

## New Brine Purification and Crystallization Plant at Bad Reichenhall

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### ABSTRACT

A new brine purification and crystallization plant has been completed and started up at Saline Bad Reichenhall in Southern Germany. The raw material of the salt plant is a so-called "Hazelstone" geological formation with its composition characterized by salt, clay and calcium anhydrite mixture, which is a characteristic salt formation in the Bavarian and Austrian Alps. The salt content in the geological formation has an irregular distribution containing between 40 and 60% of sodium chloride.

In the salt mines of Berchtesgaden the salt is mined with a so-called cavern process. Fresh water is artificially pumped to the cavern and held until it is saturated with salt from the hazelstone formation. The brine is pumped out and the undissolved fraction remains behind in the ever-increasing cavity.

The chemical composition of the brine is relatively high in magnesium and sulfate salts, which can be attributed to the slope of the natural geological formation. Thus, the brine purification process has an increased performance requirement. The raw brine, in addition to the sodium chloride, contains dissolved calcium and magnesium salts which are precipitated through the chemical lime soda-process, nearly quantitatively. The precipitation is made in a two-stage batch reactor with a daily throughput capacity of 3,000 m<sup>3</sup>. The first stage uses Ca(OH)<sub>2</sub> and the second Na<sub>2</sub>CO<sub>3</sub>. The Na<sub>2</sub>CO<sub>3</sub> consumption is reduced by transforming NaOH to NaCO<sub>3</sub> with CO<sub>2</sub> gas. The feed solution to the evaporators, following the purification, still contains a small amount of calcium and magnesium salts. The precipitated sludge is returned back into the lagoons of the salt works in Berchtesgaden and stored.

The salt is produced in three mechanical vapor recompression forced circulation evaporators which, for the first time in Europe, use titanium tubes and single-stage radial compressors. The operation of the system is highly efficient, requiring only one man per shift. The plant has an extremely low power consumption; possibly the lowest of any plant in the world and the evaporative crystallizers produce an extremely high purity salt owing to the high efficiency elutriation system.

### INTRODUCTION

A new Brine Purification and Crystallization Plant has commenced successful operation at Saline Bad Reichenhall in southern Germany. Salt deposits in the area are mined using water to create a brine solution, which, following purification, is evaporated in mechanical vapor compression units to create salt of extremely high purity. The salt is used to meet the majority of German consumer needs. The plant is highly efficient in terms of labor and power consumption and has met all performance guarantees. Although a complicated undertaking requiring five years to complete, the project met time and money budgets as well as process requirements.

### GENERAL AND PRELIMINARY REMARKS

#### Geology and exploitation of the salt deposit in the area of Berchtesgaden-Bad Reichenhall

The basic raw material of the Saline Bad Reichenhall is an extensive salt deposit in the area of Berchtesgaden and Bad Reichenhall. This deposit dates to the Triassic and Permian geological eras and is part of a narrow, salt carrying zone following the north rim of the Alps between Innsbruck and Vienna (Fig. 1). Its highly heterogeneous formation is characteristic of the alpine type of deposit. Salt, in a finely distributed form, is the main mineral present in the geological formation known as "hazelstone". The salt content is highly variable but aver-



Fig. 1. Map showing location of mine at Berchtesgaden.

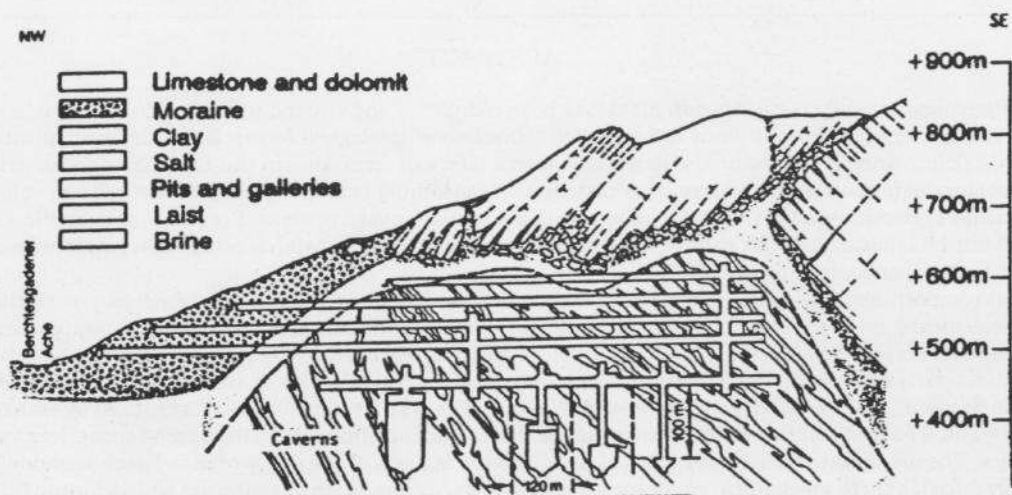


Fig. 2. Cross section of mine.

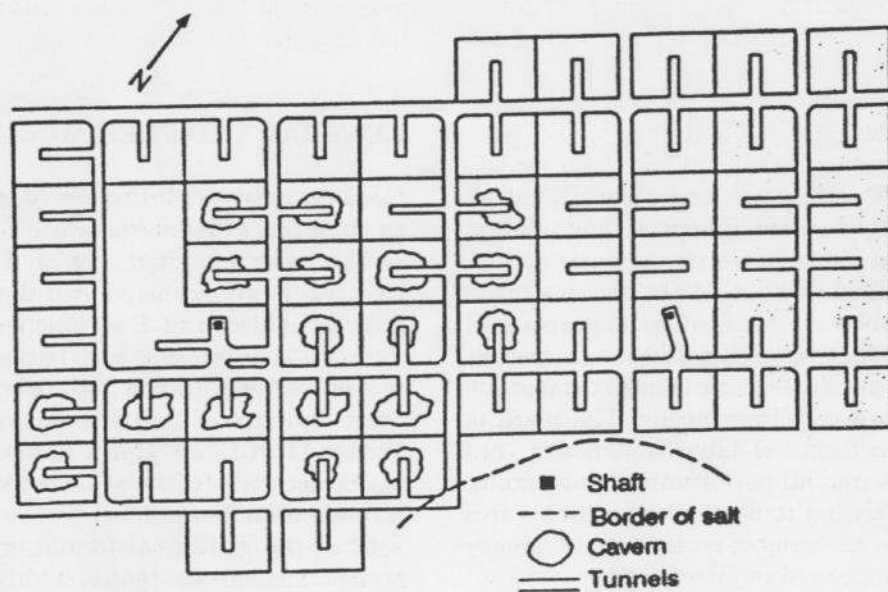


Fig. 3. Layout of mine.

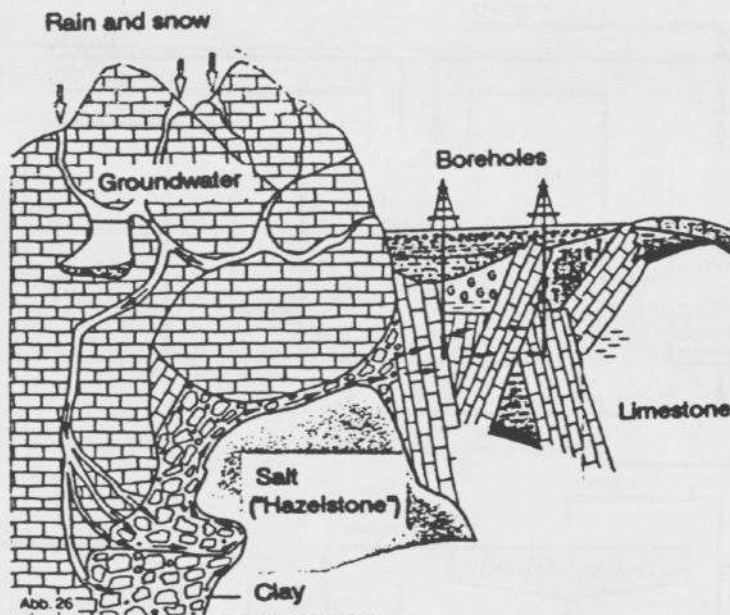


Fig. 4. Ground water passage saturated brine and brine well location.

ages about 50%. Other components are clay, anhydrite and polyhalites.

The salt mines of Berchtesgaden are interspersed with galleries and pits. Due to the strongly tectonic mixture of soluble and insoluble components, the salt can only be mined by solution mining where fresh water is pumped into the caverns. In this so-called cavern process, water is held until a nearly saturated brine is obtained with a salt content of 26–27%. The saturated brine is then pumped to the salt plant of Saline Bad Reichenhall in a 25 km pipeline. The salt mines of Berchtesgaden produce 500,000 m<sup>3</sup> of brine per year and supply approximately 65% of the brine needed by the salt plant (Figs. 2 and 3).

In addition to the solution mining, naturally generated saturated brine is obtained from wells at Bad Reichenhall. From a total of 3 "deep wells", approximately 250,000 m<sup>3</sup> per year of brine is pumped from a depth of about 600 m (Fig. 4).

#### History of the Saline Bad Reichenhall and its market significance

Based on various historical evidence, it is presumed that the salt sources of Bad Reichenhall have been exploited since the Bronze Age, i.e. for about 4000 years. The first written reference dates back to the 7th century. Numerous documents confirm many changes in the rights of salt mining between clerical and private or governmental owners. In the 15th and 16th century, the Bavarian princes acquired the salt extraction rights and claimed the exclusive control of the salt production and its trade,

a monopoly which existed until 1868. Since 1926, the salt mining has been carried out by the Bayerische Berg-, Hutten- und Salzwerke AG which was owned by the Bavarian State until 1991. The Saline Bad Reichenhall is a branch of this company. About a year ago, the ownership was acquired by the SKW in Trostberg, an enterprise of VIAG-Holding.

The Saline Bad Reichenhall produces approximately 200,000 t/year of salt. The majority of this salt is used as table salt and water softening salt. Secondary uses are for animal feed stock and for de-icing. The Saline Bad Reichenhall supplies the majority of the table salt consumed in German households.

#### JUSTIFICATION FOR THE NEW SALT PLANT

The evaporator trains that operated in the plant, most of which dated back to the sixties, were damaged by corrosion and abrasion to such an extent that, after 20 years of operation, they could not reliably guarantee the production of the plant. The acquisition of a new evaporation plant therefore became necessary. The existing evaporation plant was a combination of mechanical vapor recompression and multiple effect steam driven systems. The energy sources for these systems were natural gas and heavy oil.

The existing plant did not utilize any chemical precipitation of the dissolved calcium and magnesium salts in the brine. By running the plant with a controlled CaSO<sub>4</sub> suspension, it was possible to min-

Fig. 5 Brine Purification

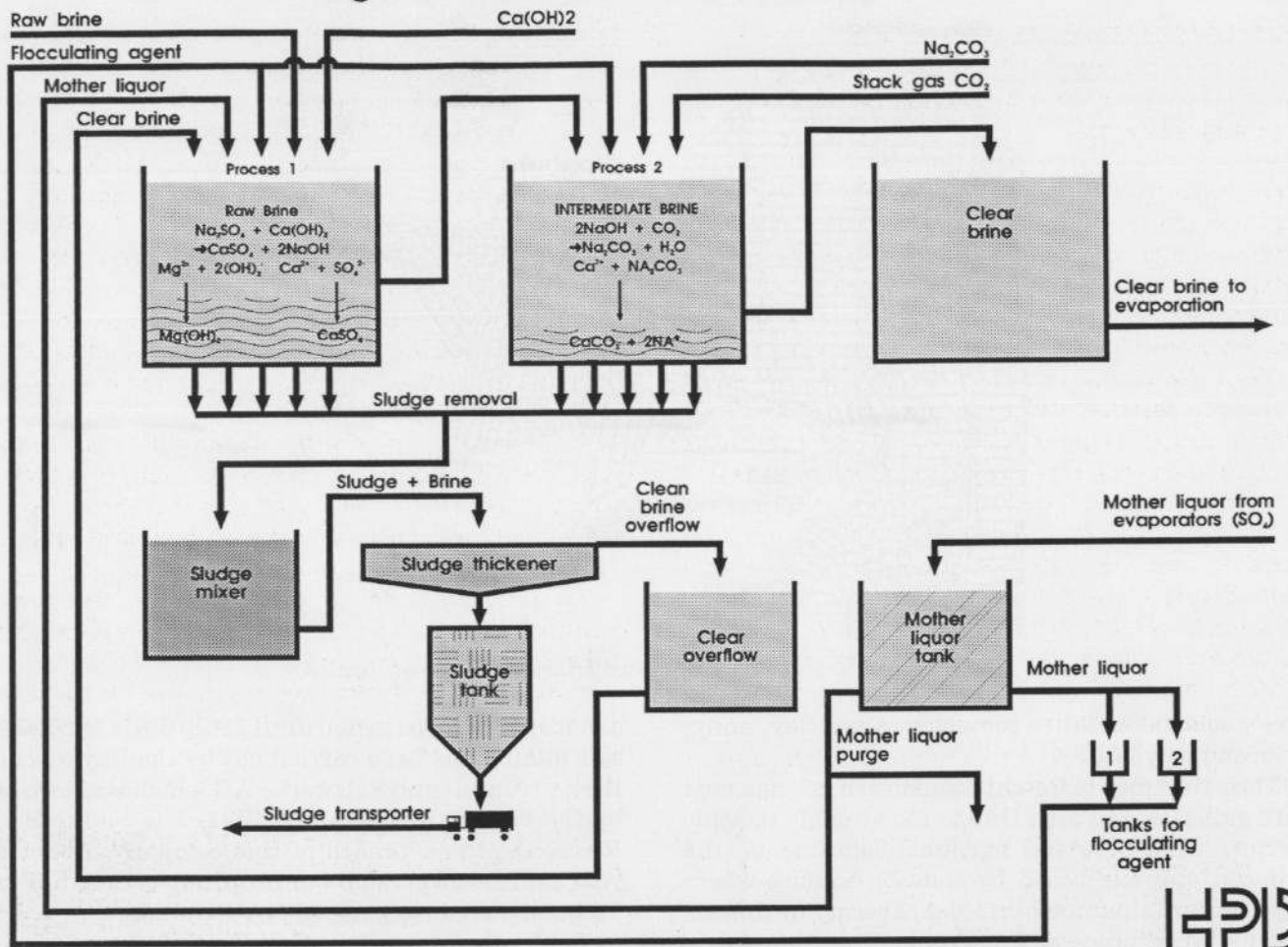


Fig. 5. Brine purification.

imize scaling of the tubes. However, the relatively high content of magnesium salts in the mother liquor led to a significant increase of the boiling point of the brine which resulted in higher energy consumption. In addition to this, the increased magnesium content of the salt proved to be disadvantageous to product storage. The higher energy cost, as well as the need for higher product quality, were the chief reasons for adapting a full chemical treatment process for the brine prior to evaporation.

#### CONDITIONS AFFECTING CHOICE OF PROCESS

The energy sources which were considered — heavy oil and natural gas — are dependent on the political situation of the exporting countries and therefore are subject to variations in availability and price with severe fluctuations of both. The consideration that in the long term electric energy would best guarantee both dependable supply and price stability was an important criteria in the design of the new

evaporation plant.

Based on available space, the new plant had to be designed to use as little room as possible.

The salt plant is situated in the center of a health resort. One of the basic requirements was therefore to minimize the air pollution by SO<sub>2</sub> and NO<sub>x</sub> gases.

In order to prevent a loss of market share, the guarantee of full salt production during the erection period was an absolute requirement.

#### REQUIREMENTS REGARDING THE NEW SALT PLANT

- High salt purity
- Uniform salt crystals (not smaller than 0.1 mm)
- Low energy consumption
- High availability (long intervals between evaporator boil-outs)
- Reduced operating labor
- Short start-up time. Frequent start-ups are required to enable optimum use of low energy rate.
- Plant life expectancy (choice of material)

## PLANT REALIZATION

Based on the above aims, the following plant concept was realized:

### Brine treatment

The chemical composition of the brine is relatively high in magnesium and sulfate salts which can be attributed to the natural geological formation. Thus, the requirements of the brine purification process are considerable. (See Fig. 5).

The raw brine, in addition to sodium chloride, contains dissolved calcium and magnesium salts which are precipitated through the lime soda process, nearly stoichiometrically. The precipitation is made in two-stage batch reactors with a daily throughput capacity of  $3,000 \text{ m}^3$ . The first stage uses  $\text{Ca}(\text{OH})_2$  and the second  $\text{Na}_2\text{CO}_3$ . The  $\text{Na}_2\text{CO}_3$  consumption is reduced by transforming the  $\text{NaOH}$  in solution to  $\text{Na}_2\text{CO}_3$  with  $\text{CO}_2$  gas. The feed solution to the evaporators, following the purification, still contains a small amount of sulfate and magnesium salts. The precipitated sludge is transported back into the caverns of the salt works in Berchtesgaden. Figure 6 shows the brine purification system.

## Evaporation plant

### Evaporation process

In order to best meet the design requirements regarding the crystallizers, the MSMR design (mixed suspension, mixed product removal) was chosen.

The evaporator was designed as a forced circulation crystallizer according to the guidelines of HPD, resulting in vessel details similar to those working successfully in numerous salt plants. A vane type demister was installed in the vapor section to provide the required vapor purity.

To prevent scaling of the tubes, the heater was designed with high velocities in the tubes prescribed by heat transfer, crystal size and morphology considerations (see Fig. 7). For corrosion and erosion reasons the tubes were made of titanium.

By providing a large recirculation flow, the supersaturation is kept low, favoring relatively slow crystal growth. The crystallization section is designed to guarantee both sufficient retention time for the crystal growth and sufficient time for the full release of supersaturation.

The  $\text{NaCl}$  crystals produced migrate down to the



Fig. 6. View of the brine purification plant.

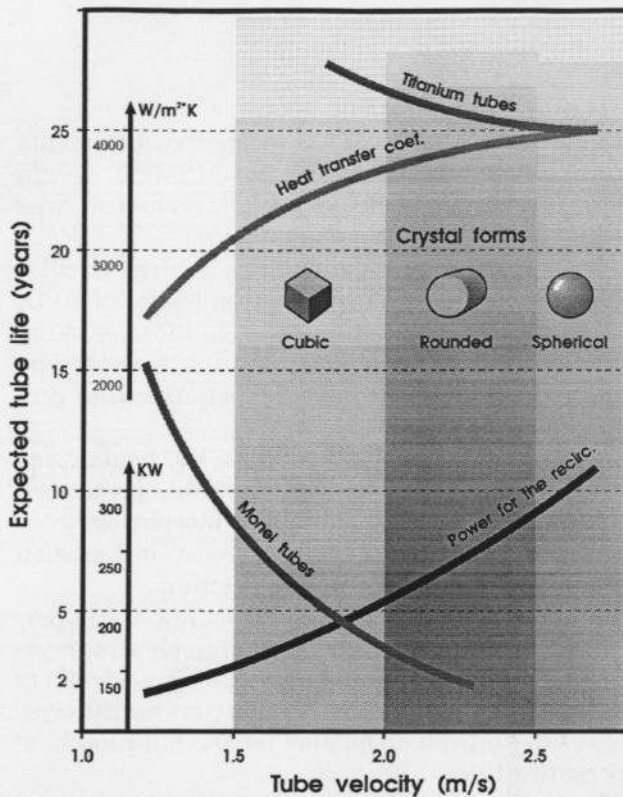


Fig. 7. Tube velocity criteria.

elutriation leg, where — by means of counter current feed brine — they are separated from the hot mother liquor and thus washed and cooled. At the same time, the salt is classified by sending the small crystals back to the evaporator with the ascending counter current brine. The salt is discharged from the salt leg by means of a control valve whereby

enough crystals are retained in the crystallizer to keep the required slurry concentration in the evaporator. This slurry concentration is important for the following reasons:

— The extended retention time of the crystals increases the size of the crystals yielding a large and uniform crystal crop.

— Due to the presence of crystals in the recirculating brine, the supersaturation is released rapidly and the NaCl crystallization occurs on the crystal surface rather than on the metallic walls of the heat exchanger tubes. Thus, scaling of the tube walls is prevented.

#### Compressor

One of the most important decisions was the choice of the vapor compressor. Prior to this project, either multi-stage radial compressors or axial compressors were used in European salt plants. Due to the risk of stress corrosion and owing to some severe failures which have occurred, the tip speeds of impellers were limited to 280 m/s when using CrNi steel alloys. In order to get a sufficiently high differential pressure to supply the driving force required for the boiling point rise and heat transfer, it was necessary to employ a multi-stage compressor with 3–4 stages of compression.

The development of the single stage compressor for high differential pressure originated in the late seventies. In the USA, such machines are used often with stainless steel impellers. Encouraged by the mostly positive results, it was decided to use this type also at Bad Reichenhall, but with titanium impellers.

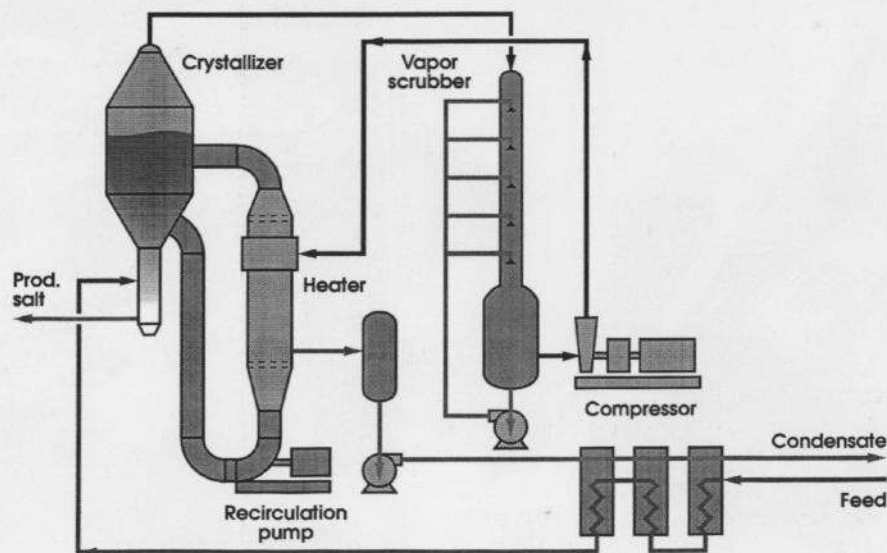


Fig. 8. Bad Reichenhall salt crystallizer.

The single stage radial compressor offers the following advantages:

- Substantially lower investment cost
- Less floor space requirement
- Sturdy construction
- High efficiency
- High availability
- Easy maintenance

The three-year operating experience with the single-stage radial compressor has justified its choice.

Control schematics of one of the three stages of the evaporation plants is shown on Fig. 8.

### OPERATION RESULTS TO DATE

Table 1 summarizes the performance of the salt plant.

### CONCLUSIONS

The construction of the new plant was a complicated undertaking which required five years of planning and execution with several stages. It involved rebuilding an existing plant without loss of production and modernization including new buildings interspersed with existing structures in the center of town. The project was completed within the time and money budgeted; fully tested, it met all guarantees which were measured over a one month test period.

TABLE 1

New plant — requirements and results

Requirements	Results
Low energy consumption	Max. 125 kWh/t NaCl at the compressor coupling 0 t steam/t NaCl (excluding dryer)
High salt purity	Ca <1 ppm Mg <1 ppm SO <sub>4</sub> <300 ppm Elutriation efficiency approximately 95%
High availability	Operation period 4–6 weeks followed by approximately 12-h shutdown for preventive washing.
Cubic, uniform crystals without fines	Cubic crystals d avg = 0.55 mm d <0.2 mm approx. 9.1% d >1.0 mm approx. 0.1%
Low operating labor	1 Operator for 3 units
Quick start-up and shut down	Start-up time with cool brine (25°C) approx. 4 h Start-up time with warm brine (90°C) approx. 0.5 h Shutdown approx. 1 h
Longevity	No visible abrasion of compressor after 3-year operation Evaporator wall thickness reduction not measurable.
Low investment cost	Installation realized within budget