Mine water of abandoned coal mines for geothermal heat storage: Hydrogeochemical modeling and predictions

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Abstract

Water samples from various hard coal mines (German Ruhr coal district, Dutch South-Limburg coal district) were modeled to evaluate a future mine thermal energy storage using the modeling software PHREEQC. Different thermodynamic databases had to be used for modeling. The geochemical reactions were simulated during charging up to 150 °C (at 5 bars).

The mineral phases calcite and anhydrite exceed the equilibrium during the operation and tend to precipitate as scaling. Depending on the redox potential, minerals like ferrihydrite, siderite and goethite tend to form deposits. A storage temperature up to about 90 °C is recommended to avoid intense scaling.

Keywords: storage, mine water, PHREEQC, scaling

Introduction

After the ending of hard coal mining in Germany in 2018, a large number of flooded galleries, shafts and converged gobs will remain in the subsurface, which are excellently suited as thermal energy storages due to the increased hydraulic permeability. A great potential for local low-temperature heating networks in cities, residential areas or industrial areas is given (compare Hahn et al. 2018). During summer it is possible to store industrial surplus heat via heat exchangers in the mine water of flooded galleries. In winter, the process is reversed and the heat is extracted with heat exchangers. Heat pumps can bring the temperature to the desired heating level. Figure 1 shows a sketch of a heat storage in a flooded Carboniferous hard coal mine. A lower flooded level is used as heat storage, whereby it is possible to use an upper flooded level as cold storage for cooling purposes.

The geology of the German Ruhr coal district and the adjacent Dutch South-Limburg coal district is dominated by typical Upper Carboniferous deposits composed of silt- and mudstones, intercalated with coal seams,

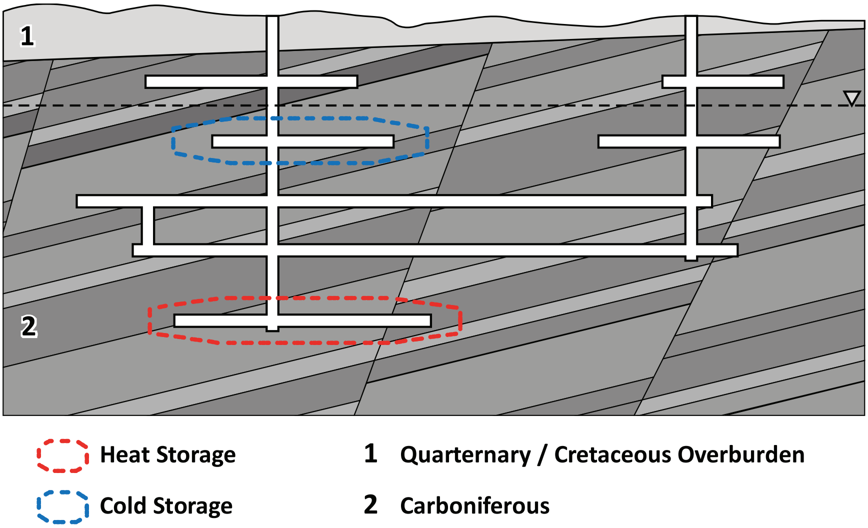

Figure 1 *Sketch of a heat storage in a flooded mine of the German Ruhr coal district (courtesy Felix Jagert).*

which can pass into sandstone beds (compare fig. 1). During the Variscan orogeny, the deposits were intensively folded. At the same time, the ductile-brittle rock tended to break and major faults were created. The resulting fault-systems are usually hydraulically effective. As a rule, the strata of the Upper Carboniferous are characterized by conjugate shear joint sets and therefore have only little hydraulic permeability. The Carboniferous deposits are superimposed by strata of the Upper Cretaceous as well as the Quaternary, which form the overburden.

Establishing a geothermal power plant for heating purposes with the ability to work as a seasonal heat storage as well in abandoned mines will cause certain hydrogeochemical reactions in the mine water. In general the mine waters of the Upper Carboniferous coal districts (Ruhr, Aachen, Ibbenbüren, Saar, South-Limburg) can be characterized as connate waters, influenced by mining activities (oxidation). The concentration of the main cations and anions (Na^+, K^+, Ca^{2+}, Mg^{2+}; Cl, SO_4^{2-}, HCO^{3-}) is rising with increasing depth from brackish waters (0.1 –1 % salinity) to brines (> 40 g/L, more than 4 % salinity). Heating mine water during charging of a thermal storage will cause precipitation and dissolution of certain mineral phases and also cause corrosion of pipes and heat exchangers. Figure 2 shows intense scaling of a historical dewatering pipe of a former hard coal mine in Bochum, obviously consisting of a mixture of different mineral phases.

***Figure 2** A historical dewatering pipe of a former hard coal mine, Bochum shows the scaling potential of mine water (courtesy Felix Jagert).*

Hydrogeochemical modeling of the thermodynamic behaviour and redox states of the mine waters enables qualitative and possibly quantitative predictions of scaling and corrosion during a future operation of a plant. In addition, a simulation of a hydraulic short circuit between mine levels or due to hydraulic active faults (mixing of waters) can help to estimate their hydrogeochemical effect on the storage.

Methods

Water analyses collected from various coal mines (table 1) were modeled to evaluate a future geothermal heat storage operation using the hydrogeochemical modeling software PHREEQC 3 (Parkhurst and Appelo 2013). Due to a large spread of ionic strengths, different thermodynamic databases had to be used for modeling. Freshwater to brackish waters were modeled with the PHREEQC or WATEQ4F databases, which are based on the Wateq-Debye-Hückel approach (theory of ion dissociation), whereas higher salinities up to brines are modeled with the PITZER approach (ion interaction theory) or the ThermoChimie database (specific ion interaction theory).

The criterion for accurate modeling is a complete, correct water analysis, which consists of the temperature, acidity as pH, the dissolved main constituents and secondary constituents (anions and cations). The redox state is also important, but it is rarely determined and often not measured correctly, because the redox electrode adjusts only slowly to a constant measurement result. It is possible to calculate the redox state via redox-couples using PHREEQC. Archives or various monitoring programs often already provide water analyses that can be used.

Most of the available databases contain hundreds of mineral phases, but often there is a lack of some desired elements (ions), species or mineral phases. In addition, many mineral solubilities were determined only under laboratory conditions at 25 °C and 1 bar. PITZER is more suitable for different pressure and temperature conditions, but it can be used to model rather few mineral phases.

Table 1 *Water analyses from various hard coal mines of Germany and the Netherlands.*

	Franz-Haniel 1/2	Robert Müser	Oranje Nassau III	Oranje Nassau III
location	Bottrop, Germany	Bochum, Germany	Heerlen, Netherlands	Heerlen, Netherlands
depth (m b.g.l.)	1148	570	692	229
temp. (°C)	20	20	28	16
pH	6.94	7.19	7.9	7.3
		cations / anions (mg/L)		
Na^+	12700	1180	1100	940
K^+	133	22	36	38
Mg^{2+}	304	54	47	100
Ca^{2+}	1050	120	62	160
Ba^{2+}	1.7	0.93	0.037	0.059
Fe(total)	5	15	3.1	6.1
Cl^-	20200	1630	850	530
SO_4^{2-}	510	76	480	1300
$HCO3^-$	160	995	940	1000
$NO3^-$	5	1	n.a.	n.a.
date	26.07.2013	14.08.2013	26.02.2016	18.09.2015
status	active mine dewatering	abandoned mine dewatering	Mijnwater-project 2.0	Mijnwater-project 2.0
source	BRA (2013)	BRA (2013)	Mijnwater B.V.	Mijnwater B.V.

Hydrogeological considerations

If shafts are already filled and the mine levels are inaccessible, the suitable gallery must be drilled into, using a directional drilling technique. An exploration borehole into the abandoned mine with appropriate water analyses and pumping tests is usually only available in later project phases. Therefore, before modeling, different hydrogeological scenarios should be considered.

The depth, extent and geometry of the galleries should be evident in the mine maps. With this information, the most suitable mine level for heat storage, cold storage and re-injection of the cooled water can be selected. Blind shafts, dams, gobs and faults increase the hydraulic permeability of the mine levels (fig. 1). In some cases, mine levels of adjacent mines were connected during the active mining phase so that the mine water flows from one mine to another.

Knowledge about the mine water level is important for further planning. Usually, in undisturbed formation waters, salinity and temperature increase significantly with depth. This is clearly documented in historical literature and in recent publications on the coal mines in the Ruhr region (e.g. Wedewardt 1995). However, the flooded mine levels are hydraulically connected via blind shafts or gobs on shallower mine levels, so that "communicating vessels" are created. Therefore, the salinity of the mine waters from deep galleries is not known exactly.

The mine dewatering of Ruhrkohle AG (RAG) provides insights into the composition of the abandoned mines (see table 1). The sodium chloride content, the sulphate content and the degree of hardness are significantly increased in comparison to groundwaters. Despite the pyrite oxidation caused by mining (air conditioning), the pH values remain in the neutral range. Barium is mostly dissolved in deep mine waters and points to deep, older formation waters, which enter the mine. High barium contents exclude sulphate contents and vice versa, because barium precipitates with sulphate as barite.

Hydrogeochemical modeling was carried out mostly with PITZER up to 150 °C. Other databases can also be used, for example, to calculate redox species, but the results are not reliable. The expected pressures will probably not exceed 50 bars since the maximum water column in the system will be around 500 m. Line pressures on the surface will barely exceed about 5 bars. The system is considered as closed. In the reality, however, air contact and a resulting shift of the redox state are expected near the pumps in the borehole or shafts.

Results

Significant changes in solubility occur in the carbonates and sulphates. Aluminium silicates were not taken into account for the modeling, since aluminium and silicon were seldom determined in water analyses and otherwise occur in very low concentrations. The pH values in the carbonate buffer range (pH 8.3 to 6.2) prevent the mobilization of certain metal ions, such as aluminium and others.

Thermodynamic Equilibria

The saturation index (SI) indicates whether a mineral phase in the solution is supersaturated at the appropriate pressure and temperature and tends to precipitate, or whether the solubility is undersaturated and the mineral remains in solution and is dissolved out of the rock respectively. Mineral phases are in equilibrium with the thermodynamic conditions at SI 0.0. Positive values, in particular values above 1 indicate a supersaturation and possibly a growth of crystals.

In general, a distinction is made between homogeneous and heterogeneous nucleation. Homogeneous nucleation describes the growth of a crystal directly from the supersaturated solution. For this spontaneous crystal formation, a high supersaturation of the corresponding mineral phase is necessary. The heterogeneous nucleation describes a much faster crystallization on already existing surfaces such as particles in the water. These existing surfaces then serve as a jump start for crystal growth.

Most mineral solubilities increase with rising temperature (e.g. Barite in fig. 3), which is beneficial for the life of the plant. However, the rapid decrease in the solubility (supersaturation) of calcite is remarkable. This also happens for mineral varieties, such as aragonite. It is evident that a temperature-induced decrease in CO_2-solubility shifts the lime-carbonic acid balance. A similar and less intense decrease in solubility is observed for gypsum / anhydrite. Modeling with PITZER shows that a pressure drop of up to 50 bars (500 m) has very little effect on the solubilities. Only very high pressure differences of a few thousand meters to the surface would induce a calcite precipitation.

In a closed system, without degassing, the pH remains stable. Though the temperature dependency of the self-ionization constant of water leads to small shifts in the pH (compare pH in fig. 3 and fig. 4).

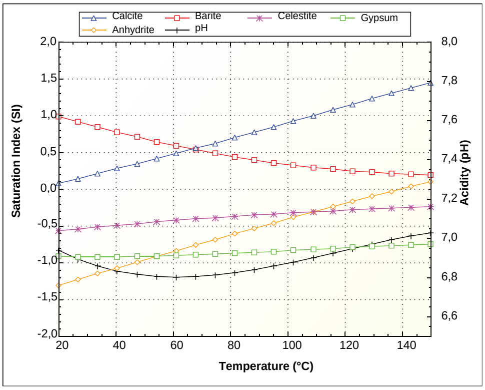

Figure 3 *Solubilities of certain mineral phases up to 150 °C (Mine water Franz-Haniel at 5 bars).*

Speciation and redox state

Some models showed that the redox state changes just due to the temperature increase. A redox-dependent specification has the consequence that different mineral phases are stable and therefore tend to precipitate. The model in fig. 4 was done with the ThermoChimie database, so the calculation of the redox state was possible. However, the database is less reliable for a temperature range above 90 °C and for acidities lower than pH 6.

Amorphous ferrihydrite is a mineral phase that forms rapidly in the presence of oxygen and then precipitates ("iron clogging"). The model in fig. 4 shows a significant increase in solubility (decreasing SI) with rising temperature due to a decreasing pE and pH. At the same time, the solubility of siderite (increasing

SI) decreases. This mineral phase generally is formed under reducing conditions. Goethite remains highly supersaturated and tends to precipitate, although its rate of formation is much slower than that of ferrihydrite.

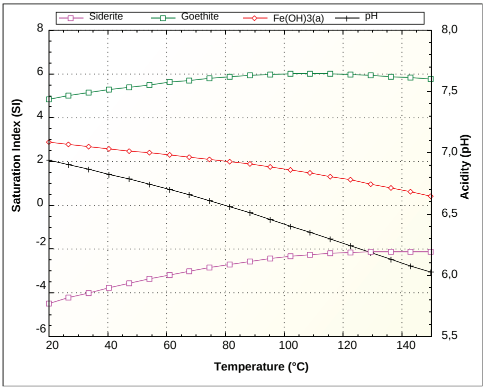

Figure 4 Solubilities of redox sensitive mineral phases up to 150 °C (Mine water Franz-Haniel at 5 bars).

Kinetics and rates of formation

The above-mentioned formation rates of minerals are of great importance in the calculation of precipitated quantities. Used mine water will only flow through the plant for a few hours and will stay in the storage for the most time. The saturation index is just a thermodynamic point of view and therefore time-independent. Plummer et al. (1978) described an approach obtaining reaction rates for the mineral phase calcite. The result adapted to the water analysis collected from Franz Haniel 1/2 is shown in fig. 5. The mine water was modeled up to 90 °C. About 55 mg/L will be precipitated after 200 hours to reach equilibrium with calcite.

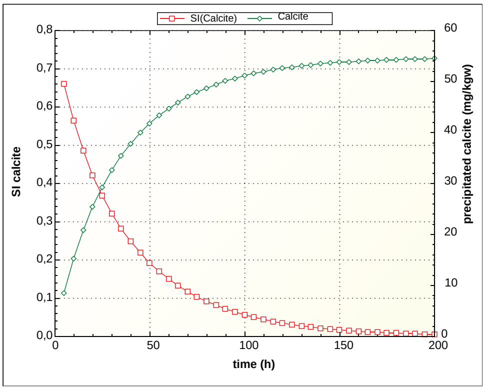

Figure 5 Kinetical reaction rates for calcite at 90 °C (Mine water Franz-Haniel at 5 bars).

Conclusions and outlook

The modeling has shown that a storage temperature only makes sense up to about 90 °C. Significantly higher temperatures in the system lead to high supersaturation, especially of the mineral phase calcite and further anhydrite. Corrosion due to high salt contents (high electrical conductivity) or due to hydrogen sulphide can hardly be described with PHREEQC. The dissolution of aluminium silicates (e.g. clay minerals like illite or smectite) or cation exchange processes on mineral surfaces are fields for further research.

In the Netherlands, galleries of the abandoned coal mine Oranje Nassau III have already been drilled for the Mijnwater-project and successfully used for geothermal installations (see Verhoeven et al. 2013 and references therein).

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References

Bezirksregierung Arnsberg (BRA) Ergebnisse Sondermessprogramm Grubenwassereinleitungen 2013 Steinkohle Ruhrrevier. published open data: https://www.bezreg-arnsberg.nrw.de/themen/w/wasserwirtschaft_untertagebau/ [14.05.2018]

Hahn, F; Bussmann, G; Jagert, F; Ignacy, R; Bracke, R (2018) Reutilization of mine water as a heat storage medium in abandoned mines. Proceedings from the 11th ICARD | IMWA | MWD 2018 Conference (this issue), Pretoria, South Africa

Parkhurst, DL; Appelo, CAJ (2013) Description of Input and Examples for PHREEQC Version 3 — A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/

Plummer, LN; Wigley, TML und Parkhurst, DL (1978) The kinetics of calcite dissolution in CO2-water systems at 5°C to 60°C and 0.0 to

1.0 atm CO2. Am. Jour. Sci.: 278, 179-216, doi:10.2475/ajs.278.2.179

Verhoeven, R; Willems, E; Harcouët-Menou, V; De Boever, E; Hiddes, L; Op 't Veld, P; Demollin, E (2013) The EC REMINING-lowex project in Heerlen the Netherlands: development of a geothermal mine water pilot project to a full scale hybrid sustainable energy infrastructure Mine Water 2.0. European Geothermal Congress 2013. Pisa, Italy, 3-7 June 2013

Wedewardt, M (1995) Hydrochemie und Genese der Tiefenwässer im Ruhrrevier. DMT-Berichte aus Forschung und Entwicklung, 39, 250 pp, Bochum