thus, it has the lowest probability of precipitating. The ions sodium, magnesium and

292    chloride also show a significant increase in concentrations with a high factor. The

293    concentrations of calcium and sulphate rise by the smallest factor. Section 1 in Bad Rothenfelde

294    is an exception. Here, the factor of sulphate is slightly higher than that of chloride. Bicarbonate

295    shows decreasing concentrations for all sites. The two graduation towers in Bad Westernkotten

296    and sections 2 and 3 in Bad Rothenfelde have the smallest factor (Table 3).

297

298 **Table 3** Calculated factors for the concentration change of ions in the natural brines and

299 concentrated brines for the locations Bad Westernkotten graduation tower 1 (G1) and 2 (G2),

300 Rheine (R) and Bad Rothenfelde sections 1 (S1), 2 (S2) and 3 (S3)

| Location | Cations (mg/L) | | | | Anions (mg/L) | | |
|---|---|---|---|---|---|---|---|
| | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Mg^{2+}$ | $SO_4^{2-}$ | $Cl^-$ | $HCO_3^-$ |
| Bad Westernkotten G1 | 3.8 | 6.8 | 1.9 | 2.8 | 2.4 | 3.1 | 0.1 |
| Bad Westernkotten G2 | 3.9 | 7.1 | 2.5 | 3.7 | 3.5 | 3.8 | 0.1 |
| Rheine | 6.3 | 8.0 | 3.2 | 6.2 | - | 6.1 | 0.4 |
| Bad Rothenfelde S1 | 2.0 | 4.2 | 1.3 | 2.3 | 1.9 | 1.8 | 0.3 |
| Bad Rothenfelde S2 | 3.4 | 4.1 | 2.0 | 3.8 | 2.9 | 3.1 | 0.1 |
| Bad Rothenfelde S3 | 4.1 | 4.6 | 2.2 | 4.6 | 3.6 | 4.2 | 0.1 |

301

302 For the comparison of laboratory results with modelled ion concentrations (Fig. 3), modelled

303 values were read from PHREEQC modelling output files for a selected sodium ion

304 concentration. The respective ion concentrations were read for the modelling step where the

305 $Na^+$ concentration best matches the measured $Na^+$ concentration in the sampled concentrated

306 brines. Therefore, the modelled and analysed $Na^+$ concentrations coincide.

307 Chloride concentrations are also in a good agreement except for Bad Rothenfelde section 1 and

308 Bad Westernkotten graduation tower 1. There, modelled values are higher. This could also

309 explain the positive error of ion balance (5.8 % and 11.9 %, respectively) observed for these

310 samples. The ion balance is below 5 % for all other sampled brines at the graduation towers:

311 3.9 % for section 2 and –0.7 % for section 3 in Bad Rothenfelde, 2.6 % for the graduation tower

312 2 in Bad Westernkotten and 1.4 % in Rheine.

313 For $Ca^{2+}$, $Mg^{2+}$, $K^+$ and $SO_4^{2-}$, laboratory results partly show different values compared to the

314 modelled concentrations (Fig. 3). These deviations have no obvious regularity regarding the

315 type of ion or location and have both positive and negative signs. In Fig. 3, it can be seen that

316    bicarbonate concentrations deviate considerably from the modelled values: modelled

317    concentrations are significantly lower for all sites.

318    Modelling atmosphere contact plays an essential role here, because it leads to a significant

319    carbon dioxide degassing already at the beginning of the modelling. This could explain the

320    significantly lower bicarbonate concentrations by modelling. Besides, it should be taken into

321    account that precipitation kinetics were neglected in the modelling, leading the model to assume

322    that chemical equilibrium has already been established. However, a supersaturated solution for

323    a mineral phase can also be obtained over a longer period of time by a slow precipitation

324    reaction (Merkel and Planer-Friedrich 2008). Its inobservance in the model could lead to

325    overestimation of carbonate precipitation. Furthermore, it should be noted that when modelling

326    with PHREEQC, weather-dependent changes (e.g., temperature fluctuations and dilution by
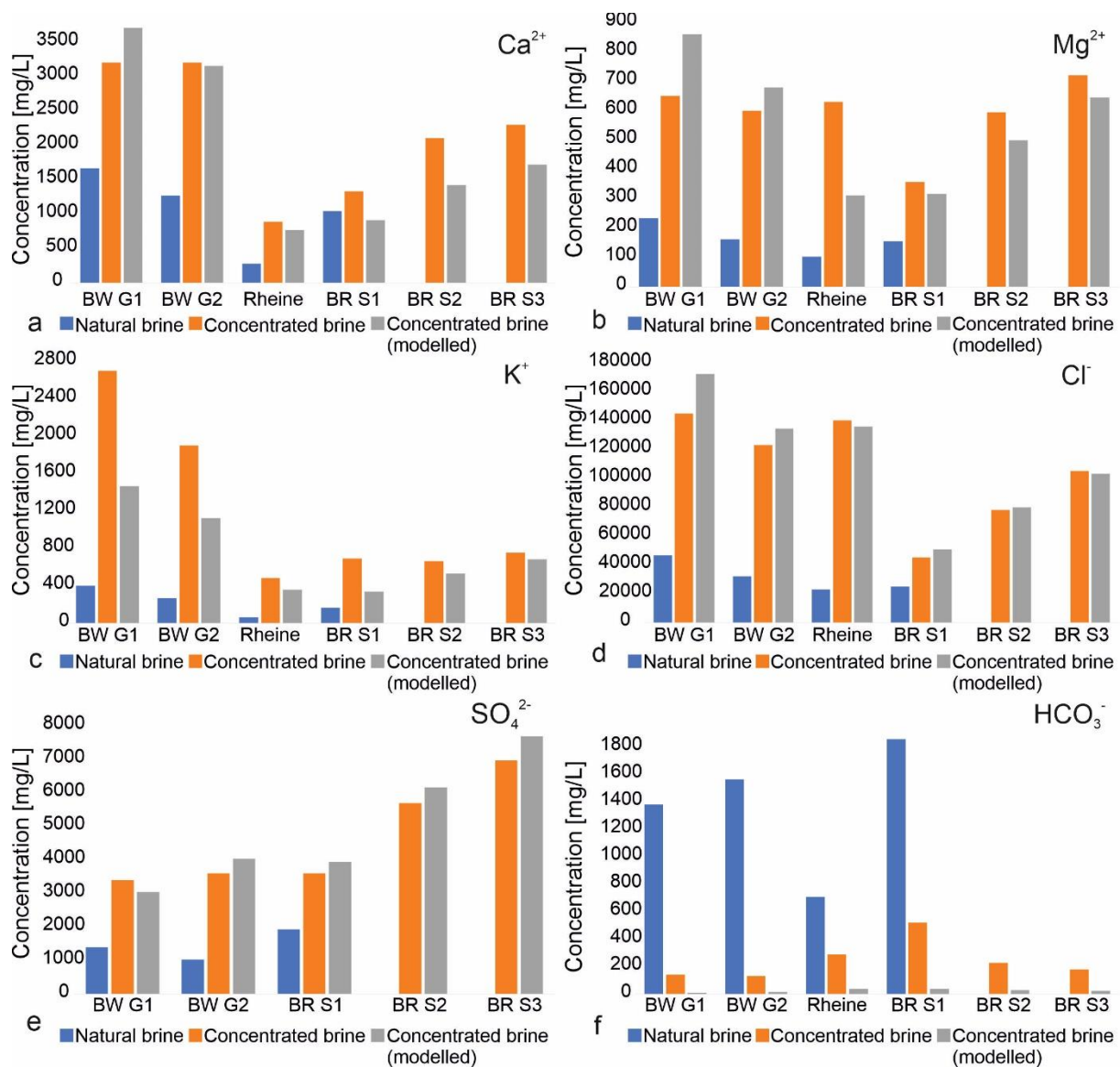
327    rain) are not included.

328

**Fig. 3** Concentration change of calcium (**a**), magnesium (**b**), potassium (**c**), chloride (**d**), sulphate (**e**), and bicarbonate (f) in the natural brines and the concentrated brine (own samples and modelled with PHREEQC) for the locations Bad Westernkotten graduation tower 1 (BW G1) and 2 (BW G2), Rheine and Bad Rothenfelde section 1 (BR S1), section 2 (BR S2) and section 3 (BR S3)

**4.3 Saturation State of Mineral Phases and Mineral Precipitation Quantities**

In Fig. 4, the courses of the modelled saturation indices (SI) are illustrated with increasing evaporation for a graduation of the natural brine in Bad Rothenfelde and Bad Westernkotten

338 graduation tower 1. Except for aragonite, all minerals reach an SI-value of 0 at different

339 evaporation rates. Manganese dioxide, hematite and calcite already precipitate at the beginning

340 of the modelling. Precipitating Fe(III) phases may therefore play a role in thornstone

341 colouration, but quantitatively appear to be of lower importance compared to the spa site Bad

342 Nauheim near Frankfurt, for example (Schäffer 2018). After that, the sulphates barite, celestine

343 and gypsum precipitate. The minerals siderite, dolomite and halite precipitate at the end.

344 Figure 4 reflects the precipitation of the ferrous carbonate siderite for the Bad Westernkotten

345 site. In contrast to that, the ferric oxide hematite precipitates in Bad Rothenfelde. Besides, the

346 sulphate, baryte reaches an SI value of 0 in Bad Rothenfelde, which results from the different

347 extent of analysis data for the different locations: for the sites Rheine and Bad Westernkotten,

348 the mineral phases including Ba, Fe(III) and Mn(III) as stoichiometric constituents were not

349 modelled due to the absence of total iron, manganese and barium values. Therefore, the

350 precipitation of hematite is more probable, because both siderite and hematite were considered

351 in the modelling for the site Bad Rothenfelde. The modelling results of the saturation indices

352 for the Bad Rothenfelde site show the precipitation of the same mineral phases as for Bad

353 Sassendorf. However, iron and manganese are removed from the natural brine in Bad

354 Sassendorf by treating it before it is used in the new graduation tower. Therefore, the mineral

355 phases nsutite and hematite are not likely to precipitate in considerable amounts at the

356 graduation tower in Bad Sassendorf. Modelled SI of the second graduation tower in Bad

357 Westernkotten have a similar course as for the first one. The natural brine used in Rheine has a

358 low Mn(II) and sulphate content. Because of this, the precipitation of sulphates and Mn(II)-

359 containing minerals was not included in the modelling. Instead, the carbonate strontianite is

360 likely to precipitate in Rheine. With the exception of aragonite, the mineral phases detected in

361 the diffractograms (Table 2) were successfully simulated in the modelling approach. The

362 absence of aragonite in modelled precipitates is probably due to its higher solubility in

363 comparison to calcite, leading to preferential precipitation of the less soluble $CaCO_3$

364     polymorph, and the highly complex interplay of parameters controlling $CaCO_3$ polymorph

365     precipitation (Jones 2017) which cannot be considered in total by the modelling approaches

366     used here.

367     Overall, the modelled precipitating mineral phases (Fig. 4) and the calculated factors for the

368     hydrochemical evolution during the graduation process (Table 3) are in agreement.

369     Precipitation of calcite already occurs at the beginning of the modelling which is one

370     explanation for the only small increase in $Ca^{2+}$ concentration and the strong decrease in $HCO_3^-$

371     concentration. The small factor for $SO_4^{2-}$ increase corresponds to the precipitation of the

372     sulphates baryte, celestine and gypsum. The significant increase of $Na^+$, $Mg^{2+}$ and $Cl^-$

373     concentrations is caused by the late precipitation of halite and dolomite at high evaporation

374     stages. Observed hydrochemical signatures and evaporite sequences are in general agreement

375     with the evolution of sabkha brines in Tunesia and playa brines in Iran and Afghanistan studied

376     and modelled by Nasri et al. (2015) and Kaseb et al. (2020), respectively, with the exception of

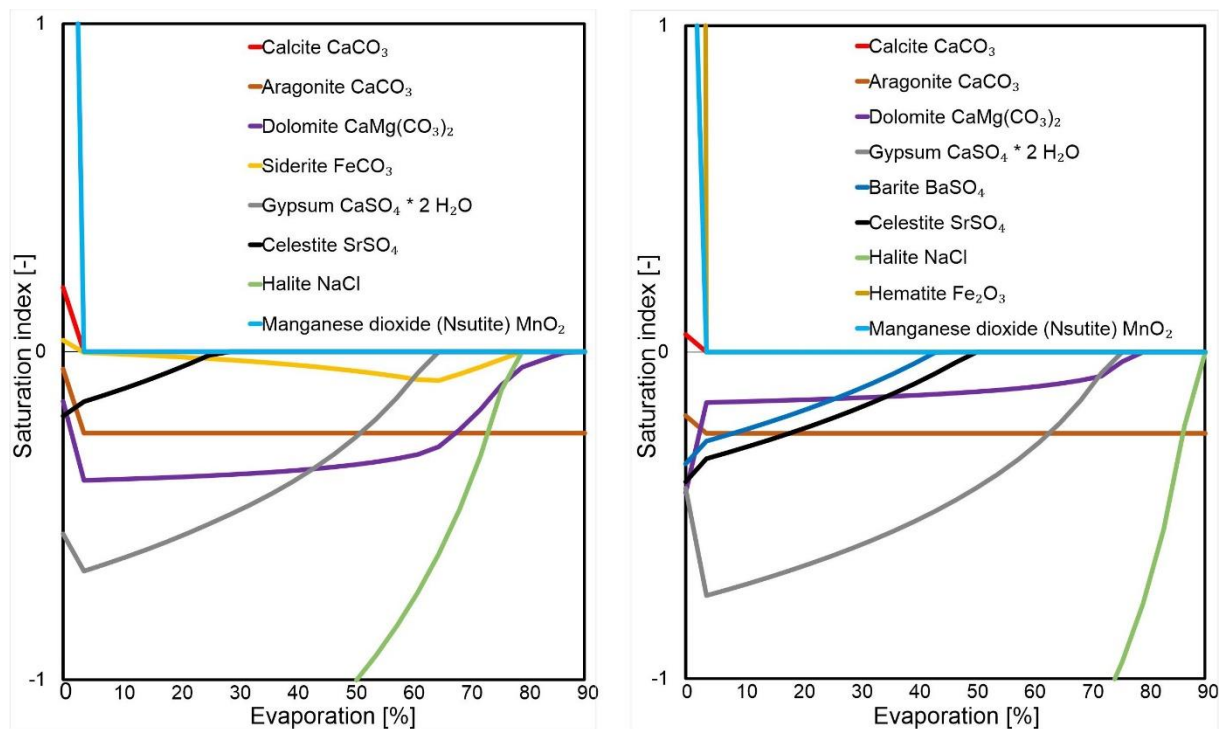377     dolomite which appears to precipitate substantially earlier in desert environments.

**Fig. 4** Saturation indices (modelled with PHREEQC) of the precipitating mineral phases and the mineral aragonite with increasing evaporation for the locations Bad Westernkotten graduation tower 1 (left) and Bad Rothenfelde (right)

The expected amounts of mineral precipitation for the graduation of natural brines in the graduation towers are specified in Table 4. Modelled precipitation quantities are listed for a salinity of 18/19% and 28/29%, respectively. Results for the sums of mineral precipitates at the different sites show substantial differences. The reason for this is the different composition of the applied natural brines, and differences in the graduation processes.

The brine of Bad Rothenfelde has the largest total amount of precipitates (2.14 g/L) and Rheine the smallest total amount (0.56 g/L) for the salinity of 18/19%. In contrast to that, both graduation towers in Bad Westernkotten show values up to 48.6 g/L for total precipitation at a salinity of 28/29%, which consists of approx. 90% halite. Corresponding to the higher bicarbonate concentrations in the natural brines of Bad Rothenfelde and Bad Westernkotten (Fig. 3), carbonates represent the main component of the precipitation quantity for these sites

394 at lower evaporation grades. At higher evaporation, gypsum forms the main part of the

395 precipitates besides halite. The only exception is the low-sulphate natural brine in Rheine.

396 Besides, the ratio of calcite to dolomite shifts within the carbonates for a higher evaporation.

397 This is probably due to higher relative accumulation of $Mg^{2+}$ in concentrated brine as compared

398 to $Ca^{2+}$ (Table 3) which is partly removed from solution by gypsum precipitation at higher

399 evaporation grades.

400 The modelled precipitating mineral quantities for an evaporation of 90% can be regarded as

401 maximum values, since the maximum obtainable salt concentration of 27% for a moderate

402 climate zone mentioned in Kalwasińska et al. (2018) is already exceeded. Nevertheless, halite

403 only reaches saturation starting from an evaporation of 90% for Rheine und Bad Rothenfelde

404 (Fig. 4) and was detected in the sampled precipitates for these two sites (Table 2). Additionally,

405 the modelling neglected the formation of aerosols, which would probably reduce precipitation

406 quantities and might be an aspect of future research.

407 Modelled precipitation amounts for carbonate phases may be questioned, because the deviation

408 between modelled and measured concentrations for bicarbonate is remarkably high (Fig. 3).

409 However, modelling results for carbonate-dominated earlier precipitation stages fit XRD results

410 for samples probably representing such stages very well.

411 The precipitation of Fe(II) and Fe(III) containing minerals such as siderite and hematite depends

412 on the respective iron concentrations which in turn is controlled by pH and pe. The same applies

413 analogously to manganese. As an assumption was made for pe during modelling and the

414 thermodynamic data for the iron and manganese ions were added from another database (cf.

415 3.2), the precipitated quantities of Fe- and Mn-containing mineral phases need to be considered

416 an estimate, but are not likely to play a major role in total precipitate compositions anyway.

417

418 **Table 4** Converted results of the precipitated mineral quantities for the indicated evaporation

419 degrees modelled with PHREEQC

| Graduation degree, expressed as… | Rheine | | Bad Rothenfelde | | Bad Westernkotten graduation tower 1 | | Bad Westernkotten graduation tower 2 | |
|---|---|---|---|---|---|---|---|---|
| …Evaporation [%] | 83 | 90 | 79 | 90 | 61 | 90 | 76 | 90 |
| …NaCl content in the brine [%] | 19 | 29 | 18 | 29 | 18 | 28 | 19 | 28 |
| Amount of precipitating minerals [g/L] | | | | | | | | |
| Calcite | 0.17 | 0.10 | 1.32 | 0.52 | 1.16 | 1.12 | 1.30 | 1.13 |
| Dolomite | 0.38 | 0.44 | 0.18 | 0.93 | - | 0.04 | - | 0.16 |
| Siderite | 0.01 | 0.01 | - | - | - | $2\times10^{-3}$ | $5\times10^{-3}$ | $9\times10^{-3}$ |
| Gypsum | - | - | 0.59 | 2.26 | - | 2.17 | 0.01 | 1.42 |
| Barite | - | - | $3\times10^{-5}$ | $3\times10^{-5}$ | - | - | - | - |
| Celestite | - | - | 0.04 | 0.05 | 0.12 | 0.16 | 0.12 | 0.14 |
| Hematite | - | - | 0.01 | 0.01 | - | - | - | - |
| Manganese dioxide (Nsutite) | - | - | $6\times10^{-4}$ | $6\times10^{-4}$ | $5\times10^{-4}$ | $5\times10^{-4}$ | $5\times10^{-4}$ | $5\times10^{-4}$ |
| Halite | - | 2.65 | - | 6.19 | - | 45.1 | - | 18.8 |
| Total precipitates [g/L] | 0.56 | 3.20 | 2.14 | 9.96 | 1.28 | 48.6 | 1.44 | 21.7 |
| Assumed evaporation amount of natural brine [L/d] | 1105 | | 17340 | | 6313 | | 3173 | |
| Total precipitates [kg/d] | 0.62 | 3.54 | 37.1 | 173 | 8.08 | 307 | 4.57 | 68.9 |

420

**4.4 Prognosis for the Newly Built Graduation Tower in Bad Sassendorf**

A forecast was made for the expected amount of mineral precipitates for the next 25 years for the newly (in 2019) built graduation tower in Bad Sassendorf. Saturation indices of considered mineral phases have a similar course as those for the location Bad Rothenfelde (Fig. 4). The precipitated solid phases and their quantities are listed in Table 5. Because iron and manganese are removed before the natural brine is used in the new graduation tower in Bad Sassendorf, the minerals hematite and nsutite are not likely to precipitate in considerable amounts, and therefore, were not considered in the calculation of the total precipitation quantities and the extrapolation to 25 years. A total amount of mineral precipitates of 1.23 g/L inserted natural brine is obtained for an evaporation of 69%. This total quantity consists of 90% calcite. The total amount of precipitates increases to 37.9 g/L for an increased evaporation of 90% and consists of 93% halite. After one year, a precipitation quantity of 1.4 t can be expected for an evaporation of 69%. This value rises to 34.4 t after 25 years. The precipitation quantities for an evaporation of 69% are projected for 365 days over a year in Table 5. This is based on the assumption that a salinity of 19% is reached after only one day. Afterwards, the quantities are extrapolated for 25 years. The brine can be concentrated in a graduation tower to a maximum salt concentration of 27% within 3 days under good weather conditions (Kalwasińska et al. 2018). This 27% is achieved for the natural brine in Bad Sassendorf at an evaporation rate of 90%. Therefore, the values given for this evaporation can be regarded as the maximum precipitation quantity to be expected (Table 5). Considering the three-day period required for a salt concentration of 27% (evaporation of 90%), the quantities were projected for one year and finally for 25 years.

444    **Table 5** Converted results of the precipitating mineral quantities up to an evaporation of approx.

445    69% and 90%, modelled with PHREEQC for the new graduation tower in Bad Sassendorf

| Graduation degree, expressed as… | Amount of precipitating minerals | | | | | |
|---|---|---|---|---|---|---|
| | [g/L] | | [g/L/yr] | | [kg/L/25 yr] | |
| …Evaporation [%] | 69 | 90 | 69 | 90 | 69 | 90 |
| …NaCl-content in the brine [%] | 19 | 27 | 19 | 27 | 19 | 27 |
| Calcite | 1.13 | 0.89 | 413 | 108 | 10.3 | 2.70 |
| Dolomite | - | 0.23 | - | 28.0 | - | 0.70 |
| Barite | $2\times10^{-4}$ | $1\times10^{-4}$ | 0.07 | 0.01 | $2\times10^{-3}$ | $3\times10^{-4}$ |
| Celestite | 0.10 | 0.15 | 36.5 | 18.3 | 0.91 | 0.46 |
| Gypsum | - | 1.21 | - | 147 | - | 3.68 |
| Halite | - | 35.4 | - | 4307 | - | 108 |
| Total precipitates | 1.23 | 37.9 | 450 | 4608 | 11.21 | 116 |
| Total precipitates for an evaporation of 3072 L/d natural brine | 3.78 kg/d | 116 kg/d | 1.4 t/yr | 14.2 t/yr | 34.4 t/25 yr | 356 t/25 yr |

446

## 5   Conclusions

448    During a graduation process, the evaporation of water leads to concentration of the natural brine

449    and related precipitation of different mineral phases. An analysis of the precipitates showed

450    they are composed of the minerals calcite, aragonite, gypsum and halite. White samples contain

451    gypsum and halite. No gypsum was detected in reddish samples, but high calcite contents were

found. A connection between increasing calcite contents and the intensity of the reddish colouring is discernible.

Hydrochemical brine evolution is assessed by comparing the changes in ion concentrations of the natural brine and the concentrated brine. Only the concentration of bicarbonate decreases with increasing evaporation. The concentration increase of the other ions varies, indicating that some ions are precipitated as mineral phases. Calcium and sulphate show smallest relative accumulation in the concentrated brine. This and the significant bicarbonate decrease is explained, among other things, by the precipitation of carbonates and sulphates. Potassium has the most pronounced concentration increase, it is contained neither in the XRD detected mineral phases nor in the modelled precipitates.

Modelled saturation indices indicate calcite precipitation already at the beginning of the modelling. Sulphates only precipitate at a higher evaporation degree of about 28% and chlorides only reach saturation at an evaporation degree of more than 78%. XRD results for three successive sections at the Bad Rothenfelde graduation site are in good agreement with this order of precipitation.

The precipitating mineral quantities modelled with PHREEQC show that a total precipitation between 0.62 kg/d and 37.1 kg/d occurs at a graduation process up to 18-19% NaCl with the carbonates calcite and dolomite as main components. Precipitation amounts are between 3.54 kg/d and 307 kg/d for a high evaporation rate of 90% and consist mainly of halite.

For the modelled prognosis of the new graduation tower in Bad Sassendorf, a total precipitation amount of about 34.4 t for a graduation process up to 19% salt content is predicted, and about 356 t if a permanent evaporation grade of 90% is considered. The applied modelling approach can provide an estimate of the expected amount and sequence of mineral precipitations depending on the quantity of evaporated water.

476 Large quantities of precipitating evaporite minerals can impair the functionality of a graduation

477 tower. These deposits have to be removed in time consuming and cost intensive procedures.

478 Therefore, besides contributing to a better understanding of hydrogeochemical and

479 mineralogical processes during brine concentration and thornstone formation, this study

480 showed that the applied modelling approach can be a powerful tool to aid in graduation tower

481 planning and management in spa towns.

482

483 **Authors' contributions**

484 Conceptualization: Andre Banning, Laura-Jane Ostwald; Methodology: Andre Banning, Laura-

485 Jane Ostwald; Formal analysis and investigation: Laura-Jane Ostwald; Writing - original draft

486 preparation: Laura-Jane Ostwald; Writing - review and editing: Andre Banning; Resources:

487 Andre Banning; Supervision: Andre Banning

488

489 **Declarations**

496

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503    Mammen (RUB) for carrying out powder X-ray diffraction measurements.

504

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