Przegląd Solny / Salt Review, 2015, **11:** 98–108

The graduation tower of Bad Kösen (Germany) – its history and the formation of thornstone

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Abstract

Graduation towers are wooden frameworks stuffed with blackthorn bundles. Brine is pumped to the top of the towers. Afterwards, the brine flows down on the bundles and drops are formed upon impact with the twigs and branches. The technique results in high evaporation rates due to the enormous surface of the drops, the high air velocity on the drop surfaces, and the dependence of the vapor pressure on the radius of a brine surface. Minerals precipitate as so-called thornstone. Gypsum crystals mostly radiate out from the twigs of the bundles and the surface of the thornstone is comparable with sandroses. A rounding of the crystals is caused by dissolution processes. Samples from the graduation tower in Bad Kösen, Germany, show that the thornstone contains layers of foreign particles, fine-grained carbonates, and sometimes traces of halite. Strontium illustrates that the brine could be evaporated until halite saturation. Due to its high efficiency, the technique made it possible to produce table and pickling salt during the 18th and 19th century, even from low-concentrated brines and under the climatic conditions in Austria, Germany, Poland, and Switzerland.

Nowadays, graduation towers are centres of recreation in spa towns. The particle inclusions of the thornstone demonstrate the cleaning of the air. Water evaporation cools the air and the resulting microclimate with fresh, salty aerosols is used for therapeutic inhalations. The trickling of brine creates a relaxing atmosphere and the brines can be used for bath therapies. In addition, the towers are technical monuments, tourist attractions, and event locations. Visitors have the opportunity to learn principles of solution mining and salt processing.

Key words: brine, evaporation, graduation tower, gypsum, inhalation, thornstone, salt

Introduction

In Germany, Poland, and Austria salt deposits are located close to the earth's surface and come into contact with groundwater. For several hundred years, the resulting brines have been accessed through boreholes, shafts, and in underground drifts for the production of table and pickling salt. In addition, salty springs were used for extraction. The salt content of many of these brines is comparable to seawater, and the low contents of sodium chloride necessitates a concentration of the solutions. Furthermore, the calcium content of calcium-containing salts, such as calcium sulphate, has to be reduced for the production of pure salt.

A historic technique for the production of salts is the evaporation of water in basins of saltworks, also called salt evaporation ponds or salterns. This technique is not applicable in Central Europe because the time periods of low relative air humidities are too short. Consequently, a two-stage process was developed that consists of a pre-concentration in graduation towers, occasionally referred to as thorn houses, and the final salt extraction by boiling. Due to the successful operation, graduation towers were built in many other countries. For example, in Australia towers were used to produce salt by a 'thorn graduation process' of seawater (ROGERS 1984). However, as a result of new techniques developed in industrial salt extraction and processing, the operation of the graduation towers became unprofitable. Since then, the towers have been used to increase the air humidity and to enrich the air with brine drops for spa treatments (cf. Langer 2014, Pawlikowska-Piechotka & Piechotka 2014). The air is cleaned from particles, and due to water evaporation, the temperature is decreased. The fresh breezes moisten the air passages and are used for inhalation therapies (e.g. Burkowska-But et al. 2014). The brines are used for relaxing baths and bath therapies, for example in the case of rheumatism and skin diseases. This way, it was possible to open new opportunities for halotherapy, which has been used throughout the world for ages. The imposing towers are tourist attractions, technical monuments, and are suitable for cultural events. All these were reasons enough to design and build new small- and large-scale towers taking into account the specific requirements of halotherapy.

The knowledge of the interactions between water evaporation, the kinds and amounts of salt precipitation, and the changes in brine composition with the degree of evaporation, are relevant for the processing of salts and the evaluation of the genesis of natural salt deposits. Many geoscientific models are based on research results gained in salt ponds, however, investigations of graduation towers can be used to verify the findings and to expand the models. Moreover, the salt precipitations of graduation towers can be used to detect changes of the earth atmosphere (e.g. Oczkowski et al. 1996). This paper describes the functioning and operation using the graduation tower of Bad Kösen as an example because the construction of this tower is similar to many old facilities. One focus of the investigations was the mineral precipitation on the blackthorn bundles of the tower walls. These precipitations are called thornstone and brine or saline stone. Samples of the brine and the thornstone were subjected to chemical analysis. The mineral content and the thornstone structures were determined. The results were evaluated in context with climate data to obtain information about the conditions of thornstone formation.

Basic Structure And Operation of Graduation Towers

The technique to increase the evaporation rate by the formation of drops (curvature effect according to the KELVIN equation) was first used in Lombardy in about 1400. In the 16th century, brines were distributed over large straw-filled boxes. Over time, the size of these structures increased and walls with straw bundles were constructed. North of the Alps the first "Leck" or "Lepperwerk" was built in Bad Kissingen (Germany) in 1563. New plants were increasingly being built. A famous example is the plant of Nauheim (1579), which was initiated by the physician Matthäus Meth (Hermbstädt 1815). Approximately in the year 1700, the straw was replaced by blackthorn, which allows the collection of particle-free brines (Emons & Walther 1982). The shrub of blackthorn is traditionally used in Europe to make hedges, because of its woody thorns and thick brambles. The invention of the graduation towers dates back to Joachim Friedrich Freiherr von Beust (1697 – 1771), who initiated the construction of the facilities in Bad Salzungen (1740) and Bad Salzuflen (1767) (e.g. Vogel 2008). The technique was refined by Jacob Sigismund Waitz von Eschen. His activities covered the expansion of the royal Prussian saline in Salzelmen near Schönebeck (Elbe) to the largest state owned enterprise with a 1,837-m-long graduation tower. The largest graduation tower, which is still in use, was designed by Jakub Graff, a former professor at the Mining Academy in Kielce. It is located in Chiechocinek, Poland, and is about 16 metres high and 1,742 metres long. The name of the towers originates from the graduation or marking of hydrometers to the scale of Antoine Baumé, which allows determining the density of fluids and the percent by mass of sodium chloride. Fig. 1 shows basic elements of a graduation tower.

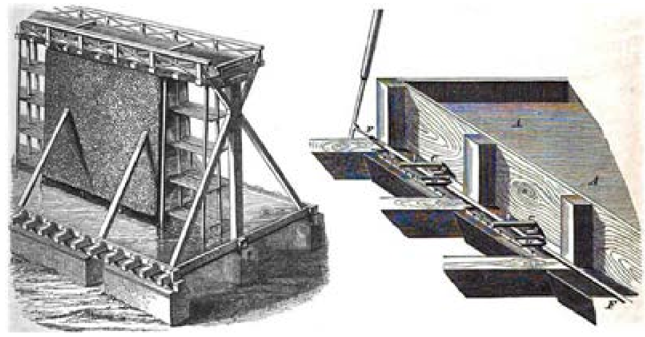

Fig. 1. – Antique illustration of a graduation tower (KNAPP 1848).

The constructions have to be built on a sturdy foundation and consist of basins or cisterns, a strong framework made of spruce or oak wood and stuffed with bundles of brushwood, pumps, pipelines, dropping channels, valves, taps, and often a roof that covers the framework (cf. Affelt, 2003; Harding, 2013; Langer, 2014; Ritz, 1996). Towers used for salt production have an elongated form, which allows a maximum evaporation rate. Contrary to this, aesthetic aspects significantly influenced the construction of new towers that were built for therapeutic purposes. A characteristic feature of the elongated graduation towers are tilted wooden beams on both sides of the framework. These beams are necessary to transfer the wind load. The bundles were laid with a downward inclination to the outer faces in order to direct the movement of brine. The complex brine distribution system is necessary to control the brine flow in accordance with the wind velocity and wind direction. Nevertheless, a considerable loss of brine is unavoidable, as small drops are always being blown away. However, this disadavantage during salt production is an advantage for inhalation therapy. In former times, the basins or cisterns were covered with boards to protect the brine from dilution by rainwater. Today, this measure is no longer necessary.

The brine is pumped to a platform at the top of the framework with pumps that are driven by water or wind power (e.g. Bad Dürrenberg, Bad Rothenfelde, Germany and Chiechocinek, Poland). After controlled distribution, the brine falls down on the branches. Due to the formation of drops, the brine surface increases and high evaporation rates can be achieved. Low-soluble salts, especially gypsum ($CaSO_4 \cdot 2\, H_2O$), crystallize on the brushwood twigs and the framework as so-called thornstone. Despite this effective technique, it is necessary to repeat this process until a sodium chloride content close to halite saturation is reached and the brine can be transported to the boilery.

Salt Production and Spa Facilities in Bad Kösen

Bad Kösen is located in the German federal state Saxony-Anhalt near the tri-border with the federal states Thuringia and Saxony. The region is called Saale-Unstrut, after the Saxon/ Thuringian river Saale and the river Unstrut. Kösen is located at the Via Regia. In earlier times, this trade route connected the urban centres Frankfurt, Leipzig, and Wroclaw in Silesia. Up until the middle of the 19th century, Kösen was the main wood trading place along the Saale. This facilitated the further town development.

In this region, salt production goes back as far as 1730 with the exploitation of a salt spring. At the beginning of the 18th century, Kösen was part of Saxony, which was ruled by Augustus the Strong, King of Poland and Grand Duke of Lithuania. He instructed the mining engineer Johann Gottfried Borlach to explore and investigate salt deposits. A new phase of salt production using graduation towers began (cf. Budde, 2012; Wirth, 1987). In 1733, Borlach built his first graduation tower in Artern, just 67 km from Kösen. From 1737 he worked in Kösen and received the title of Saxon mining councillor in 1740. In addition, he was the founder of the salt production plants in Dürrenberg and headed the Royal Polish mines in Wieliczka and Bochnia. Many similarities exist between the towers in Kösen and Dürrenberg. The latter is the largest contiguous facility of Germany (length 636 m).

Facilities that characterize the town image of Bad Kösen until today are the waterwheel (in German Kunstrad), the rod-operated pumping system (Mager & Gericke 1987), the main shaft house, and one of the two graduation towers (cf. Wagenbreth & Wächtler, 2015a). The wooden waterwheel and its housing were built in 1780. The wheel has a diameter of 7 m and a width of 2.4 m. It is rotated by the water of a dammed branch of the Saale river and is an undershot wheel. The water strikes at the bottom of the wheel. The speed of rotation is about 8 to 9 revolutions per minute. The crankarms of the wheel are connected with the pumping system, which can be divided into three main elements. A 180-m-long double flatrod construction, also known as art linkage, bar work, or rod line art, transmits the water power to a shaft, which is equipped with the brine pump. This shaft has a depth of 175 m and an average diameter of 3.5 m. It was partially lined with wooden planks and was covered with a wooden house. The shaft and house are named after Johann Gottfried Borlach (Budde, 2012). The Borlach shaft is connected to a second shaft via a 243-m-long drift at a depth of approx. 165 m. The construction of the underground structures was completed in 1737.

From the shaft, a single-flatrod system was constructed to drive a piston pump, which was necessary to transport the brine to the top of the graduation tower. Since 1959, electric pumps have been used. The wooden constructions were restored and are famous technical monuments of the 18th century. The technique to use such constructions for power transmission to a waterwheel was adopted from the mining districts in the Harz and Erz (Ore) mountains. Flatrod systems were also constructed in England. The technique dates back to the period before the invention of the steam engine (16th century) and was used to transmit power for up to four kilometres. Fig. 2 illustrates the original use of the water delivery systems.

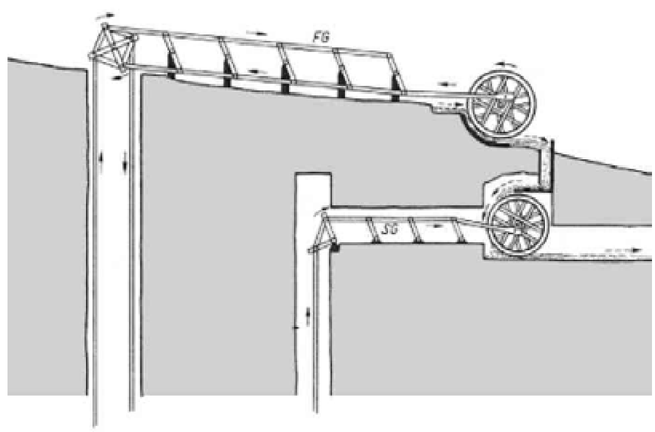

Fig. 2. − Single- (SG) and double-flatrod systems (FG) for the transmission of power in historical ore mining after Wagenbreth & Wächtler, 2015b (cf. Fürer 1900).

With about 1,600 hours of sunshine per year and low precipitation, the Saale-Unstrut-region has exceptional conditions for the cultivation of grape vines and the operation of a graduation tower. The Harz mountain range, reaching an elevation of 1,141 m (Brocken), and the mountains of the Thuringian Forest (Großer Beerberg 983 m) protect this region from heavy precipitations. Westerly winds predominate. The existing tower of Kösen, which is located at 149 m elevation above sea level, was built in 1780 on a hill (Rechenberg) perpendicular to the main wind direction (cf. Knapp, 1848). In 1797, a chemical plant was constructed for the processing of residual materials from the production process. The wooden framework has a length of 320 m and a height between 18 m and 20 m. It is stuffed with 34,400 blackthorn (*Prunus spinosa*) bundles, which are called fascines, over a height of 12.5 m up to 14.4 m (13 m on average). The bundles form a surface area of about 7,500 square metres. The flatrod system ends at the middle section of the tower, where the pump lines are mounted and a passageway exists. At the northern wing of the tower, a platform was built, which permits direct access to the blackthorn walls on the western and eastern side. At the end of the northern wing, a staircase enables the visitors to reach the platform at the top of the graduation tower. From here, the visitors have a good view across the town with its spa facilities and the surrounding landscape. In addition, visitors use this platform for sunbaths. The roof of the graduation tower was removed a long time ago.

Fig. 3. − Section of a postcard from 1928 showing the graduation tower of Kösen on the Rechenberg. The framework has a length of 320 m.

Initially, some towers were filled with straw, however, blackthorn is harder, thorny, and can be used in thick bundles. The drops of brine are separated more finely, and the brine contains lower amounts of particles. The brushwood has to be changed every 5 to 10 years as it becomes encrusted with mineral deposits over time. Currently, the blackthorn used in Bad Kösen is delivered from Poland.

Table salt, cattle salt, Glauber salt (sodium sulphate, cf. Strecker, 1929), and fertilizing salt were produced. Initially, Glauber Salt was gained by cooling and later through the use of sulphuric acid. Between 1731 and 1859, the white salt (e.g. table salt) was produced with pans. The annual production amounted to around 2,500 tons. In 1799, the plan was to produce 50,400 hundredweights (2,590 tons) of white salt. Before the rules of the German Customs Union came into force, a hundredweight corresponded to 51.4 kg in Saxony. In 1849, the annual salt production was about 51,000 hundredweights or approx. 2,620 tons. In 1868, Kösen was granted town privileges. At that time, 6,200 people lived in Kösen.

The end of salt processing with the graduation technique is related to the beginning of mining in the Staßfurt region. In 1858, shaft sinking began. In 1864, 40,000 hundredweights of rock salt and more than 1 million hundredweights of potash salt were extracted. It is likely that another reason for the end of salt production in this region was a failed attempt to explore salt with a boring from a Saale island (Große Radinsel).

The salt mining on the nearby Roßleben anticline began later and did not affect the closure of the facilities. The boiling houses do no longer exist. The dismantling of the disused plants along the small Saale and of the housing of the lower, secondary shaft was carried out in 1860. Despite the end of the graduation technique during this time, it is important to stress that the use of brines for salt production had experienced a comeback in the form of the solution mining process. With this technique, the minerals are dissolved by freshwater or seawater, which is pumped into salt deposits. Solution mining is comparable with classical salt mining because the resulting brines are characterized by high sodium chloride contents and high NaCl-$CaSO_4$-ratios.

In Kösen, a physician described the healing effects of the brine from the mill spring (Mühlbrunnen) already in 1726. Within the next fifty years, the use of the brine for therapeu-

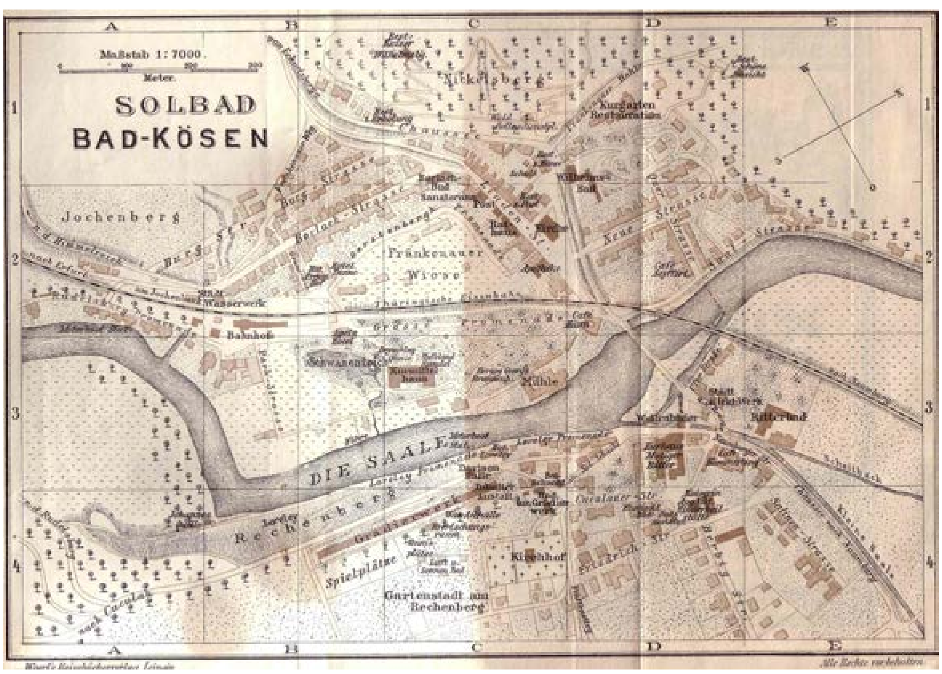

Fig. 4. − Map of Kösen before 1910. The locations of some baths are highlighted in bold typeface, such as the „Bad am Gradierwerk“ (bathhouse at the graduation tower), the „Wellenbäder“, and the „Ritterbad“ (knight’ bathhouse).

Fig. 5. − A section of a historical map (BUDDE 2007) and an overview of the current center of Bad Kösen. The flatrod constructions are positioned north of the graduation tower. They connect the waterwheel with the brine pumping equipment of the Borlach shaft (yellow arrow) and the graduation tower.

tic treatments became more and more popular. Bathers were already mentioned in 1794. Initially, not more than 40 guests visited Kösen. For the summer of the year 1826 61 visitors are documented. Brines of the mill and of the Johannes well were given to drink in the Herzog-Georgs-hall. Nowadays, the mill spring does no longer exists. In 1859, Kösen already had 1,300 guests. Generally, the spa institutions experienced a huge upturn during the period of the Belle Époque. In October 1892, the first German conference of health resorts (Deutscher Bädertag) took place in Kösen. Two important supporters of salt therapies were the Prussian court physician Wilhelm Hufeland and Carl Theodor Groddeck, who opened the most modern and elegantly furnished spa facilities and set new standards for the bathing culture (Martynkewicz, 1997).

In 1903, the secondary (lower) shaft was closed because penetrating water diluted the brine. At the site of the first hall for inhalation therapies of 1888, a spa treatment centre was built between 1910 and 1911. Two boreholes with depths of 280 m and 680 m were drilled, which feed the Beyschlag and the Hufeland well. In 1927, a medical bath was opened. Since 1935, Kösen has been a state-recognized health spa, and the town carries the predicate Bad (spa). Between 1990 and 1992, most spa facilities were modernised. Rehabilitation centres and a thermal bath were built. One of the clinics is located on the south-eastern edge of the graduation tower, which is now an open-air inhalatorium. It allows enjoying the beneficial health effects of moist, salty air far from the seaside. Due to the increasing demand in high-quality brine, a PVC pipeline was installed into the Borlach shaft down to a depth of 123 m. Nowadays, the shaft is an entrance to the nature preserve Saale-Unstrut-Triasland and a starting point of a geology trail. Fig. 4 and Fig. 5 show the town center and give an impression of the urban development. Currently, Bad Kösen has about 5,500 inhabitants.

Brine Composition

Bad Kösen is located in the eastern part of the Thuringian Basin, which consists of rocks of the Triassic period. The town was built on limestones of the Muschelkalk that form an aquifer. The underlying Upper Buntsandstein (Röt) is an aquifuge (cf. Hecht & Jungwirth, 1996; Hecht & Mai, 1999). Consequently, springs are located at the boundary of the Lower Muschelkalk and the Röt unit, which contains salt layers. Below the Triassic sediments occurs the salts of Zechstein age. Generally, the composition of brines depends on the composition of the groundwater, the composition and content of the soluble rock compounds, the contact time of the water with the rocks as well as on pressure and temperature. In this context, the dependence of the salt solubilities from pressure and temperature can be neglected, because no deep boreholes are used for the extraction of the brine. The depth of the main shaft is 175 m. In addition, the solubility of halite increases slightly with increasing pressure and this salt has a low positive temperature coefficient of solubility. Due to the interaction between density and temperature, the maximum mineralization of pure NaCl brines shows a minimum at about 20 °C (317,100 mg/l). The maximum mineralization increases to approx. 317,600 mg/l at 10 °C and 30 °C. The brines from Bad Kösen were sampled at the top and on the wall of the graduation tower. The major elements and the content of bromide

Table 1a. Content of major and trace elements (Sr^{2+}, Br^{-}) of brines used in spa towns in Brandenburg, Thuringia, and Saxony-Anhalt (cf. Fürer, 1900; Knapp, 1848). Values in milligram per litre (mg/l). N.A.: not analyzed or not stated. The data of the towns are valid for different springs or for brines, which are sampled at different points in times.

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Br^-
Bad Dürrenberg	34,246	363	445	1,792	25.1	53,575	4,640	290	35.6
Bad Frankenhausen	30,020	797	684	1,911	N.A.	48,565	4,920	328	N.A.
Bad Frankenhausen	11,268	252	275	1,225	N.A.	17,986	3,268	283	N.A.
Bad Kösen	16,693	142	210	1,280	15.2	25,491	4,190	284	14.8
Bad Kösen	17,100	140	217	1,220	19,9	26,000	4,022	273	19,9
Bad Kösen	22,000	210	315	1,260	N.A.	33,580	4,800	N.A.	N.A.
Bad Salzungen	3,157	24.3	92.7	246	3.6	5,123	0.43	0.27	2.5
Bad Salzungen	22,685	167	317	507	10.3	35,925	1,120	0.39	15.6
Bad Salzungen	121,035	560	1,405	1,405	27.9	190,907	3,899	0.21	83.2
Bad Sulza	40,680	280	391	1,893	N.A.	64,520	3,857	188	N.A.
Burg (Spreewald)	88,175	666	1,180	3,550	98	143,183	1,350	213	56.5

Table 1b. Content of major and trace elements (Sr^{2+}, Br^{-}) of brines used in spa towns in Hessen, Lower Saxony, and North Rhine-Westphalia (cf. Fürer, 1900; Knapp, 1848). Values in milligram per litre (mg/l). N.A.: not analyzed or not stated. The data of Bad Salzuflen are valid for different springs.

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	Br^-
Bad Harzburg	7,040	106	200	1,120	N.A.	10,700	3,620	70	N.A.
Bad Orb	5,190	318	240	894	23.4	8,860	102	1,678	47.5
Bad Salzdetfurth	20,160	410	468	1,304	16.6	33,275	3,782	250	N.A.
Bad Salzuflen	17,750	142	429	1,566	35.9	28,700	2,920	1,447	10.2
Bad Salzuflen	44,465	465	869	1,873	34.5	70,500	5,786	2,313	N.A.
Bad Salzuflen	45,261	515	914	1,753	43.1	70,850	5,485	2,324	21.4
Bad Sooden-Allendorf	41,300	442	497	1,790	25	63,880	5,300	412	32
Soltau	113,000	993	736	1,200	21.8	178,000	5,260	74	61

Table 2. Fictive salt components of the brines of Bad Kösen and Bad Sulza (Saale-Unstrut-region) as well as of seawater and the brine of a salt cavern in milligram per litre (mg/l).

	NaCl	KCl	$MgCl_2$	$MgSO_4$	$CaSO_4$	H_2O
Bad Kösen	41,739	0	0	1,040	3,704	984,790
Bad Kösen	42,865	0	0	1,075	3,536	984,476
Bad Kösen	55,556	0	0	1,549	4,250	980,526
Bad Sulza	103,413	534	1,532	0	5,466	963,307
Seawater	28,475	763	3,207	2,559	1,080	988,586
Salt cavern	290,000	1,160	3,100	2,100	4,100	891,670

(Br^-) were measured with a Metrohm ion chromatograph. The ionic balance of the analytical results was less than 1.0 percent. In addition, the density of the brines was calculated and compared with measurement results. Trace elements were determined with an iCAP Q mass spectrometer. Table 1 shows the results and an overview of the ion content of the brines that are used in spa towns in Germany. Table 2 lists so-called fictive (calculated) components of brines in Bad Kösen and the nearby Bad Sulza. This table allows a comparison of these brines with seawater and salt solutions of cavern leaching. Moreover, the values give an impression about the amount of graduation that is necessary for a salt production.

All brines are dominated by chloride and sodium ions, followed by sulphate and calcium. Accordingly, halite and gypsum are the most important minerals leached by groundwater, however anhydrite is the calcium sulphate of the unaffected Röt rock salt. Except for the high-concentrated brines of Bad Salzungen and Soltau, the Na/Ca-ratio is in a range of 5.8 up to 44.7, with an average value of 17.8. The Na/Ca-ratio of seawater is about 26. This comparison demonstrates the need for separating Ca-containing minerals prior to salt production. However, with 20.3 to 65.4, the brines have much higher Na/(K+Mg)-ratios in relation to seawater (6.4). In this case, the only exception is the brine of Bad Orb (9.3). Consequently, it is not necessary in each case to dispose of residual solutions with high magnesium and potassium content. Lower amounts of potash salts crystallize during the final salt boiling.

The specific composition of the low-concentrated brines makes it advisable to use these brines for therapeutic applications. In medicine, physiological or isotonic saline is a general phrase referring to a solution that contains 9,000 mg NaCl per litre or 3,540 mg Na^+ and 5,460 mg Cl^-. A hypertonic has a higher NaCl concentration and a hypotonic saline contains less solute. With the exception of a brine in Bad Salzungen, all brines are hypertonic salines.

Graduation of the Brine

The amount of water that evaporates from a brine depends on the relative humidity and the wind velocity. The relative humidity is a function of the air water content and temperature. These relationships explain why a historical technique; i.e., the production of solar salt in salt works, is applied in dry and warm climates; e.g., at the coast of the Mediterranean Sea. In the Mid- and North-European countries, an ancient production technique is the evaporation of brines in metallic pots and pans. However, this technique needs much firewood and can lead to a substantial air pollution as experience in Lüneburg shows (Brimblecombe et al., 2011). The pollution would have a sustained negative effect on spa activities.

Graduation towers made it possible to reduce the energy consumption. This is above all due to the increase of the brine surface available for water evaporation as a result of the formation of fine drops. Regardless of this optimization, sufficient low relative humidities must be given for the initiation of evaporation. Although the evaporation of pure water already starts when the humidity is less than 100%, a humidity of less than 70% is necessary to increase the concentration of an NaCl solution up to 25 wt.-% (cf. Kinsman, 1976; Usdowski & Usdowski, 1970). Fig. 6 and the Fig. 7 show climate data of Bad Kösen. According to Fig. 6, the wind blows mainly from the west. The western winds have the highest velocity with 15.5 km/h. The highest temperatures come with eastern and south-eastern winds. The relative humidity ranges between 56% (E) and 81% (SW). During the summer, the relative humidity can sink temporarily to less than 40% (Fig. 7).

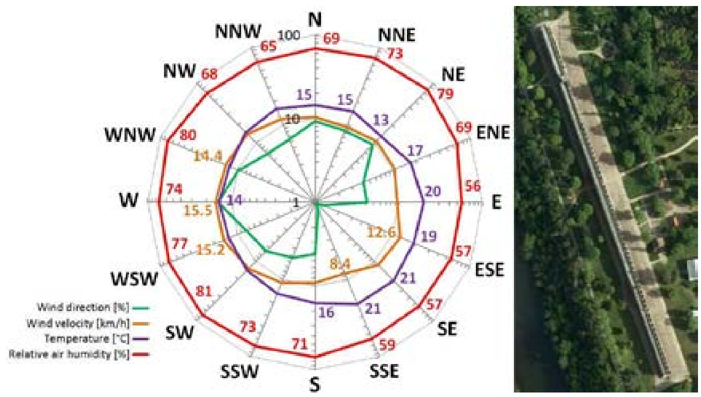

Fig. 6. − Relative air humidity (red), temperature (dark blue), and wind velocity (orange) in dependence of the wind direction (green). Measurement results from May to July 2014.

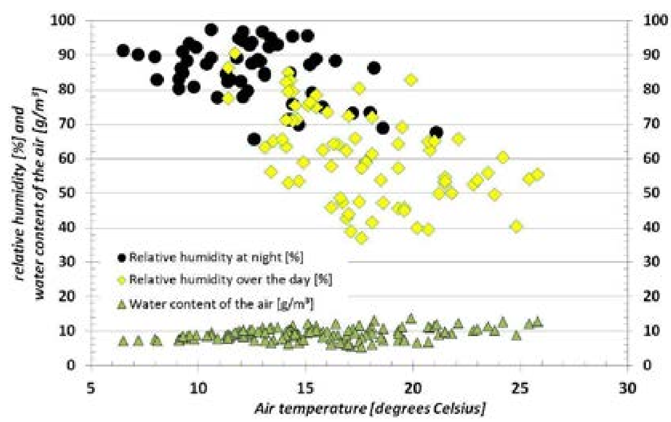

Fig. 7. − Relative humidity and water content of the air in Bad Kösen, August 2014.

The final salt content of the graduation process depends on the initial sodium chloride concentration of the brine and the efficiency of the graduation tower. In addition, high production costs of the production process in the boilery lead to the effort to reach higher salt contents by graduation. However, the possibility of salt crystallization, in particular of halite, in

Table 3. Sodium chloride content of the brine in the Borlach shaft and after the 1st, 2nd, 3rd, and 4th grading in wt.-% after Emons & Walter, 1988 (cf. Knapp, 1848).

wt.-% NaCl in brine	1st grading	2nd grading	3rd grading	4th grading
2.7	8.5	13.2	19.9	24.8

basins and pipelines limits the achievable degree of graduation. Consequently, the graduated brine had a sodium chloride concentration between 16 wt. % (Nauheim) and 25 wt.-% (e.g. Lüneburg). In Kösen, about 860 g H_2O per litre brine evaporated to reach a NaCl-content of the residual brine of 24.8 wt.-% (Table 3), taking into account the amount of water, which is fixed in the structure of gypsum. These values and the information that the annual production amounted to around 2.500 tons salt allows an estimation of the processed brine volume. It was approximately 60,000 m³, and about 50,000 tons of water evaporated. Currently, the brine flow into the Borlach shaft is 260 litres per minute or about 11,220 m³ per month. In the summer, more than 1,000 m³ of brine were pumped per month. In the winter, the volume is reduced to 100 m³ per month. For example, in November 1999, the brine volume that was pumped to the surface amounted to 450 m³.

Due to the lack of measurement results, it was not possible to calculate an evaporation rate during the graduation process. However, for a flat water surface and a hypothetical production period of 230 days, an evaporation rate between 650 mm and 750 mm was estimated by means of Dalton's law. For comparison, the amount of precipitation in the Saale-Unstrut-region is about 550 mm per year.

To evaporate 50,000 tons of water; about 10^{11} kJ of energy are necessary, taking into account an average latent heat of vaporization of 2,000 kJ/kg. This energy demand explains the cooling of the air in the vicinity of the graduation tower. For this reason, graduation towers can be compared with wet cooling towers, however, the heat transfer from the air to the brine can be neglected. Consequently, it is not surprising that some graduation towers were used to remove the surplus process heat from condensers of steam power plants.

Crystallization of thornstone

The crystallization of the minerals depends on the ion content of the won brine, the extent of water evaporation, and the solubility limits of the minerals. Fig. 8 shows the composition of the brines that are used in Bad Kösen and Bad Sulza in a NaCl-$CaSO_4$-H_2O diagram. For comparison, the evaporation path of seawater (cf. Baseggio, 1974; Herrmann et al., 1973; McCaffrey et al., 1987) and the composition of brines produced during solution mining of caverns in Staßfurt rock salt are outlined. The ion contents of the cavern brines can be explained with the high halite-anhydrite-ratio of the cavern surface. In addition, the diagram shows the line of gypsum saturation as a function of the NaCl-concentration (cf. Li & Duan, 2011). The diagram is limited on the right side by the halite saturation in pure solutions of NaCl and $CaSO_4$ at 25 °C. The arrows illustrate the changes of the brine composition during water evaporation. The arrows end below the gypsum saturation line because, in addition to calcium sulphate, the brines contain other types of sulphates. In the brines of Bad Kösen and Bad Sulza a content of about 1,130 mg SO_4/l is bound with other salts, and seawater contains about 1,690 mg SO_4/l as magnesium sulphate.

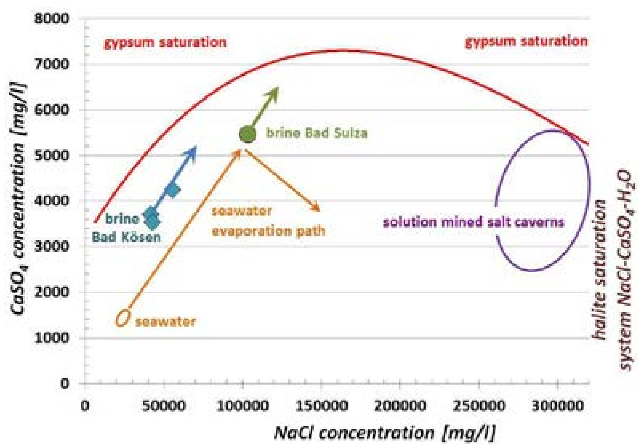

Fig. 8. – Diagram of the system NaCl-$CaSO_4$-H_2O with the points of the brines in Bad Kösen and Bad Sulza. The red line separates the field of gypsum saturation and undersaturation in NaCl-$CaSO_4$ solutions. The arrows mark the shift of the points during evaporation.

The salts of magnesium and potassium are enriched during the evaporation process even during the stage of halite precipitation. However, the magnesium and potassium content of many brines is rather low. This can be demonstrated by the $(K^+ + Mg^{2+})/Na^+$-ratio, which is about 0.03 for the brines of Bad Kösen, and approximately 0.16 for seawater.

Behaviour of the trace element strontium

Strontium and bromide are the most important trace constituents of the brine gained. The concentrations are around 15 mg/l (Sr^{2+}) and 15 mg/l (Br^-). During the graduation process bromide remains in the solution and would be fixed together with chloride in the structure of chlorides, such as halite, at a later stage. However, strontium is incorporated into the structure of calcium-bearing minerals; e.g., calcium carbonates and sulphates. Samples of the thornstone were collected at the passageway and near the platform of the graduation tower. The samples were dried with absorbent cloths and by means of storage in an exsiccator containing a desiccant. For chemical and mineralogical analysis, several of the samples were crushed manually in an agate mortar. Chemical analyses with an Axios PANalytical X-ray fluorescence spectrometer show that the Sr content of some of the thornstone samples reaches values of up to about 0.2 wt.-% (2,000 µg/g or ppm). According to the investigations of thin sections and the analysis with an X'Pert PANanalytial diffractometer, almost all of the Sr is incorporated into the structure of gypsum.

In an open system, the Sr-content of seawater is about 8 mg/l. The content increases during evaporation and precipitation of carbonates, gypsum, and halite. The Sr-content of the gypsum ranges from several hundred µg/g to up to about 2,300 µg/g due to a high distribution coefficient (b=50, Usdowski, 1973). In some cases, values of up to 2,700 µg/g are described (e.g. Rosell et al., 1998). These similarities and the assumption of a comparable behaviour of Sr^{2+} ions in the brines and seawater suggests using the knowledge about seawater evaporation to determine the salinity of the thornstone mother liquors. It is not possible to use the chemical results of brine in the catch basin due to the very different contact time of the brine on the gypsum surfaces and brine mixing. At the time the thornstone samples were taken, the brine in the catch basin did not reach gypsum saturation. Fig. 9 shows Sr-values of brines and gypsum that crystallized during seawater evaporation in salt works. In addition, the chemical results of samples of the graduation tower are entered into the diagram.

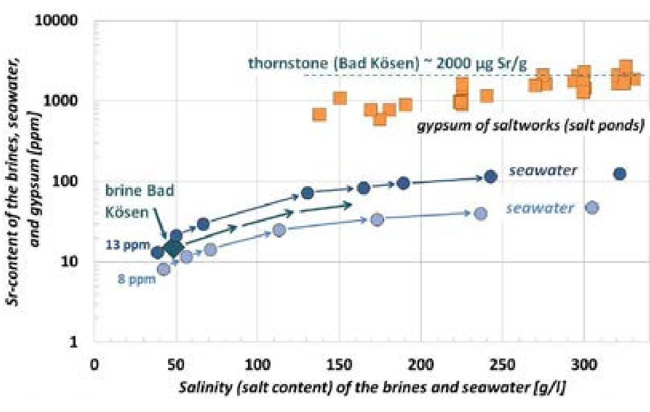

Fig. 9. – Sr-concentrations of evaporating seawater (cf. Rosell et al., 1998) and Sr-content of gypsum. The crystallization of halite begins at a seawater salinity of about 300 g/l. Yellow squares mark results of Engelhardt (2016).

Appearance and Structure of the Thornstone

According to the brine composition, the behaviour of the salts during water evaporation and the information about the annual salt production (around 2,500 tons), about 300 tons of low-soluble minerals, e.g. gypsum and carbonates, precipitated annually as thornstone. If the porosity of the thornstone is neglected, this amount corresponded to a volume of marginally more than 130 m³. According to the current observations, two types of thornstone can be distinguished. Plates of crystal aggregates are formed on wooden boards and planks. These layers deform, peel off the wood, and the pieces fall into the catch basin. An example of such a piece is shown in Fig. 10 and Fig. 11.

The thornstone forms layers and tubers on the branches, in particular at the outer surface of the formwork. These crystallizations can be visually compared with the calcite precipitations of travertine. Both types of crystallizations are yellowish-red to beige-coloured. Most probably, iron and manganese oxides are responsible for the colouring of the thornstone. Analyses of the brines show values of about 2 µg Fe/litre and approximately 0.2 µg Mn/litre.

Fig. 10. – Part of a gypsum layer with an average thickness of 0.4 mm. The layer was formed on a timber profile at the passage of the graduation tower in Bad Kösen. The width of the photo corresponds to 11 cm.

Fig. 11. – Close-up of the gypsum crystals shown in Fig. 10. The width of the photo corresponds to approx. 3 cm.

The surface of the thornstone on the branches is characterized by crystals with sharp edges. It can be compared with sandroses. However, in some areas of the graduation tower, the crystals have round shapes. Due to the arrangement and size of these areas, it can be assumed that the crystals are partially dissolved by brine that was not gypsum saturated. Darker areas also indicate alternating depositing conditions. Irrespective of the surface, cross-sections of the thornstone show radiating crystals (Fig. 12 and Fig. 13). Deviations from the circular cross-section and differences of the crystal morphology between the upper and lower parts of the thornstone can be explained by the flow of the brine along the surface of the thornstone and the formation of drops that hung for a while. Consequently, different time periods are available for crystallization and dissolution processes. Sometimes, small stalactites of halite grow. This demonstrates the high efficiency of the graduation techniques.

Fig. 12. – Thornstone on a twig of blackthorn. The divergent orientation of the crystals becomes visible on the broken surfaces. The picture width corresponds to about 7.5 cm and the diameter of the divergent oriented crystals at the upper picture margin is 1.4 cm.

Fig. 13. – Gypsum crystals of the thornstone, graduation tower Bad Kösen. The width of the upper photo corresponds to approx. 3.0 cm and the width of the lower photo to approx. 1 cm.

Thin-sections can be used to visualize the crystal aggregates and the inner structure of the crystals. The visual inspection was performed with a Leitz Laborlux 12 POL-microscope and a Keyence digital microscope. The investigations showed that the carbonates and non-transparent, foreign particles are arranged along stripes or zones that extend over a large number of crystals (Fig. 14, Fig. 15). The stripes are not flat because the particles were incorporated during the crystal growth along crystal layers. Although it is not possible to determine growth rates, the inclusions indicate differences of crystal growth.

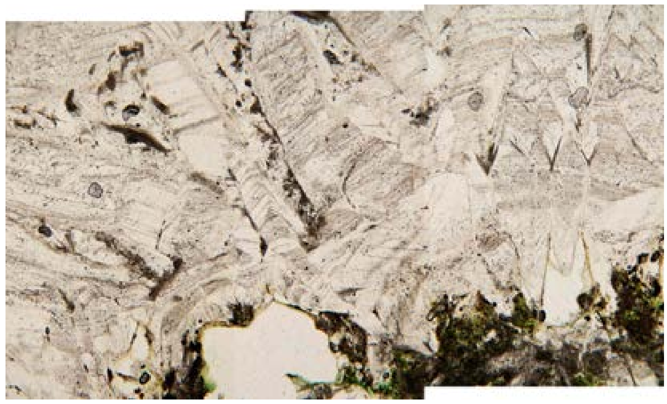

Fig. 14. – Photograph of a thin section with gypsum crystals (parallel polarisers) that grow on a wooden plank (lower border of the image). The first layer consists of fine-grained gypsum and organic materials. The gypsum crystals with a length of 6 mm at maximum, which are characterized by carbonate inclusions and foreign particles, are visible. The height of the image corresponds to approx. 3 mm.

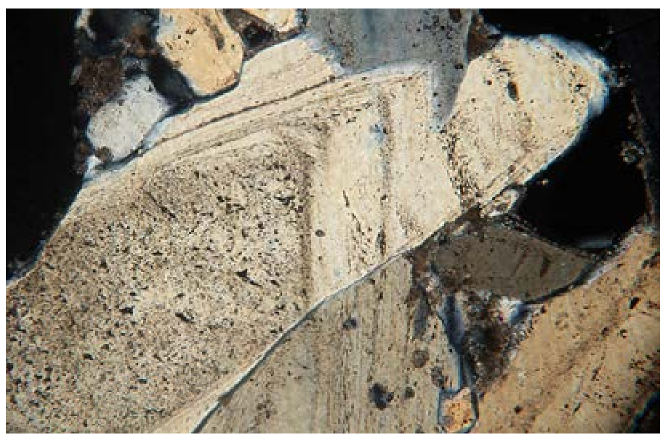

Fig. 15. – Microscopic close-up of gypsum crystals (crossed polarisers). The image diagonal corresponds to approx. 1 mm.

Acknowledgments

We are very grateful to Dr. Thomas Schirmer from the Technical University of Clausthal, Germany, for carrying out the chemical and X-ray diffraction analyses. We would like to thank also Mr. Thomas Budde from the Kurbetriebsgesellschaft Bad Kösen GmbH for the information about the graduation tower. Last but not least, we would like to give our thanks to Dr. Nina Müller-Hoeppe (DBE TECHNOLOGY GmbH) for her review of the draft.

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