# The potential of raw material extraction from thermal brines – Successful milestones of the BrineMine project

By V. GOLDBERG, D. WINTER, F. NITSCHKE, M. RATH, S. HELD, L. SPITZMÜLLER, I. BUDACH, M. PAVEZ, D. MORATA, J. KOSCHIKOWSKI and T. KOHL\*

\*Valentin Goldberg<sup>a</sup>, Daniel Winter<sup>b</sup>, Fabian Nitschkea, Moritz Rath<sup>a</sup>, Sebastian Held<sup>a</sup>, Laura Spitzmüller<sup>a</sup>, Ingmar Budach<sup>d</sup>, Maximilliano Pavez<sup>a,e</sup>, Diego Morata<sup>c</sup>, Joachim Koschikowski<sup>b</sup>, Thomas Kohl<sup>a</sup>, <sup>a</sup>Institute of Applied Geosciences, Division Geothermal Energy and Reservoir Technology, Karlsruhe Institute of Technology, Germany, <sup>b</sup>Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany, <sup>c</sup>Department of Geology and Andean Geothermal Center of Excellence (CEGA). Facultad de Ciencias Fisicas y Matemáticas, Universidad de Chile, <sup>d</sup>Geothermie Neubrandenburg GmbH, Germany, <sup>e</sup>Institute of Nuclear Waste Disposal, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany, E-mail: valentin.goldberg@kit.edu

0179-3187/21/3 DOI 10.19225/210306 © 2021 DVV Media Group GmbH

#### Abstract

The BrineMine Project is a German-Chilean multidisciplinary research project realized by research and industry partners. The focus is on development of strategies for raw material and water extraction from geothermal springs (Brine Mining) in Chile. The topics can be separated into a geological/geochemical part and a mechanical engineering part, which are processed in close cooperation by the project consortium. In the first part, the economic potential of the dissolved raw materials in thermal spring waters in Chile is assessed by analyzing existing geochemical data of different sites. This is complemented by hydrogeochemical and geophysical exploration campaigns. The second part focuses on the development, construction and implementation of a prototype for pre-treatment and concentration of geothermal brines. With the comprehensive expertise of the team, a treatment strategy was developed and tested in a geothermal power plant, enabling controlled silica precipitation in order to overcome this limiting factor for geothermal energy production and associated raw material extraction. In this study, successful milestones of the BrineMine project are presented. The economic potential of elements in Chilean thermal waters is demonstrated. Additionally, the global potential of Brine Mining is outlined. The development of the silica treatment strategy is further described, as well as a possible integration of a prototype into an operating geothermal power plant. Finally, the construction and implementation of a large-scale first-generation prototype are presented with promising field results.

#### Introduction

The energy transition and the associated demand for non-energy, mineral raw materials have prompted the German government to expand research and development activities along the entire value chain. The focus is on economically strategic raw materials, of which the availability for future technologies and the high-tech industry must be secured to reduce dependence on the world market. The development of new resources offers the potential to complement conventional raw material extraction and thus to achieve the

### ELEK Letter to Editor

Don't hesitate to contact us and share your opinion and know-how with us. We look forward to getting your letter to the editor – leserbriefe@eid.de

(Photo: stock.adobe.com)



### **GEOTHERMAL ENERGY**

strategic goals set by the German government.

It is known that the highly mineralized thermal waters, which are circulated during the production of geothermal energy, sometimes have significant enrichments of economically strategic elements such as lithium, rubidium, antimony, tungsten, etc. [1, 2]. The BrineMine project aims to describe, qualitatively and quantitatively, the occurrence of these chemical elements in geothermal waters in Chile against the background of raw material extraction. The extraction of mineral raw materials from thermal waters is still challenging in terms of the process technology, but new sustainable methods are preparing the path to an economical production as an alternative to conventional extractive mining. An important milestone is the development of a large-scale prototype enabling effective precipitation and enrichment of selected raw materials from geothermal brines. The process used in the BrineMine project for the enrichment of the target substance is based on reverse osmosis and membrane distillation. It is driven by geothermal heat securing energy-neutrality and reduced greenhouse gas emissions. To ensure the longevity of the plant, an effective configuration of fluid pre-treatment and membrane modules is crucial. Due to overall high salt concentrations, selective separation of scale-forming minerals is required in a pre-treatment stage to avoid scaling or membrane fouling in the later process steps. The focus is on controlling silicate precipitation, which can be expected due to the change in temperature and pressure conditions. In laboratory and pilot plant tests, effective methods have been identified that allow instantaneous precipitation of up to 98% of the initial silica concentration.

The application of the developed prototype takes place in two steps, first in an operating geothermal power plant in the Upper Rhine Valley in Germany and afterwards in Chile. The test location in Chile is selected according to the results of hydrogeochemical exploration campaigns supported by geophysical methods to determine the size of the subsurface reservoir and thus the economic viability.

The BrineMine project is a 3-year research project funded by the German Federal Ministry of Education and Research. The project is realized as a bi-national research project between German and Chilean research and industrial partners. The project structure features two focal points: 1) Determination of the economic potential of thermal waters as a raw material resource and 2) Pre-treatment of thermal waters prior to raw material extraction. The Fraunhofer Institute ISE (Institute for Solar Energy Systems) leads the international consortium in close cooperation with the Karlsruhe Institute of Technology (KIT) and the Andean Geothermal Centre of Excellence (CEGA) at the Universidad de Chile. Further collaborates are the companies SolarSpring membrane solutions and Geothermie Neubrandenburg (GTN). Further Chilean partners are CSET, GTN Latin America and Transmark Renewables.

The comprehensive expertise of the consortium is required to deal with the multiple targets of the BrineMine Project. From a geological perspective, the purpose is to gain a better understanding of the resource potential from geothermal wells in Chile, as well as to carry out a large-scale exploration campaign to find appropriate locations for a prototype implementation. The project's engineering part focuses on the design, production and installation of the prototype.

#### Potential of geothermal Brine Mining in Chile

In geothermal waters, a large potential of raw materials is stored, already dissolved in water. This provides several benefits in comparison to traditional mining methods by virtue of a lower environmental impact, smaller land use and a minimized water consumption. While hydrothermal mineral deposits such as iron-oxide, copper and gold deposits are well known, thermal fluids as a deposit themselves are playing yet a minor role. The high temperatures and pressures that typically prevail in geothermal reservoirs are catalysts for water-rock interaction. In combination with the interaction time, this leads to an increase in mineralization of brines with increasing depth [3]. The salinity of geothermal brines can reach values up to 400 g/l [1]. The chemical composition itself is highly variable and depending on the reservoir rocks, the fluid genesis history and the regional flow system [4].

For a long time, production-induced uncontrolled mineral precipitation known as scaling or fouling was seen as a challenge for the geothermal industry [5]. However, it is also an opportunity, as large-scale studies [1, 6] indicate significant amounts of valuable raw materials dissolved in these waters. Nevertheless, accessible data are often limited to the main ions. More detailed hydrochemical analyses can therefore reveal further raw material potentials especially in areas with high geothermal potentials.

Chile has one of the highest geothermal potentials worldwide (Fig. 1), recently affirmed by commissioning the first geothermal power plant in Chile – Cerro Pabellón with an installed capacity of 48 MW<sub>e</sub> which will be expanded to 81 MW<sub>e</sub> during 2021. The high potential arises from Chile's unique geological framework within the Andean volcanic arc, which yields more than 200 active volcanoes [7]. By now, approximately 70 geother-



Fig. 1 Distribution of thermal springs in Chile. Marker size indicates the amount of total dissolved solids. The color represents the reservoir temperature. The highlighted springs were selected due to their high values of elements, which are of economic interest in Chile.

www.oilgaspublisher.de

47. Edition · Issue 1/2021 GAS 27

mal areas are considered to potentially host high-enthalpy geothermal systems and even more are yet to be explored [8].

In terms of raw material extraction in the past years, the salt lakes in the Atacama Desert in Chile have received high interest as an important source for lithium. The mining in this area is accompanied by serious environmental impact as well as high water consumption since 95% of the Li-bearing salt lake brine has to be evaporated for the Li-enrichment [9]. This bears obvious conflict potential in one of the world's driest deserts. Furthermore, Chile has the largest copper reserves on Earth [10], which is produced by hard-rock mining. This extraction method as also for other elements is accompanied by high water consumption [11, 12]. Yet, the Chilean economy is dependent on these resources. Both elements, lithium and copper, are enriched in different thermal brines worldwide [2, 13, 14]. If springs with sufficient contents of these elements are identified and viable extraction methods are developed, Brine Mining has the potential to serve as a water-saving alternative.

Part of the BrineMine Project is the geochemical exploration in Northern Chile to identify potential springs and associated target minerals. In the course of the project, a geothermal fluid sampling campaign will be conducted to analyze the associated raw material potential of Northern Chile and create a broad and consistent data set of the thermal springs within this area. Beyond standard measurements, a holistic and standardized dataset shall be created. It focuses on springs with high temperatures and a high content of total dissolved solids (TDS). Its overall goal is an appraisal of the economic resource potential in this area. Beyond the composition, the chemical analysis allows an estimation of the geothermal resource via geothermometers, which have been adapted for Chilean systems in previous studies [15]. Furthermore, fluid age determinations, which have been approved in Chile [16], will be conducted to assess the dilution with shallow cold waters and the recharge of the system. Using these geochemical exploration tools, which are continuously developed [17], a sustainable exploitation scenario can be designed. Complementary geophysical surveys using magnetotelluric methods allow the determination of hydrothermal fluid circulation within faults and the visualization of alteration zones. An associated reservoir characterization provides additional information on the potential storage capacity [18].

Due to the global COVID-19 pandemic, the geochemical sampling campaign was postponed. In order to develop different extraction scenarios, already collected literature data (Fig. 1) were used.

# Scenario calculation for the economics of raw material extraction from geothermal brines

To exhibit the economic potential of thermal springs in terms of raw material content six simplified scenario calculations were conducted. The basis for the calculation are assumptions based on typical geothermal power plant operation parameters as e.g. at Cerro Pabellon [19], hydrochemical literature data of different thermal springs in Chile and market prices for different commodities.

Figure 1 shows the distribution of thermal springs in Chile and presents maximum values for selected, potentially relevant chemical elements. To quantify the potential of different raw materials, trace elements such as lithium (scenario El Tatio 3), rubidium (scenario El Tatio 2) and cesium (scenario El Tatio 1) were chosen as well as more enriched elements like boron (scenario Puchuldiza-Tuja), magnesium (Scenario Gorbea) or silica (scenario Termas Jahuel). The economic potential of trace elements results from their high market prices, while the more enriched elements benefit from their higher concentrations in combination with average prices (Fig. 2). A location-specific economic factor (third column in Tab. 2) results from the stated element contents and the price per unit.

The extremely high prices of cesium and rubidium result from small trading units and the lack of public trading [20]. The units are traded in grams and thus exceed the price per ton of the other bulk raw materials by far. Furthermore, the achievable price is highly dependent on the purity and the pro-





Tab. 1Typical geothermal production scenario. The<br/>scenario assumes a flow rate of 80 l/s and<br/>an availability of 90% of the year (329<br/>days). The extraction rate is a conservative<br/>assessment based on the research in lithi-<br/>um extraction.

Flowrate	80 [l/s]	
Availability (runtime/year)	90%	
Σ Annually circulated brine	2,270,592 m <sup>3</sup>	
Extraction rate for raw materials	80%	

duced compound of the raw material. For quantifying the circulated mass of raw materials, a representative volume stream was calculated (Tab. 1). A typical flow rate for geothermal power plants is assumed [19]. An availability of 90% was selected, corresponding to 36 days per year when the power plant is not running due to maintenance work. As a sum of these two parameters, the total volume of circulated brine per year is calculated. The extraction rate of 80% for the raw material is based on literature data for lithium using ion sieves [26]. Note that lithium recovery from thermal brines recently received increased research and industry interest resulting in an improvement of recovery technologies. For each element, an individual extraction methodology must be developed resulting in different extraction rates.

#### **Resulting economic potential**

To assess the economic potential for each scenario, the circulated mass for each element was calculated using the volume of the circulated brine, the extraction rate and the concentration of the elements in the springs (Tab. 2). For boron and lithium, the mass for compounds is calculated, based on the circulated amount of substance of the pure elements. If different prices were available depending on the grade, the lower price is chosen to keep the model as conservative as possible.

The resulting economic potential displays the theoretical value of the raw materials circulated in a virtual power plant, considering the chemistry of the different springs. Extraction costs, infrastructure, processing, or any further investments are not taken into account in this simplified model.

The results show that the elements with the lowest occurrence, cesium (Scenario El Tatio 1) and rubidium (El Tatio 2), possess the highest economic potentials due to their extremely high market prices. They exceed the maximum achievable value for lithium (El Tatio 3) by far, although the latter is currently the most discussed within the geothermal community for Brine Mining. Yet, there is no concept to selectively extract cesium from thermal brines at the moment. However, the model shows, that even at an extraction rate of 1% (~22.6 Mio. \$/yr) the potential still widely exceeds each of the minerals which are present in higher concentrations. Like-

# 28 **GAS** 47. Edition · Issue 1/2021

www.oilgaspublisher.de

Tab. 2 Economic potential of the production scenarios. The circulated amount results from the element content multiplied with the volume of circulated brine and the extraction rate. For boron and lithium, the amount was calculated as resulting compounds that can be produced from the pure element content.

Scenario	Compound	Economic factor spring [\$/I]	Circulated mass per year [t]	Specific price [\$/t]	Resulting economic potential [\$/yr]
Termas-Jahuel	SiO <sub>2</sub>	0.0001	690	300 [21]	207,078
Gorbea	Mg	0.0023	2,089	2,000 [22]	4,177,889
Puchuldiza-Tuja	$H_3BO_3$	0.0034	10,414	600 [23]	6,248,663
El Tatio 1	Cs	0.9954	29	63,000,000 [24]	1,808,117,821
El Tatio 2	Rb	0.1067	12	15,920,000 [25]	193,752,340
El Tatio 3	LiCO <sub>3</sub>	0.0029	585	9,000 [22]	5,263,383



Fig. 3 Solubility behavior of silica. The plot shows the solubility of different silica polymorphs/phases in relation to the temperature (Data Source reference [30]).



Fig. 4 Flow chart summarizing the problem-solving approach in the BrineMine project. Based on the challenge of silica fouling, a treatment strategy was developed in the laboratory. This approach was upscaled first using a numerical design calculation. The simulation results were subsequently reproduced in a technical center leading to the construction of a 1st generation prototype.

wise, also compounds such as boric acid  $(H_3BO_3)$  with the second-lowest price per ton have an economic potential in the range of lithium carbonate due to their higher occurrence (scenario Puchuldiza-Tuja). A similarly high potential is obtained for magnesium (scenario Gorbea). It is shown, that in addition to materials for the high-tech industry, bulk raw materials can be a lucrative target for geothermal Brine Mining. The market value for SiO<sub>2</sub> (scenario Termas-Jahuel) is by far the lowest. However, even though it is not lucrative to sell  $SiO_2$  as raw material,  $SiO_2$ -extraction might be of economic interest as a means to mitigate silica scaling, which could increase power plant efficiency. Furthermore, the specific price for the precipitates can be increased by purifying or optimizing the produced silicon compound. The overall potential further increases when the processes are coupled in a cascade approach, where different elements from one brine are produced in one process chain. This is demonstrated by the high potential of the three scenarios El Tatio 1–3 which all analyze the same spring. Here it is to be said that the element contents represent a minimum value since the data are from surface springs that could be diluted by meteoric waters. In a geothermal project where the reservoir is accessed via boreholes, higher values are consequently expected.

Still, as in all mining projects, the potential is site-specific, requiring an extensive exploration and exploitation strategy. To extract raw materials from liquids, various extraction methods are developed such as adsorption, liquid-liquid extraction, ion sieves, electrochemical precipitation, co-precipitation, or membrane distillation. The choice of a particular technique depends on the composition of the fluid, the initial concentration as well as the desired compound to be processed [27]. Furthermore, it must be compatible with the challenges imposed by the chemistry of thermal waters.

#### **Pretreatment of thermal waters**

#### Methodology

In high-enthalpy geothermal fields, precipitation of amorphous silica is the limiting factor for the possible amount of extractable energy [28]. With 16 GW, installed worldwide capacity in high-enthalpy geothermal power plants in 2020 [29] this challenge concerns major parts of the geothermal industry worldwide. Furthermore, the efficiency of raw material extraction from brines can be improved by pre-concentration of the target minerals [27]. Both processes, cooling for energy production and concentration for enhancing the extraction process, potentially increase silica precipitation. To avoid damage to the power plant or the extraction facility, silica precipitation must be controlled.

The solubility of silica phases is strongly driven by temperature as displayed in Figure 3. Geothermal brines are assumed to be in equilibrium with the surrounding lithology under reservoir conditions [30]. This typically results in saturation with respect to quartz under the given reservoir conditions. During production, this equilibrium is perturbed and the fluid tends to oversaturate, which leads to a risk of unwanted precipitation. Likewise, oversaturation can also result from increasing the general SiO<sub>2</sub> content (Fig. 3) during the pre-concentration step. In order not to limit the potential concentration rate, the method of selective precipitation was preferred over precipitation inhibition. The challenge was to find a compound and an associated precipitation process that is cost-efficient, integratable into the power plant process, and selective for silica to not affect the content of valuable elements. With the comprehensive expertise of the research consortium in a multi-stage and interdisciplinary process (Fig. 4), a treatment strategy was developed and implemented in a largescale prototype in less than 12 months.

www.oilgaspublisher.de

Various precipitation methods were compared in small-scale lab experiments using artificial brines, which were designed according to the chemistry of Chilean thermal waters. The successful method results from changing the species distribution of the silica. SiO<sub>2</sub> dissolves in water under the formation of silicic acid (H<sub>4</sub>SiO<sub>4</sub>) as shown in equation 1.1 [31]. An increase in pH leads to ionization of the silicic acid (Equation 1.2 and 1.3) [31]. At a pH value of  $10.5 H_3 SiO_4^{-1}$  is the dominant species. This negatively charged species react in the presence of double or higher valent cations (e.g. Ca<sub>2</sub><sup>+</sup>/Mg<sub>2</sub><sup>+</sup>) under the formation of Calcium/Magnesium-silicate-hydrate (C/MSH) phases. The associated precipitation is almost instantaneous. This enables controlled silica precipitation as a pre-treatment before concentrating. Silica species reaction [31]:

$SiO_2 + 2H_2O \leftrightarrow H_4SiO_4$	(1.1)
$H_{4}SiO_{4} + OH^{-} \leftrightarrow H_{3}SiO_{4} H_{2}O$	(1.2)
$H_{3}SiO_{4} + OH^{-} \leftrightarrow H_{3}SiO_{4} + H_{3}O$	(1.3)

After successful small-scale testing in the laboratory the process was transferred to a larger scale at the technical center in the Fraunhofer Institute (ISE) in Freiburg. The precipitation experiment was reproduced successfully. Based on this intermediate step a large-scale prototype was developed. A numerical geochemical model was set up for extrapolating the results for the application with complex natural brines and to quantify the mass flows. Based on these results, the prototype was designed and dimensioned.

#### **Prototype Design**

The prototype plant is developed, built, and operated in a real-life environment to demonstrate the suitability and flexibility of the full pre-treatment process chain. The process scheme and integration strategy for

the demonstrator are visualized in Figure 5. The demonstration plant is designed to be hooked-up either to the pressurized thermal brine flow of a geothermal power plant or a non-pressurized thermal brine well. A bypass stream of the geothermal brine is extracted from the main flow path and fed into the demonstrator. The design flow rate here was a continuous stream of 20-50 l/h. In the first process stage, the problematic typical high load of silica is selectively precipitated following the developed strategy. The system continuously adjusts the condition within the reactor to an optimal set of molar Ca/Si ratio as well as pH, also taking into account the natural content of calcium in the currently processed geothermal brine. The precipitates are extracted from the water stream by filtration. In the second stage, the brine is pre-concentrated with the efficient pressure-driven reverse osmosis (RO) process, which extracts fresh water through a semi-permeable membrane through which the dissolved solids cannot pass. The pre-concentration potential of this process stage depends on the natural salinity of the given brine and will reach a salinity level of about 70,000 mg/l at a typical operation with a pressure of 60 bar. Consequently, for low saline thermal brines (e.g. El Tatio, Chile, ~10,000 mg/l [32]) a significant pre-concentration is possible, for super saline brines (e.g. Upper Rhine Valley ~110,000 mg/l [2]) the pre-concentration stage is bypassed and the brine is directly forwarded to the post-concentration stage. The post-concentration relies on the thermally driven membrane distillation (MD) process, in which water is extracted from the brine by evaporation through a vapor-permeable membrane. Since MD basically relies on the phenomenon of an evaporative separation, it is not fundamentally limited to a certain final concentration. The limitation is indirectly given by energy efficiency considerations



Fig. 5 Process scheme and hydraulic/energetic integration strategy for the BrineMine continuous flow demonstrator



Fig. 6 Geothermal power plant Insheim (Source: Pfalzwerke geofuture GmbH)

or supersaturation of specific species that induce crystal nucleation and consequently membrane scaling or flow channel clogging. The MD process stage is considered energetically highly attractive since it is driven by low-grade heat (60-90 °C) that was previously extracted from the geothermal brine. The MD permeate is considered high-quality freshwater due to the super-selective nature of evaporative separation. The concentrate outflow offers a brine with a high content of valuable resources, ready to be used in arbitrary extraction processes. With this design, the first step of the prototype application was conducted by installing it in an actively operating geothermal power plant located in the Upper Rhine Valley in Germany.

#### **Prototype Testing**

Due to the COVID-19 pandemic, the prototype could not to date be tested in Chile. An alternative was found at the geothermal power plant Insheim in the Upper Rhine Valley (Germany) operated by Pfalzwerke geofuture GmbH (Fig. 6). Consequently, the prototype was calibrated for geothermal waters with higher salt load and lithium concentration, and a lower silica concentration. It was successfully implemented in a running power plant cycle operating in a continuous flow system (flow rate 20–50l/h), while handling total dissolved solids of up to 120,000 mg/L of highly corrosive brines (Fig. 7).

Figure 8 shows the results of the successful treatment. Silicon and magnesium immediately (within 5 minutes) underwent a reduction of 98 %, while calcium showed a delayed reaction. Importantly, the concentration of lithium, a potential target mineral, is not affected during the entire process time. Furthermore, preliminary results indicate no incorporation of other trace elements such as cesium or rubidium. This proves that the developed silica controlling process is replicable for complex brines without affecting target elements. The results indicate that the risk of silica scaling is greatly reduced, even in the context of further cooling and concentrating. Subsequently, the brine was concentrated by constricting the water through membrane distillation. This step facilitated the concentration of lithium up to 500 mg/l (and a total salt load of 300,000 mg/l),

www.oilgaspublisher.de

# **GEOTHERMAL ENERGY**



Fig. 7 Prototype installed at the geothermal power plant Insheim. The left picture shows the prototype. Precipitates are shown in the two pictures on the right. (Source: Valentin Goldberg / Sebastian Held).

which corresponds to a concentration factor of ~3 and puts it into the realm of Chilean salt lake brines. If once applied to fluids with lower initial salt loads a higher relative raw material concentration is possible. If the El Tatio fluid with approx. 10,000 mg/l TDS and 61 mg/l of Lithium, is concentrated to the same total salt load, a lithium content of 1,830 mg/l can be achieved. Also, note that the silica and magnesium concentrations did not reach critical levels in terms of oversaturation during the application of the membrane distillation. The measurements of the permeate of the MD showed the integrity of the membrane and thus the production of pure water.

The promising results of the large-scale prototype application represent an important milestone for future mineral extraction from geothermal loops. It provides important information for a potential full-scale and longterm implementation. The kinetics were much faster than in the laboratory experiments using artificial brine. This can be explained by the higher salt load resulting in an increased salting-out effect and activity coefficient of the water [33]. In a flowthrough system, the reaction time is a function of vessel size and flowrate. Fast kinetics thus enable the processing of high flow rates without requiring large reaction tanks. This improves a possible implementation in a running geothermal loop without extensive changes to the geothermal plant design and facilitates an application in geothermal power plants worldwide.

#### **Outlook and global potential**

The scenario analysis of Chilean hot springs showed the promising economic potential of thermal waters. Furthermore, the implementation of the 1st generation prototype in the Upper Rhine Valley (Germany) illustrated successfully the feasibility of installing a mineral extraction facility in an operating geothermal power plant. To extrapolate these two locally demonstrated potentials, a preliminary worldwide database was compiled (Fig. 9). The aim is to collect international geothermal chemistry data to assess the global potential of Brine Mining. Beyond the economic aspect, the database can serve as a tool for upcoming exploration projects in terms of geochemical exploration or scaling risk assessment.The preliminary database contains about 10,000 data points, summarizes global chemical data from hot springs and thermal wells and complements the US database collected by Neupane and Wendt [1]. The economic potential of raw materials demonstrated in particular thermal brines can thus be transferred to other geothermal areas. A first preliminary analysis of the collected data indicates a high worldwide potential. As dis-



Fig. 8 Effectiveness of silica treatment. The graph shows the relative change of chosen elements during the prototype testing. Within 5 minutes, the total content of Si is reduced by 98 %. Li as raw material reference stays unaffected and varies within the scope of measurement inaccuracy.

played in Figure 10, 12 of 30 elements defined by the European Commission as critical raw materials can be enriched in geothermal brines [63]. Further elements of high economic value are also frequently found worthy of enrichment.



Fig. 9 Preliminary worldwide database of geothermal brines. The database currently contains data of ~10,000 springs and provides the basis for the evaluation of the global economic potential of Brine Mining [1, 2, 32–62].



Fig. 10 Economic valuable elements in thermal waters. In red: Elements found in thermal waters that are classified as critical elements by the European Commission [63]. In blue: Other elements that are of high economic value and were found enriched in thermal waters in the global brine database.

www.oilgaspublisher.de

## **GEOTHERMAL ENERGY**

#### Conclusion

During the first phase of the BrineMine project, the potential of raw material extraction from geothermal waters in Chile was analyzed. Not only elements used in the high-tech industry (e.g. lithium) should be in the focus for extraction, but also bulk raw materials that occur in higher quantities (e.g. boric acid). Our investigations indicate an enormous worldwide economic potential for the extraction of raw material from thermal waters. To unleash this economic potential of thermal waters with their complex chemistry an effective method to control silica precipitation was developed. Tests in an operating geothermal power plant demonstrated the possibility of treating brines for specific components like silica and simultaneously concentrating valuable raw materials like lithium. The precipitated silica-calcium-hydrate phases can themselves also be seen as a resource. The almost total reduction of silica is a potential means of silica scaling mitigation, which could increase the efficiency of conventional geothermal power plants independent of raw material extraction. The large-scale prototype demonstrated the feasibility of the developed treatment strategy during continuous operation. Furthermore, important parameters for the optimization of the prototype were identified. Based on these experiments the prototype will be adjusted to Chilean brines and implemented at its original destination.

The first real-life application of mineral extraction at an operating geothermal power plant is a huge milestone for the realization of Brine Mining's global potential. Compared to conventional mining methods the raw materials are already dissolved in thermal waters and do not have to be leached out of a hard rock deposit. Since the fluid serves as the media of transport bringing the target minerals to the surface, efforts in terms of mining and infrastructure as well as land use are greatly reduced compared to conventional open-pit mining. Consequently, Brine Mining has a great potential for a more sustainable and environmentally friendly raw material production.

The potential has been proven. Now, economical extraction technologies for each element have to be developed, adapted to the individual brines and implemented in geothermal power plants. For entering the large economic and ecologic potentials of Brine Mining, a site-specific raw material and extraction concept will be mandatory. A buried treasure lies beneath our feet, considering the high volumes of thermal water circulated in geothermal power plants and the contents of valuable elements dissolved in these waters. Lifting this treasure will be beneficial for the geothermal industry and beyond.

#### Acknowledgment

The authors gratefully acknowledge research funding by BMBF Client II for the BrineMine Project (Federal Ministry of Education and Research, FKZ: 033R190B). We thank Prof. Dr. J. Kolb and Dr. E. Eiche of the department of Geochemistry & Economic Geology (Karlsruhe Institute of Technology, Division of Applied Geosciences) for the support in developing the measurement strategy and the access to laboratories and equipment, as well as for fruitful discussions. The team of Pfalzwerke geofuture GmbH is thanked for enabling the prototype implementation at the powerplant Insheim and the pleasant cooperation during sampling. Further, we thank Transmark Renewables for the productive discussions and for enabling a joint sampling campaign. Finally, we appreciate the support of the Chilean ANID-Fondap program (projects 15090013 and 15200001).

#### References

- G. Neupane and S. Wendt, Eds., "Assessment of Mineral Resources in Geothermal Brines in the US," 2017.
- [2] B. Sanjuan, R. Millot, C. Innocent, C. Dezayes, J. Scheiber, and M. Brach, "Major geochemical characteristics of geothermal brines from the Upper Rhine Graben granitic basement with constraints on temperature and circulation," Chem. Geol., vol. 428, pp. 27–47, 2016, doi: 10.1016/j. chemgeo.2016.02.021.
- [3] I. Stober, M. Wolfgramm, and J. Birner, "Hydrochemie der Tiefenwässer in Deutschland," Z. geol. Wiss., no. 5–6, pp. 339–380, 2014.
- [4] I. Stober and K. Bucher, "Hydraulic and hydrochemical properties of deep sedimentary reservoirs of the Upper Rhine Graben, Europe," Geofluids, vol. 15, no. 3, pp. 464–482, 2015, doi: 10.1111/ gfl.12122.
- [5] I. Stober and K. Bucher, Geothermie. Heidelberg: Springer Verlag Berlin, 2012.
- [6] A. Hauser, Catastro y caracterización de las fuentes de aguas minerales y termales de Chile. Servicio Nacional de Geolog{\'\i}a y Miner{\'\i}a, 1997.
- [7] L. Siebert, T. Simkin, and P. Kimberly, Volcanoes of the World: Third Edition. 2010.
- [8] D. Aravena, M. Muñoz, D. Morata, A. Lahsen, M. Á. Parada, and P. Dobson, "Assessment of high enthalpy geothermal resources and promising areas of Chile," Geothermics, vol. 59, pp. 1–13, 2016, doi: 10.1016/j.geothermics.2015.09.001.
- [9] V. Flexer, C. F. Baspineiro, and C. I. Galli, "Lithium recovery from brines: A vital raw material for green energies with a potential environmental impact in its mining and processing," Sci. Total Environ., vol. 639, pp. 1188–1204, 2018, doi: 10.1016/j.scitotenv.2018.05.223.
- [10] C. A. Peña and M. A. J. Huijbregts, "The blue water footprint of primary copper production in Northern Chile," J. Ind. Ecol., vol. 18, no. 1, pp. 49–58, 2014, doi: 10.1111/jiec.12036.
- [11] C. A. Peña and M. A. J. Huijbregts, "The Blue Water Footprint of Primary Copper Production in Northern Chile," J. Ind. Ecol., vol. 18, no. 1, pp. 49–58, 2014, doi: 10.1111/jiec.12036.
- [12] G. M. Mudd, "Sustainability Reporting and Water Resources: a Preliminary Assessment of Embodied Water and Sustainable Mining," Mine Water Envi-

ron., vol. 27, no. 3, pp. 136–144, 2008, doi: 10.1007/s10230-008-0037-5.

- [13] F. Tassi et al., "Geochemistry of fluid discharges from Peteroa volcano (Argentina-Chile) in 2010-2015: Insights into compositional changes related to the fluid source region(s)," Chem. Geol., vol. 432, no. April, pp. 41–53, 2016, doi: 10.1016/j. chemgeo.2016.04.007.
- [14] S. Regenspurg, H. Milsch, and J. Schaper, "Copper in Geothermal Brine: Origin, Reactions, Risks, and Chances," World Geotherm. Congr. 2015, no. April, p. 5, 2015.
- [15] F. Nitschke, S. Held, T. Neumann, and T. Kohl, "Geochemical characterization of the Villarrica geothermal system, Southern Chile, part II: Site-specific re-evaluation of SiO2 and Na-K solute geothermometers," Geothermics, vol. 74, no. March, pp. 217–225, 2018, doi: 10.1016/j.geothermics.2018.03.006.
- [16] S. Held et al., "Geochemical characterization of the geothermal system at Villarrica volcano, Southern Chile; Part 1: Impacts of lithology on the geothermal reservoir," Geothermics, vol. 74, no. October 2017, pp. 226–239, 2018, doi: 10.1016/j.geothermics.2018.03.004.
- [17] L. H. Ystroem, F. Nitschke, S. Held, and T. Kohl, "A multicomponent geothermometer for high-temperature basalt settings," Geotherm. Energy, vol. 8, no. 1, 2020, doi: 10.1186/s40517-020-0158-z.
- [18] M. Pavez, E. Schill, S. Held, D. Díaz, and T. Kohl, "Visualizing preferential magmatic and geothermal fl uid pathways via electric conductivity at Villarrica Volcano, S-Chile," J. Volcanol. Geotherm. Res., vol. 400, p. 106913, 2020, doi: 10.1016/j.jvolgeores.2020.106913.
- [19] G. Cappetti, "Cerro Pabellón geothermal plant: a success story Geothermal resources in Chile," 2019.
- [20] W. C. Butterman, W. E. Brooks, and R. G. J. Reese, "Mineral Commodity Profiles: Cesium," U.S. Geol. Surv., pp. 1–10, 2005, [Online]. Available: https:// web.archive.org/web/20070207015229/http:// pubs.usgs.gov/of/2004/1432/2004-1432.pdf%0Ahttp://pubs.usgs.gov/of/2004/1432/index. html.
- [21] T. Dolley, "2017 USGS Minerals Yearbook Silica," 2017.
- [22] D. Bastian, "DERA Preismonitor Oktober 2020," 2020.
- [23] A. Brioche, "2017 USGS Minerals Yearbook Boron," 2017.
- [24] C. Tuck, "CESIUM USGS Report," 2020.
- [25] C. Tuck, "RUBIDIUM USGS Report," 2020.
- [26] X. Xu et al., "Extraction of lithium with functionalized lithium ion-sieves," Prog. Mater. Sci., vol. 84, no. September, pp. 276–313, 2016, doi: 10.1016/j. pmatsci.2016.09.004.
- [27] T. Ryu et al., "Recovery of Lithium Ions from Seawater Using a Continuous Flow Adsorption Column Packed with Granulated Chitosan-Lithium Manganese Oxide," Ind. Eng. Chem. Res., vol. 55, no. 26, pp. 7218–7225, 2016, doi: 10.1021/acs.iecr.6b01632.
- [28] I. Gunnarsson and S. Arnórsson, "Impact of silica scaling on the efficiency of heat extraction from high-temperature geothermal fluids," Geothermics, vol. 34, pp. 320–329, 2005.
- [29] G. W. Huttrer, C. Rica, and E. Salvador, "Geothermal Power Generation in the World 2015-2020 Update

Report," pp. 1-17, 2020.

- [30] R. O. Fournier and J. J. Rowe, "Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells," Am. J. Sci., vol. 264, no. 9, pp. 685–697, 1966, doi: 10.2475/ajs.264.9.685.
- [31] R. K. Iler, The Chemistry of Silica. 1976.
- [32] W. F. Giggenbach, "The isotopic composition of waters from the El Tatio geothermal field, Northern Chile," Geochim. Cosmochim. Acta, vol. 42, no. 7, pp. 979–988, 1978, doi: 10.1016/0016-7037(78)90287-9.
- [33] W. L. Marshall and J. M. Warakomski, "Amorphous silica soluhilities-II. Effect of aqueous salt solutions at 25°C," Geochemica Cosmochem., vol. 44, pp. 915–924, 1980.
- [34] D. M. Allen, S. E. Grasby, and D. A. Voormeij, "Determining the circulation depth of thermal springs in the southern Rocky Mountain Trench, south-eastern British Columbia, Canada using geothermometry and borehole temperature logs," Hydrogeol. J., vol. 14, no. 1–2, pp. 159–172, 2006, doi: 10.1007/s10040-004-0428-z.
- [35] L. Aquilina et al., "Origin, evolution and residence time of saline thermal fluids (Balaruc springs, southern France): Implications for fluid transfer across the continental shelf," Chem. Geol., vol. 192, no. 1–2, pp. 1–21, 2002, doi: 10.1016/ S0009-2541(02)00160-2.
- [36] S. Arnórsson, E. Gunnlaugsson, and H. Svavarsson, "The chemistry of geothermal waters in Iceland. II. Mineral equilibria and independent variables controlling water compositions," Geochim. Cosmochim. Acta, vol. 47, no. 3, pp. 547–566, 1983, doi: 10.1016/0016-7037(83)90277-6.
- [37] . H. Karamanderesi and K. Ölçeno, "Geology of the Denizli Sarayköy (Gerali) Geothermal Field, Western Anatolia, Turkey," World Geotherm. Congr. 2005, no. April, pp. 24–29, 2005.
- [38] G. Cortecci, T. Boschetti, M. Mussi, C. H. Lameli, C. Mucchino, and M. Barbieri, "New chemical and original isotopic data on waters from El Tatio geothermal field, northern Chile," Geochem. J., vol. 39, no. 6, pp. 547–571, 2005, doi: 10.2343/geochemj.39.547.
- [39] G. Tarcan, S. Filiz, and Ü. Gemici, "Geology and Geochemistry of the Salihli Geothermal Fields, Turkey," World Geotherm. Congr. 2000, pp. 1829–1834, 2000.
- [40] W. Giggenbach, D. Sheppard, B. Robinson, M. Stewart, and G. Lyon, "Geochemical structure and position of the Waiotapu geothermal field, New Zealand," Geothermics, vol. 23, no. 5–6, pp. 599–644, 1994, doi: 10.1016/0375-6505(94)90022-1.
- [41] W. F. Giggenbach, "Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin," Earth Planet. Sci. Lett., vol. 113, pp. 495–510, 1992.
- [42] A. Gokgoz, I. E. Yilmazli, I. Gungor, and I. Yavuzer, "Hydrogeology and Environmental Study at the Karahayit Geothermal Field (Western Turkey)," no. April, pp. 25–29, 2010.
- [43] E. González-Partida et al., "Hydro-geochemical and isotopic fluid evolution of the Los Azufres geothermal field, Central Mexico," Appl. Geochemistry, vol. 20, no. 1, pp. 23–39, 2005, doi: 10.1016/j.apgeochem.2004.07.006.
- [44] S. E. Grasby, I. Hutcheon, and H. R. Krouse, "Erratum: The influence of water-rock interaction on the

chemistry of thermal springs in western Canada (Applied Geochemistry (2000) 15 (439-454) PII: S0883292799000669)," Appl. Geochemistry, vol. 15, no. 7, p. 1069, 2000, doi: 10.1016/S0883-2927(00)00020-2.

- [45] C. W. Karingithi, S. Arnórsson, and K. Gródienvold, "Processes controlling aquifer fluid compositions in the Olkaria geothermal system, Kenya," J. Volcanol. Geotherm. Res., vol. 196, no. 1–2, pp. 57–76, 2010, doi: 10.1016/j.jvolgeores.2010.07.008.
- [46] K. Kato, A. Ueda, K. Mogi, H. Nakazawaka, and K. Shimizu, "Silica recovery from Sumikawa and Ohnuma geothermal brines (Japan) by addition of CaO and cationic precipitants in a newly developed seed circulation device," Geothermics, vol. 32, pp. 239–273, 2003.
- [47] T. Kaya and A. Kindap, "Kizildere New Geothermal Power Plant In Turkey," Int. Geotherm. Days Conf. Summer Sch., no. Slovakia 2009, 2009.
- [48] J. Lowstern et al., "A geochemical reconnaissance of the Alid volcanic center and geothermal system\ Danakil depression\ Eritrea," Geothermics, vol. 28, pp. 161–187, 1999.
- [49] C. Nicolau, M. Reich, and B. Lynne, "Physico-chemical and environmental controls on siliceous sinter formation at the high-altitude El Tatio geothermal field, Chile," J. Volcanol. Geotherm. Res., vol. 282, pp. 60–76, 2014, doi: 10.1016/j.jvolgeores.2014.06.012.
- [50] M. Özkaya, "NUMERICAL MODELING OF KIZILDERE GEOTHERMAL FIELD," 2007.
- [51] H. M. Ozler, "Hydrogeology and geochemistry in the Curuksu (Denizli) hydrothermal field, western Turkey," Environ. Geol., vol. 39, no. 10, pp. 1169– 1180, 2000, doi: 10.1007/s002540000139.
- [52] H. Pauwels, C. Fouillac, and A. M. Fouillac, "Chemistry and isotopes of deep geothermal saline fluids in the Upper Rhine Graben: Origin of compounds and water-rock interactions," Geochim. Cosmochim. Acta, vol. 57, no. 12, pp. 2737–2749, 1993, doi: 10.1016/0016-7037(93)90387-C.
- [53] F. Risacher, H. Alonso, and C. Salazar, "Hydrochemistry of two adjacent acid saline lakes in the Andes of northern Chile," Chem. Geol., vol. 187, no. 1–2, pp. 39–57, 2002, doi: 10.1016/S0009-2541(02)00021-9.
- [54] B. Sanjuan, R. Millot, C. Dezayes, and M. Brach, "Main characteristics of the deep geothermal brine (5 km) at Soultz-sous-Forêts (France) determined using geochemical and tracer test data," Comptes Rendus - Geosci., vol. 342, no. 7–8, pp. 546–559, 2010, doi: 10.1016/j.crte.2009.10.009.
- [55] U. Serpen and N. Aksoy, "Reassessment of Reinjection in Salavatli-Sultanhisar Field of Turkey," no. April, pp. 25–29, 2010.
- [56] S. Simsek, "Hydrogeological and isotopic survey of geothermal fields in the Buyuk Menderes graben, Turkey," Geothermics, vol. 32, no. 4, pp. 669–678, 2003, doi: 10.1016/S0375-6505(03)00072-5.
- [57] S. Simsek, "Present status and future development possibilities of Aydın-Denizli Geothermal Province," Production, pp. 11–16, 2003.
- [58] F. Tassi, F. Aguilera, O. Vaselli, T. Darrah, and E. Medina, "Gas discharges from four remote volcanoes in northern Chile (Putana,Olca, Irruputuncu and Alitar): A geochemical survey," Ann. Geophys., vol. 54, no. 2, pp. 121–136, 2011, doi: 10.4401/ ac-5173.
- [59] S. Tekin, "ESTIMATION OF THE FORMATION TEM-

PERATURE FROM THE INLET AND OUTLET MUD TEMPERATURES WHILE DRILLING GEOTHERMAL FORMATIONS," 2010.

- [60] J. Wrage et al., "Geochemistry of thermal waters in the Southern Volcanic Zone, Chile – Implications for structural controls on geothermal fluid composition," Chem. Geol., vol. 466, no. July, pp. 545–561, 2017, doi: 10.1016/j.chemgeo.2017.07.004.
- [61] K. Yeltekin and S. Akin, "Analysis of Long Term Tracer Test," Production, pp. 1–6, 2006.
- [62] N. Yildirim, S. Önc, and U. A. Akman, "High Enthalpy Geothemal Potential Possibility in SW of Büyük Menderes Graben, Turkey," Proc. World Geotherm. Congr., no. 16, pp. 25–29, 2010.
- [63] E. Kommission, "Mitteilung der Kommission an das Europäische Parlament, den Rat, den Europäischen den Europäischen Wirtschafts- und Sozialausschuss und den Ausschuss der Regionen," 2020.

www.oilgaspublisher.de