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Energetic use of highly mineralised deep waters as an aspect of material co-production of minerals

Timm Wunderlich, Lukas Oppelt, Tom Ebel, Fritz Raithel, Thomas Grab, Tobias Fieback
Technische Universität Bergakademie Freiberg

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Abstract

Reducing Europe's dependence on imported raw materials with alternative and innovative local extraction methods is becoming a matter of critical importance. Brines of existing deep wells in various European countries contain recoverable concentrations of raw materials of , as well as a great geothermal heat potential. This paper summarises potentials from wells on the continent from which raw materials and heat can potentially be extracted (raw material and heat source). Moreover, the paper presents novel extraction processes (raw material and heat sink) that have been developed by research institutions and have been enhanced by the integration of heat and mass flows to reduce the energy consumption. Challenges and potentials of the developed processes as well as their suitability to provide utilizable excess heat and cold for external demands are described. The paper determines the boreholes’ potentials for the extraction of raw materials, their heating and cooling and possible CO_2 savings.

1. Introduction

Brines from deep geothermal wells in hydrothermal systems have extremely individual compositions and mineralisation depending on the location (from a few mg/l to several g/l). The water contains elements such as Fe, Sr, Ar, Li, Mg, Sr, which are dissolved at great depths under high pressure and high temperature should be extracted in technical plants. Due to technological improvements, it is possible to extract these dissolved elements locally in Europe and make them available as raw materials for the import-dependent high-tech and battery industry. In addition to material utilisation, the energy potential of brine water can also lead to a significant improvement in economic efficiency. Accordingly, the resource of highly enriched brines contains both material and energy components that need to be considered. Heat integration provides an all-encompassing view of the material and energy utilisation as well as the increase in efficiency.

2. Reasearch aspects

In the BrineRIS research project, open research data relating to public scientific information, which are available free of charge and are usually provided by public data sources, are collected from six different countries in the European Union. In addition, individual sites in various countries were re-examined and samples were taken. The aim is to provide users and the public with data on the extraction of valuable metals from geothermal brines. Data will be processed in such a way that it fulfils the specific requirements of the institutions providing the data and those wishing to use it, providing quality evidence and making the primary source easy to locate. [1] A task of the BrineRIS project is the mapping of brine resources, which requires reliable data on the location of exploration facilities, environmental characteristics, brine exploitation parameters and formal and legal information. Furthermore, an important part is to analyse the legal requirements for water extraction and environmental protection. Therefore, data should be obtained from various sources such as public administration, governmental institutions or research organisations. In addition to the data on the boreholes, three research institutions are working on the enrichment of the lower lithium concentrations in Europe (<100mg/L Li) to an economically feasible level. Parallel three different processes are being developed to test a wide range of process technologies. In addition to the used evaporation processes, solvent extraction (SX), capacitive deionisation (CDI), mebrane electrolysis (ME) or synthesised adsorption (SAD) are included in the various processes to increase the lithium concentration. In order to reduce the high energy requirements of the processes, geothermal heat and waste heat streams are to be utilised in the processes to achieve a reduction in CO_2 emissions and energy requirements. [2]

2. Methods

2.1 Heat integration

Heat integration is an essential tool for rational energy utilisation and is playing an increasingly important role in process engineering in particular, but also in energy technology. The principle of heat integration is to link processes that need to be cooled down with processes that need to be heated up. This networking takes place through the use of heat exchangers. The heat demand of process streams to be heated up must be covered and the heat supply of process streams to be cooled down must be dissipated. The amount of energy added from outside or dissipated to the outside can be reduced by the suitable interconnection of the individual flows, thus minimising exergy losses and reducing costs. [3,4]

The analysis of the energy system to be carried out should provide various information, including determining the minimum required useful energy demand and the corresponding heat integration potential:

- Determining the minimum heating and cooling requirements.
- How much primary energy actually needs to be used for heating and cooling.
- What can be utilised in the process through skilful interconnection to determine the minimum exergy losses.

In conclusion, it can be recognised that the exergetically optimal heat integration in processes with numerous material flows can be very complex. Heat integration has been a key component of process optimisation since 1979 with the publications by Linnhoff and Cerda. [5] It described for the first time the reduction of the use of conventional plants/systems for heat and cold supply using heat transfer networks. Preliminary work was carried out by Linnhoff and Flowe, whereby the developed temperature interval method represents an approach to the mathematical procedure for determining the energetically optimal heat transfer networks, taking thermodynamic limits into account. [6,7]

2.2. Pinch Methode

The concept of pinch analysis, in its strict definition according to Linnhoff, is used as a thermodynamic analysis method with a focus on minimising heat consumption. [4] According to Mann and Liu [8], the common feature of all approaches to process integration is the system-orientated, integrated analysis, synthesis and modification of processes based on thermodynamic or physical, chemical correlations. The analysis aims to optimise the integration of the processes within a process, which is either only subject to technical limits, such as the fact that heat transfer only works in the direction of the colder system, or economic limits due to the necessary investments. The term pinch analysis originates from a graphical representation in which the smallest distance (pinch point) between the aggregated curves of all cold and all hot process streams is of key importance (Linnhoff and Hindmarsh 1983). [3]

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These principles describe the objective of minimising waste streams or total costs by integrating processes. The following three main principles serve to describe process integration:

- Considering all processes as comprehensively as possible as an integrated system of connected units, in which all process, supply and waste flows are analysed to achieve a more efficient design
- the application of process engineering methods such as mass and energy balances to the relevant process steps to obtain prioritised achievable target values for consumption of resources and generation of emissions and waste,
- and the subsequent detailed design of the processes to come as close as possible to the specified target values. [8]

2.3 Boreholes as heat source

The wells and the abysmal brine to be extracted from these wells are to be utilised as a starting product for raw material coproduction. The thermal energy contained therein is also to be efficiently coupled in order to provide thermal support for the extraction process. The data on boreholes and other relevant information was provided by different institutions. A database of all boreholes investigated, their location and other information such as their concentrations and hydrogeological characteristics was implemented. A total of 2400 boreholes in the six countries were compiled. [9] It can be assumed that the data basis is not complete, as private boreholes etc. could not be included. In addition, data can't always be found in full in the literature or different samples with different characteristics were taken, which means that further analyses or new measurements should be carried out on the boreholes in the future if a site proves to be promising. The geothermal potential could be calculated for 626 locations as the required data was fully available. Due to missing volume flows, the number could not be increased. One reason for the lack of volume flows were different samples and the age of the primary sources. Pump tests were not carried out at all locations. The data are essential when it is about estimating the potential for a continuously running process. This literature research revealed that unfortunately no borehole data and water samples were freely available in this area, and the analysis did not reveal any suitable Li concentrations. [10]

2.4 Extraction processes as heat sink

Communication between research institutes aiming to extract the lithium using their own processes and the simultaneous attempt to integrate the geothermal heat and the various mass flows within the process is a key component and provided the basis for the following results. The framework parameters of the process were presented and explained in several discussions with regard to their integration capability. Despite the completed integration of all individual processes, the relevant processes and procedures are still at an early stage, so some assumptions were made about the process variables. The exact orders of magnitude, e.g. in relation to an automated assembly line process, were assumed as these are currently batch processes which will be changed in the future. Accordingly, time spans and transport routes have been partially neglected. The temperature level is based on laboratory data. Mass flows were attempted to be intersected as real data through multiple exchanges and communication. The processes are still on a laboratory scale, so that the transferability to larger industrial scales is not yet fully known.

2.5 Integration using an example process (TU Gent)

This pinch procedure was carried out for all processes in order to achieve the best possible intersection of the mass flows in the process.It is is briefly explained using the Membrane Electrolysis (ME) process developed by the TU Gent as an example. The other processes are listed in an overview in part 2.6.

Procedure TU Gent process

Capacitive deionization (CDI) is a technical process for separating removal of charged ionic species from water, for this process espezially for brines. The aim is to primarily targeting desalination applications. The CDI relies on the application of an electrical potential difference across two electrodes, which are analysed and researched by the TU Gent in particular. [11] After an initial separation or concentration of the ions, electrolysis takes place. During electrolysis, hydroxide ions accumulate in the water. These first react with the carbon dioxide introduced to form hydrogen carbonate ions and then reduce these further to carbonate ions. These are able to react with the lithium ions contained in the water to form the salt lithium carbonate, which precipitates out of the solution and can be separated.

These process can be simplified for heat integration. For heat integration, the following must be considered at the beginning as shown in Figure 1. As the mass flows are mainly water-carrying, these are shown in the diagram. As evaporation takes place between the ME and the CDI, the water vapour is also used for preheating. The vapour, which has a Latent Heat Transfer and a Higher Heat Capacity: in contrast to the water Sensible Heat Transfer and Lower Heat Capacity, would not be justified in a diagram.
Four streams can be considered as shown in Figure 2. The incoming streams, lithium-rich water after the CDI and CO_2, are cold and must be preheated, while the outgoing streams, lithium-poor water and lithium carbonate, are hot and must be cooled. The stream that heats the lithium-rich water is not considered, as it is determined in the heat integration. In the given diagram, the volumes of the flows are specified independently of the time. It was assumed that these are litres per second. The volume flows were also converted into mass flows. The typical substance values for liquid water were used for all water-based flows. The mass flow rate for CO_2 was determined using the mass flow rate of the lithium carbonate.

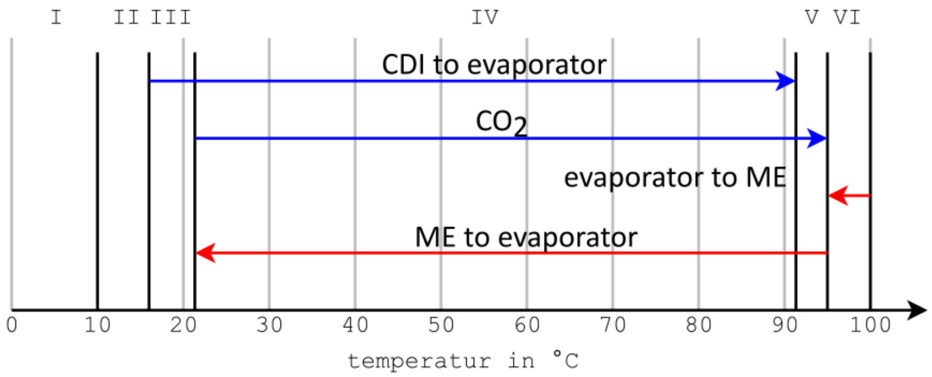

Figure 1 Mass flows with the respective temperature levels of the process involving capacitive deionisation and membrane electrolysis before a pinch analysis

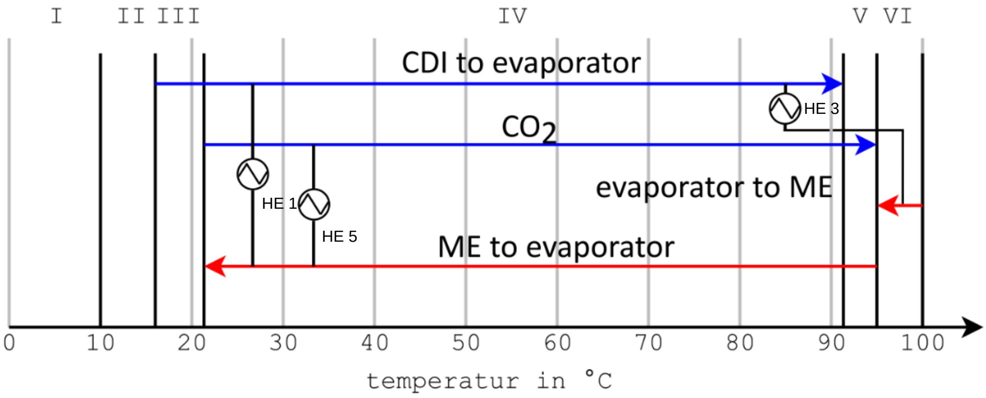

Figure 2 Mass flows with the respective temperature levels of the process with capacitive deionisation and membrane electrolysis with interconnected heat exchangers (the steam flow within the process is not shown)

HE 1 shows that the waste flow of the fluid from the ME, after HE 4 can be used to preheat the red CB flow. The "waste water" that is separated during evaporation can also be included in the preheating of the red stream (HE 2) and thus reduce any energy savings that are still required during evaporation as can be seen in Figure 3. As the ME can't be operated with 100°C water, the concentrated brine (purple line) must be cooled down, which can be perfectly used for preheating (red line) HE 3. As the waste water flow from the ME is considered around 95°C, this temperature is used to preheat the CO_2 in black (H4). Since there is still heat potential and the CO_2 can be heated further, the HE 5 was installed. After a reactor, the products still have to be cooled, which allows the CO_2 to be preheated for the first time.

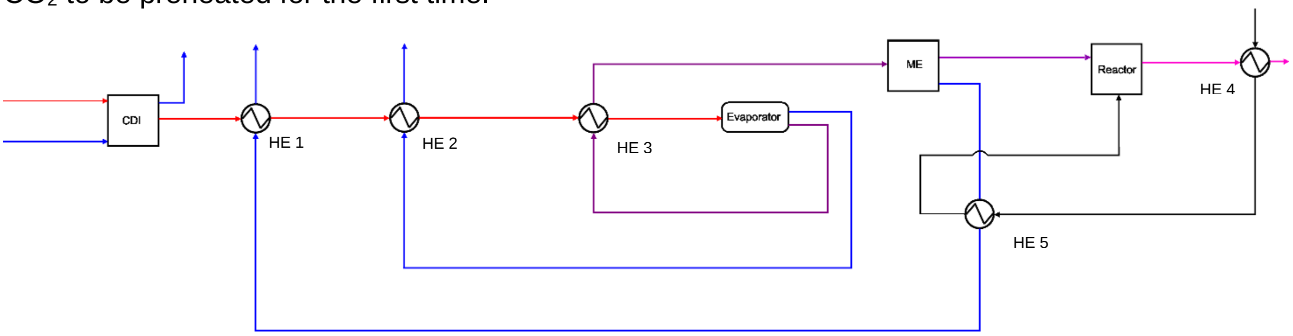

Figure 3 Lithium extraction process at TU Gent after pinch analysis with the components CDI, Evaporator, ME and CO2 Reactor and the corresponding heat exchangers

Final integration of other processes

The second process was developed by the Polytechnic University of Wroclaw and is shown in Figure 4. The aim of the solvent extraction (SX) process is to extract a specific substance (NaCl) from a mixture (concentrated brine) using a suitable solvent (ethanol). The basic principle is based on the different solubility of substances in different solvents. For a more detailed overview as well as the extraction rates, please refer to Ochromowicz et. al. 2024. [12] From a thermodynamic point of view, there are various ways of improving the dissolution of the substances in the solvent, such as preheating, heating or cooling. In addition, thermal processes can be used to separate the phases and recover the substances to provide a cycle in the process.

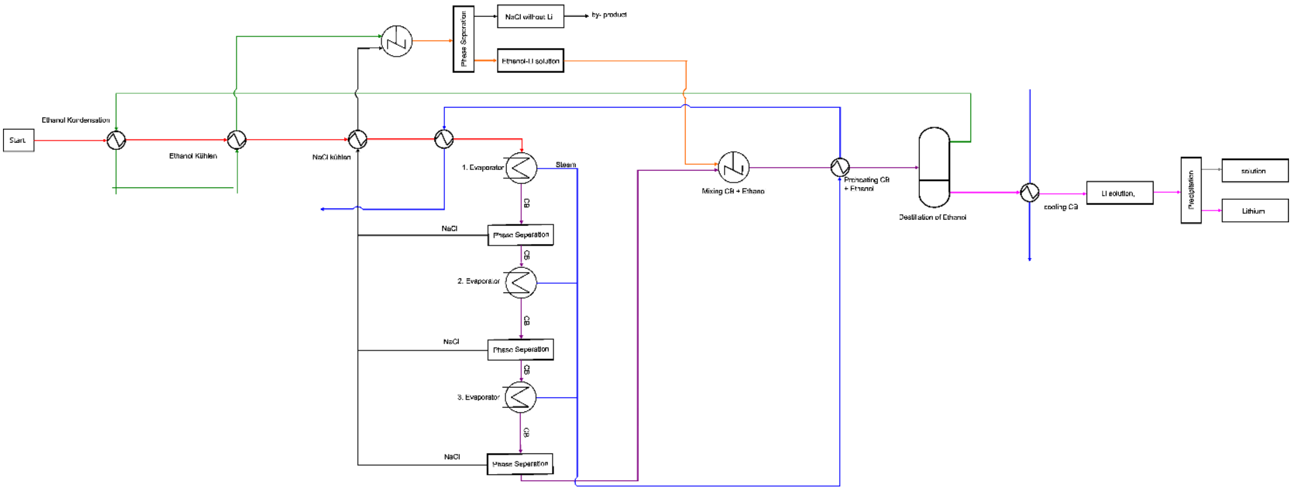

Figure 4 Lithium extraction process of the University of Wroclaw after pinch analysis with the components such as evaporator, distillation unit and the corresponding heat exchangers

The third process developed by GTK consists of two sub-processes as it is and synthesised adsorption (SAD) process, as shown in Figure 5. Before the brine is used, the synthetic adsorbent must be produced, as shown in the upper Figure 5. This process can be compared, for example, to burning lime After the manufacturing of the adsorbent a certain amount of adsorbent is brought into contact with the brine, followed by evaporation and washing of the products with a liquid.

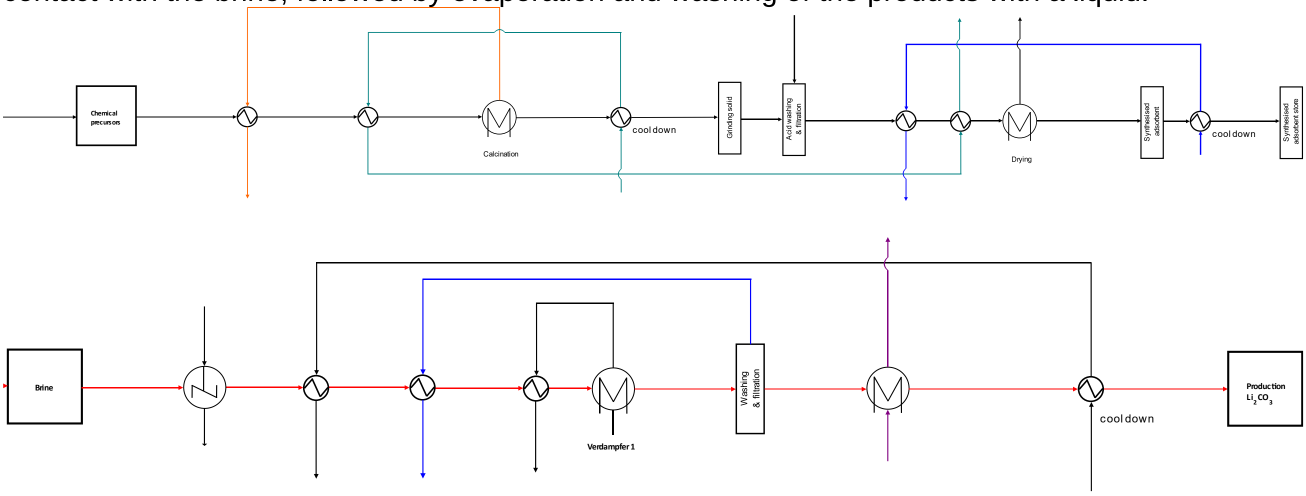

Figure 5 Lithium extraction process of GTK after pinch analysis upper process to create a synthesised adsorption lower process for lithium extraction

3. Results

3.1 Techno-economic evaluation

The analysis of the wells shows that most of them are not directly suitable for process heat or electricity generation: the average temperatures of all the wells, such as in Hungary (57.4 °C),

Poland (27.4 °C) and Slovakia (16.3 °C), make the general use of an ORC (Organic Rankine Cycle) uneconomical. Nevertheless, individual sites have been identified as worthwhile.
The pinch method has already achieved savings in the processes, even if not all process peaks can be covered. Nevertheless, the existing geothermal potential could be integrated into all processes. Residual mass flows with temperatures up to 100 °C, which the process can no longer use, could be used as an additional benefit with heat pumps and made available to other consumers. An example is given to illustrate the potential.

3.2 Comparison on an example location

It analyses how the three processes compare in terms of efficiency, energy requirements and technology, savings potential and cost effectiveness. The comparison takes into account the specific conditions of the site and the requirements of the process chains, so that the processes can still be compared well. The aim is to identify the best solution for using geothermal energy to maximise both environmental and economic sustainability. To compare the three processes, an example site is taken from the database. All three methods are applied to this site to determine the comparability of the individual assessment factors. The example site is Ln-1 in Czech Republic with the following data

Dataset	1961
Well yield	1,15 m³/h
Temperature	21 °C
Li- concentration	21,8 mg

3.3 Energy

The results of the pinch method are shown in the following Tabel 1.

Tabel 1 Energy data and requirements of the three processes for the selected location

Figure		Process 1	Process 2	Process 3
Energy Demand	MWh/a	106	526	2.530
Energy-saving	MWh/a	153	4.070	2.283
Energy-saving	%	40,8	10,1	52,6
CO_2- Demand	t CO_2	21	105	508
CO_2-Savings	t CO_2	31	944	458
Cooling Potential	MWh/a	28	/	/
Heating Potential	MWh/a	150	3.238	2.700
Lithiumcarbonat	kg/a	≈93,1 (±20%)	≈83,6 (η= 76%) [12]	missing data from the lab

As the processes were laboratory scale, the analysis is based on up-scaling for industrial applications, which means that results may differ on a large scale. For site Ln-1, the energy requirements of the three processes may be as follows:

- Process 1: Figure 6 shows that about 41% of the energy requirement could be saved by internal connections and is therefore highly efficient. With a total energy requirement of 259 MWh/a, this process is the most energy efficient because most of the mass flows could be integrated into the system. In addition, only small mass flows have to be evaporated compared to the other processes.

- Process 2: Figure 7 has the lowest energy savings of only 10%. It also has a much higher total energy consumption of 5.226 MWh/a. This is due to the three evaporation steps and the distillation where 100% of the heat could be recovered. Process 2 has the highest energy consumption.
- Process 3: Figure 8 has the greatest potential to cover its own energy needs through internal connections with over 50%. However, it is the most energy intensive process with 4.813 MWh/a. This high energy consumption is due to the equally high quantities of brine to be evaporated.

A comparison shows that process 1 requires the least energy and is the most efficient. Processes 2 and 3 have significantly higher energy consumption, with process 3 having the highest integration potential. A comparison shows that process 1 is the most efficient and has the lowest energy consumption for extraction, while process 3 has the highest demand.

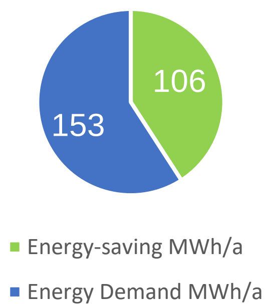

Figure 6 Figure Energy demand (blue) and savings (green) by a total demand of 259 MWh/a (without heat integration) using the TU Gent process

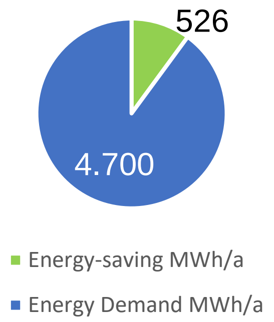

Figure 7 Energy demand (blue) and savings (green) by a total demand of 5.226 MWh/a (without heat integration) using the WUST process

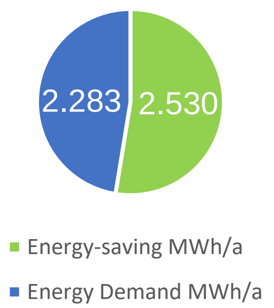

Figure 8 Energy demand (blue) and savings (green) by a total demand of 4.813 MWh/a (without heat integration) using the GTK process

3.4 Ecological

As with the energy requirements, a similar pattern emerges in the environmental domain. Process 1 has the lowest energy requirement and the highest overlap potential. If the requirements are completely covered by gas in CO_2 equivalents, process 1 emits 31 tonnes of process 2 944 t and process 3 emits 458 tonnes per year. The calculation is based on a factor of 200.8 g CO2/kWh natural gas equivalent.

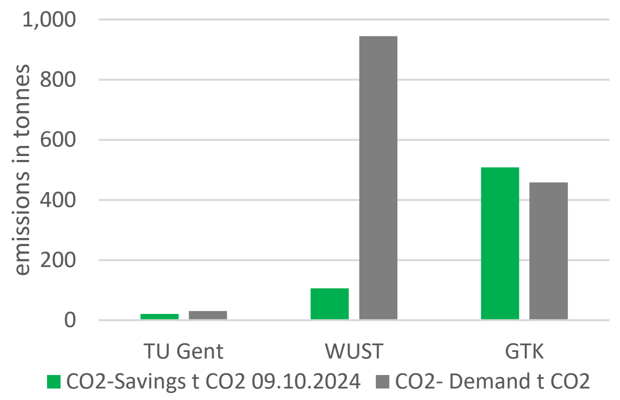

Figure 9 CO_2 emissions (grey) and savings (green) of the three processes for location Ln-1

For the site Ln-1 and the production of 1 kg of further processable lithium product (e.g. lithium carbonate), this resulted in the following key figures, which are listed in Tabel 2 for the three processes. For the energy costs, the current gas cost (non-household) for land (Czech Republic) was assumed to be € 0.11/kWh (the cost for the EU-27 gas price of € 0.12/kWh is given in brackets). [13] If production under the Green New Deal is to move away from the use of gas or fossil fuels, one option for the future is to rely on the heat pumps mentioned above, which can raise the temperature level using electrical energy. Other options include electric heating rods and heaters that can be used to evaporate water or, if available, hydrogen. For the renewable variant, a fictitious heat pump with a COP of 4 has been chosen with electricity costs for non-households of 0.21 kWh (Czech Republic) and 0.21 kWh (EU-27). [14] The share of renewables in the electricity mix is 37.5% in the EU-27 . [15] A factor of 107g CO_2/kWh equivalent has been used for the calculation of renewable electricity. [16]

It is difficult to determine the exact performance of the processes analysed as there are no fixed parameters from the laboratory and the efficiencies achievable by the processes are not known. The analysis focused primarily on the energy situation, with results based on assumptions and interim reports from the laboratory. Upscaling effects were only hypothetically included, as no efficiencies are known for the large scale or laboratory scale. Improved methods and more detailed analysis are needed to optimise the processes. In order to illustrate the uncertainties in the yield, ranges are given to illustrate possible deviations.

The energy costs and CO_2 emissions for 1 kg of lithium are shown in Tabel 2. 1 kg of lithium would require about 1140 kWh in process 1 at Gent University, which corresponds to renewable energy costs of 60 € and a carbon foot print of 6,4 kg of CO_2 for 1 kg of Li. For process 2, the most energy-intensive, the cost would be about €330 using the current laboratory scale with the assumptions. For process 3, which is in a similar energy range to process 2, no data are available on efficiency or extraction success. Therefore, no information can be given on this process.

Tabel 2 Standardising energy costs and CO_2 emissions for 1kg of lithium

		TU Gent	WUST	GTK
energy/ 1 kg	kWh	1140,70	6297,10	No data available from the laboratory
$Cost_{fossil}$ /1 Kg	€	125,50	692,70	
$Cost_{renew}$ /1 Kg	€	59,90	330,60	
$CO_{2\text{-fossil}}$/1 kg	kg	25,20	139,10	
$CO_{2\text{-renew}}$/1 kg	kg	6,40	35,40	

3.5 Surpluses

The utilisation of surplus mass flows from processes is a major advantage, as residual heat that would normally be released to the environment can be efficiently reused. Residual flows at different temperature levels offer the potential to be used for both heating and cooling purposes. By making good use of this waste heat, additional processes can be supported and energy costs reduced. For example, several buildings can be heated, further increasing overall energy efficiency.

The following framework parameters can be provided for the processes:

Process 1 (CDI/ME): 120 MWh/a at a temperature level of approximately 100°C
Process 2 (SX): 3.238 MWh/a at a temperature level of approximately 100°C
Process 3 (SAD): 2.700 kW at a given temperature level
These surpluses can be used, for example, to heat several buildings, increasing the efficiency of the overall system.

3.6 Geothermal potential of all other analysed boreholes

As not all boreholes have sufficiently high lithium concentrations, these boreholes can´t be used for further evaluation of resource extraction.
However, the data does provide information on the geothermal potential of older boreholes in each country. Maps showing the regional geothermal potential of deep boreholes can be published. This allows local authorities and stakeholders to draw conclusions for the heat transition in their countries and to initiate projects. One such map is available to interested parties through the project and can be seen in Figure 10 [8]

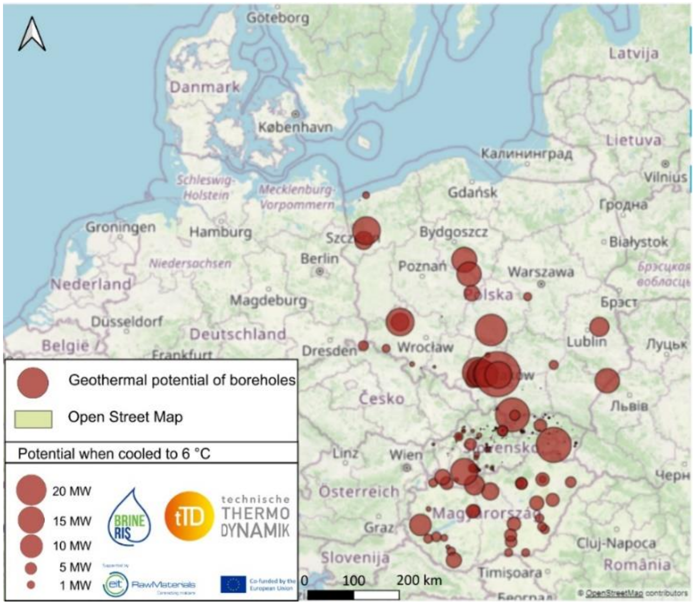

Figure 10 Illustration of the investigated boreholes regarding their geothermal potential in different countries, shown in an interactive map, see source [9]

4. Conclusion

The production of raw materials in Europe is an important component of independence from imports from other parts of the world. In recent years, processes have been and are being developed to intensify the extraction and co-production of raw materials. One focus is on economic efficiency and energy use, as the natural evaporation of water in open basins, such as in South America, is not possible when using brine water, for example. To this end, three innovative processes, still at laboratory scale, were investigated and energy improvements were demonstrated using a pinch analysis. Energy savings were achieved in each process, with the Gent University of Technology process being the most promising, with energy savings of 40%, as it uses the least energy. In addition, the processes shown are on a laboratory scale and the WUST and GTK processes can also contribute to Europe's independence from raw materials, for example by using renewable energies for evaporation. In addition to the production of raw materials, it can also be seen that geothermal potential is available from over 600 boreholes. These can make a significant contribution in the regions, for example by supplying heat to residential areas or businesses.

5. Acknowledgement

We would like to thank the project partners at the Technical University of Gent, the University of Wroclaw and GTK for providing us with the data from their processes so that we could carry out the analyses. Special thanks go to Magdalena Worsa-Kozak, who led the BrineRIS project for 3 years as a very persistent and reliable coordinator. We would also like to thank Leonard Worm, who helped us with the research as a student assistant.

Postadresse, Gustav-Zeuner-Straße 7, 09599 Freiberg
E-Mail-Adresse, Timm.Wunderlich@ttd.tu-freiberg.de

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