Introducing a New Approach for the Stowage of Waste Brines from Potash Mines of the Werra District in Germany as a Measure to Ensure the Safe and Sustainable Continuation of Potash Extraction and Processing

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Abstract

The global fertiliser production industry has been and, considering world population development, will be vital for intensive agricultural land use. However, waste brine discharge from the production of fertilisers poses environmental challenges. The German potash deposits of the Werra District are unique resources for the production of special fertilisers. A new approach to waste brine management will need to ensure a responsible and sustainable continuation of fertiliser production in the Werra District. This approach entails the conditioning of waste brines and subsequent stowage in a former potash mine thereby eventually eliminating discharge of waste brines in rivers and/or in aquifers.

Keywords: potash mining

Introduction

The importance of global potash (i.e. Potassium with symbol **K**) extraction and processing has been substantial for well over a century (Darst, 1991). Potash based fertilisers will, considering the growing world population, continue to be a vital resource for intensive agricultural land use. The German potash deposits of the Werra District, high in sulphatic and magnesium containing minerals, are unique in their ability to provide resources for the production of special fertilisers, i.e. potassium sulphate and magnesium sulphate (K+S AG, 2018). Globally the production of potash fertilisers is however not without controversy due to waste brine discharges into surface and ground water and saline run-off from stockpiles for solids salt wastes (Tallin, Pufahl, & Barbour, 2011), (Ladrera, Canedo-Argüelles, & Prat, 2016), (BMUB/UBA, 2016), (Rauche, 2015).

To ensure a responsible and sustainable continuation of potash extraction and processing in the Werra District, K-UTEC AG Salt Technologies (K-UTEC), in collaboration with K+S AG and K+S KALI GmbH (K+S), has proposed a new approach which can gradually decrease, and in future even eliminate, the discharge of waste brines from the production of fertilisers in rivers and/or their injection in deep aquifers. This approach entails the conditioning of waste brines and subsequent stowage in former potash mines in the Werra District and will, after successful implementation, gradually reduce and eventually eliminate the discharge of approximately 3 million m³ waste process brine in the Werra-district into surface water and/or injection of waste brines into deep aquifers. A critical condition for stowage is the chemical composition of the waste brines in relation to the host minerals in the mines of the Werra District which must be adequately considered since the stowage process can potentially initiate dissolution processes weakening the mines' pillars consequently leading to surface subsidence and/or seismic events.

In the newly developed approach waste process brines are conditioned by increasing the concentration of magnesium chloride. The (conditioned) brines can be stowed in the following states: as a geotechnically supporting or location-stable backfill and as a liquid (FGG Weser, 2019). The performed research has thus investigated the required chemical composition of conditioned waste brine, evaluated the preferred state for stowage and engineered the stowage process and sequence. The resulting reports on the research comprise mainly proprietary knowledge and are not publicly available. For the purpose of this paper however the relevant research insights and results have been presented with references to all public and non-public sources included in the reference list at the end of this paper.

The Werra Potash District

In 2018 the Werra District celebrated 125 years of potash mining based on the first drilling core brought to surface, proving the presence of potash in this region, on the 5th of October 1893 (Stadt Heringen, 2018). In the years following this discovery many shafts and potash processing plants were commissioned in this region, e.g. shaft Grimberg in 1900 and shafts Hattorf and Sachsen-Weimar in 1905 (K+S Kali GmbH, 2017). Potash mining in the Werra District in combination with the mining of potash in other German regions such as Staßfurt, Hannover and the southern Harz area allowed Germany to maintain a monopoly position in the production and sales of potash based fertilisers for more than 50 years until the signing of the Treaty of Versailles on the 28th of June 1919, formally ending World War I (Rauche, 2015). The several individual potash mines and processing plants were consolidated in 1997 into the current K+S Werra District comprising the sites Merkers (including Springen), Wintershall, Hattorf and Unterbreizbach. The Merkers site ceased production in 1993. The mines of the Werra Potash District are presented in Figure 1 and span approximately 30 km (East-West) by 25km (North-South).

In the Werra District approximately 19 million tons of potash bearing salt is extracted per year which constitutes to circa 45% of total potash bearing salt mining by K+S KALI GmbH (K+S Kali GmbH, 2017), (K+S AG, 2018). The extracted potash bearing salts in the Werrra District originate from two horizons, i.e. the Hesse and Thuringia seams, both of Permian Zechstein age (Reinhold, 2014). The potash seams in the Werra District are relatively flat-lying deposits at a depth of approximately 500 to 1000 meters (K+S AG, 2019-1) which are mined using mainly the room-and-pillar mining method (K+S Kali GmbH, 2017).

The production of potash fertilisers in the Werra District has caused high salt concentrations in the River Werra and the subsequent Weser River for over 100 years (Braukmann & Böhme, 2011), (FGG Weser, 2018). The volume of saline wastewater originating from the production of fertilisers and other potassium- and magnesium-based products for the chemical industry has been reduced by K+S from approximately 20 million m³ per year in 1997 to approximately 7 million m³ in 2015. With the erection and commissioning of the so-called KCF-facility (i.e. Kainite Crystallization and Flotation) a further reduction of 1.5 million m³ per year has been made possible reducing the total volume of saline wastewaters to approximately 5.5 million m³ per year in 2019 (K+S AG, 2019-2). This volume comprises approximately 3,1 million m³ waste brine from the production process and another 2,3 million m³ of saline run-off from the solid waste salt heaps (FGG Weser, 2018). At this time approximately 1.5 million m³ per year of waste brine from the production is permitted to be injected into a deep aquifer while the remainder is discharged into the River Werra (K+S AG, 2018). The injection of waste brine into the deep aquifer will be discontinued from 2022 onwards (K+S AG, 2018) parallel to a gradual phasing out of the waste process brine discharge practice in the River Werra. Consequently, other responsible and sustainable disposal methods must be established. One possible disposal methods entails the stowage of waste brine in former potash mines in the Werra District (FGG Weser, 2018) of which the Springen Mine is one and most likely the first candidate for a stowage operation (K+S AG, 2018-1 (not publicly available)).

The Springen Mine has been developed in several stages, initially as two separate mines (Baumgart, 2019). Currently a total 7 shafts are still open and general gradient of the potash seams dips towards the Southwest (K+S KALI GmbH, 2018 (not publicly available)). Due to the structure of the potash seams, the mine can be sub-divided in several

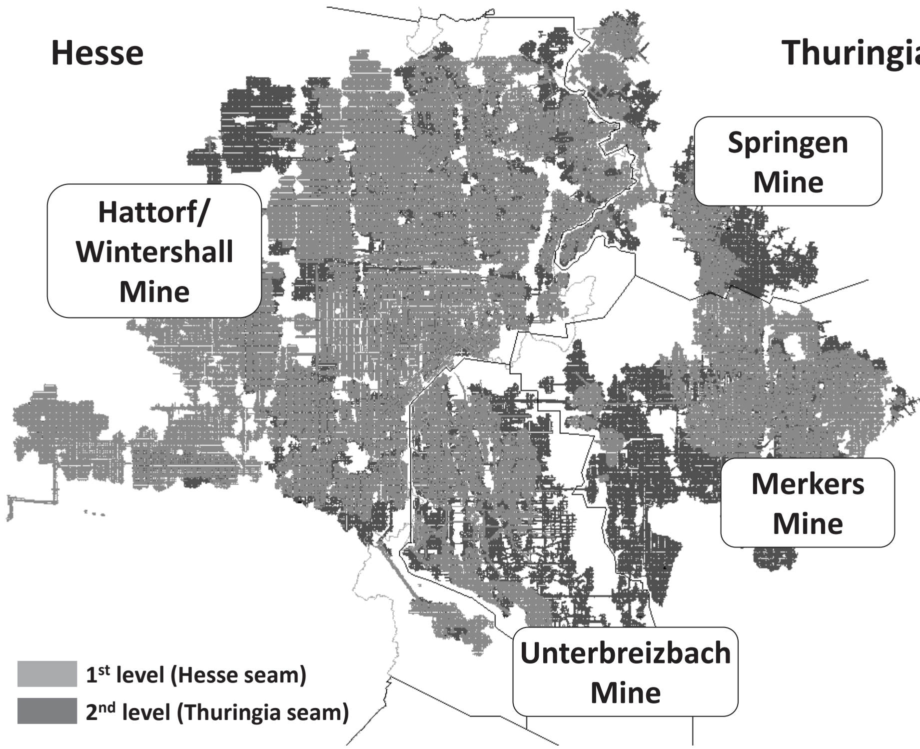

Figure 1 The potash mines of the Werra District, Germany (adapted from (K+S KALI GmbH, 2018 (not publicly available)))

mining panels which are isolated from each other through topographic depth differences. The potential isolation of mining panels have dictated the stowage sequence which is described later in this paper.

Waste brine stowage options

Independent from each other, K-UTEC and K+S have devised the following three options for stowing waste process brines in the former potash mines (K-UTEC AG, 2018 (not publicly available)), (K+S AG, 2018-1 (not publicly available)), (K+S AG, 2018-2 (not publicly available)).

- **Stowage as geotechnically supporting backfill:** using magnesium chloride (MgCl2(aq.)) as the main component, a backfill slurry can be produced which has the ability to cure and harden which is achieved using either primary binding agents or waste materials with binder properties. To improve the strength characteristics of the cured backfill sodium chloride (NaCl) grains, can be added to the backfill composition. This NaCl can either be sourced from a primary resource, i.e. mined locally in the former potash mines, or from a secondary resource, i.e. solid waste from the fertiliser production. The backfill slurry can be produced at the ground surface and pumped underground or, in case curing time is short, produced underground. In both cases the final backfill mixture is transported to the stowage area by hydraulic transport using pipelines. Strength characteristics of this type of backfill mixture are such that after curing it will provide geotechnical support to the pillars and hanging wall of the mines.
- **Stowage as location-stable backfill ('gel'):** similar to the geotechnically supporting backfill, the location-stable backfill mixture comprises MgCl2(aq.), binding agents and potentially NaCl grains. Rather than having to reach sufficient strength to support the pillars and hanging wall, the location-stable backfill composition is only aimed at supporting its self-weight. The general binding behaviour

of the backfill is based on the so-called 'Sorel-reaction' creating magnesium oxy chloride phases by combining MgCl2(aq.) with magnesium oxide (MgO(s)) (Popp, 2018). Whereas traditional Sorel concrete can reach very high strengths, K-UTEC has developed backfill compositions using alternative binding agents such as calcium oxide (CaO(s)) and calcium magnesium hydroxide (CaMg(OH)4 (s)). These mixtures reach a strength after hardening as low as 0,1 MPa (using the direct shear testing method) thus resembling a type of 'gel' in its appearance and mechanical deformation behaviour. The use of NaCl grains in the backfill mixture can improve its ability for self-support.

- **Brine stowage in a liquid state:** the final option for stowing waste process brine in the former potash mines of the Werra district is stowage in a liquid state. The several different waste brine types from the fertiliser production process have differentiated salt concentrations and can have a dissolution potential in relation to the host rocks. As stowage in a liquid state allows convective transport of the brines within the stowage volume, the dissolution potential must be carefully considered as stowage should not weaken the bearing capacity of pillars or support capacity of room beams. The waste brines are generally not completely saturated for all salt types in the mine and they thus need to be conditioned, i.e. increasing their salt concentration, before stowage can take place. The conditioning of waste brines is further detailed in the next paragraph.

As part of the research by K-UTEC and K+S, the three proposed options for waste brine stowage have been evaluated using both economic and non-economic criteria. Although an economic evaluation is, at first sight, straight forward, the challenge is how to address non-economic factors such as the permitting process, the opinion of stakeholders and the ease with which a stowing process can be incorporated in the existing fertiliser production processes. The factor time has also been an important criterion in the evaluation as the period in which the selected stowage process must be implemented is relatively short when considering K+S decided to discontinue the injection of waste process brines in deep aquifers from 2022 onwards. The result of the performed evaluation by K-UTEC and K+S (independently) is that stowage of waste brines in a liquid state, after conditioning to increase salt saturation, is the preferred option.

Main boundary conditions to brine stowage in the Springen Mine

The two potash bearing seams in the Werra District comprise so-called 'Hartsalz' (potassium chloride (KCl) and NaCl), Carnallitite (mainly hydrated potassium magnesium chloride ($KMgCl_3 \cdot 6H_2O$)) and kieseritic 'Hartsalz' (a mixture of Kieserite ($MgSO_4 \cdot H_2O$) and Sylvin (potassium chloride (KCl)) (K+S AG, 2018-1 (not publicly available)). Stowage of waste brine in the Springen Mine cannot lead to an increased subsidence and/or seismic risk. The dissolution potential of stowed brine in relation to the host rocks thus needs to be carefully considered. As the distribution of the mentioned salt types is not uniform, nor are they isolated in single mining panels, the stowage brine needs to be (largely) indifferent to all salt types. A stowage brine with a chemical composition that approximates the chemical equilibrium point in the quinary system of oceanic salts, i.e. the so-called 'Q-Point' with ca. 320 g/L $MgCl_2$, is largely indifferent to the host minerals in the mines of the Werra District (Bach, 2010), thereby enabling a safer and more sustainable stowing practice by limiting the dissolution of the host rocks, thus avoiding subsidence and seismic risk. As the waste process brines from the fertiliser production in the Werra District do not sufficiently approximate the Q-Point, lacking $MgCl_2$, they need to be conditioned. This is possible by mixing them with Bischofite ($MgCl_2 \cdot 6H_2O$ (s)) flakes (K+S AG, 2019-3 (not publicly available)) and/or a brine with a very high $MgCl_2$-concentration (K+S AG, 2018-2 (not publicly available)) or alternatively by an evaporation process (K-UTEC AG, 2018 (not publicly available))

The second boundary condition for the stowage of waste process brines is the remediation of a limited number of water inflow locations in the Springen Mine. At these locations a mostly NaCl-saturated brine, but not nearly approximating the Q-Point, is entering the mine from the underlying Rotliegend formation (Deppe & Pippig, 2002). The inflow system of this brine must be sealed before the mine is abandoned and the shafts are sealed as this brine will dissolve the pillars, destabilising the hanging wall and thus potentially causing severe subsidence and/or seismic events. The static pressure of the inflowing brines, when the inflow system is sealed, is above 60 bar above atmospheric (K+S AG, 2018-2 (not publicly available)). As the inflow system is a complex network of faults and fissures extending over a large area (Deppe & Pippig, 2002), installing a seal and proving its integrity for thousands of years is very challenging. K-UTEC suggests an alternative approach which uses the stowage of conditioned waste brines. By stowing a largely indifferent waste brine approximating the Q-Point and allowing this brine to reach a pressure equal to the pressure of the Rotliegend brine, a pressure equilibrium can be reached thus avoiding the need for an extensive and complex sealing system able to maintain a high differential pressure for thousands of years. The stowage of conditioned waste brine can thus also be an advantage for a sustainable and secure abandonment of the Springen Mine.

Engineering the preferred waste brine stowage option

The stowage of waste process brine in the Springen Mine Waste requires careful planning and engineering to satisfy the boundary conditions, meet the 2022 deadline, be cost efficient, comply with relevant laws and regulations, fulfil permitting conditions and be acceptable to the many stakeholders involved. Both K+S and K-UTEC have independently engineered the stowing process comprising a waste brine conditioning plant, a pipeline transport infrastructure for the stowage brine and a stowage sequence for the Springen Mine which will be detailed in the following (K+S AG, 2018-2 (not publicly available)), (K-UTEC AG, 2018 (not publicly available)).

- The options for the conditioning of the waste brines have been mentioned in previous paragraphs. Not mentioned is the fact that conditioning waste brines produces not only a stowage brine but also additional solid waste salts due to crystallisation reactions during the conditioning process. Two basic options for the disposal of these solids are possible: separation directly after the conditioning process, i.e. in an above-ground plant requiring a responsible disposal method, or transport of the solids with the stowage brine to the mine and separation in an underground sedimentation basin or a separation plant, e.g. based on hydrocyclones.
- The pipeline infrastructure comprises shaft pipelines, potential pumping stations boosting the pipeline pressure to overcomes topographic height differences in the mine and a stowage brine outlet system. The shaft pipeline is a API-style steel pipe (casing) with screw connections and will be suspended from the shaft hoist structure. The pressure created in the shaft pipeline through the geodetic height difference between the shaft top and bottom can either be reduced using pressure reduction (i.e. orifice) plates installed at the shaft bottom or the pressure is used to transport the stowage brine horizontally through the mine. In the latter case the horizontal pipeline must be able to withstand high pressure (e.g. PN64) and will be laid out in (lined) steel. Alternatively, the pressure is reduced and the horizontal transport can take place through HDPE-pipes with a lower pressure class (e.g. PN16). The total horizontal pipeline length will be several dozens of kilometres to span the distance between the shaft pipelines and the stowage area in the Springen Mine. The outlet of the horizontal pipelines will need to avoid scouring of the host rock at the outlet location for which several options have been suggested.
- The sequence in which the several isolated mining panels of the Springen Mine will be flooded by the stowage brine has been devised on the basis of the following design conditions:
  - o Using the topography of the mine allows stowage without the need for dams having to withstand the static

pressure of brine stowed behind them, i.e. stow brine as much as possible 'downhill'. Stowage of waste brine will thus start in the lowest areas of the mine.
- o Allow access, i.e. for maintenance and repairs, to the underground horizontal pipeline..
- o Allow access to the water inflow locations as long as possible to enable the installation of flow barriers as part of the remediation works.

Conclusions and outlook

The extensive work performed by K+S, K-UTEC and an array of other specilised firms on devising alternative waste brine disposal options has gained a wealth of knowledge and experience which can be applied to secure the production of potash based fertilisers in the Werra District. This knowledge and experience is however also potentially applicable to other mining operations (e.g. salt, metals, coal) which involve waste waters or brines. The options for creating hardening backfill compositions are also transferable outside the potash mining industry, i.e. to lower risks connected to extensive tailing ponds (e.g. avoiding incidents such as recently in Brasil) and/or increase underground resource extraction efficiency through pillar re-mining after backfilling. K+S and K-UTEC currently work together on the preparation of an optimised Process Design and subsequent engineering documents for the waste process brine stowage plant and infrastructure. Although time is short, the parties involved are confident the deadline, i.e. an infrastructure able to stow up to 1.5 million m^3/year in operation from 2022 onwards, can be met.

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