The new Wallula CO₂ project may revive the old Columbia River Basalt (western USA) nuclear-waste repository project

Michael O. Schwartz¹

Received: 18 April 2017 / Accepted: 19 June 2017 / Published online: 15 July 2017
© The Author(s) 2017. This article is an open access publication

Abstract A novel CO₂ sequestration project at Wallula, Washington, USA, makes ample use of the geoscientific data collection of the old nuclear waste repository project at the Hanford Site nearby. Both projects target the Columbia River Basalt (CRB). The new publicity for the old project comes at a time when the approach to high-level nuclear waste disposal has undergone fundamental changes. The emphasis now is on a technical barrier that is chemically compatible with the host rock. In the ideal case, the waste container is in thermodynamic equilibrium with the host-rock groundwater regime. The CRB groundwater has what it takes to represent the ideal case.

Keywords Groundwater protection · Hydrochemistry · Volcanic aquifer · Waste disposal · USA

Thirty years ago, the Columbia River Basalt (CRB) in the western USA (mainly Washington State; Fig. 1) was a candidate for a high-level nuclear waste repository and possibly will be again, as a novel CO₂ sequestration project has generated new interest in this attractive target for underground storage of natural gas, supercritical carbon dioxide and solid nuclear waste. On April 14, 2011, the US government decreed to stop funding the construction of the repository for spent nuclear fuel and other types of high-level nuclear waste in the Yucca Mountain, Nevada. Some days before that, Washington State granted a permit to inject 1,000 t of carbon dioxide into the CRB at Wallula, only a few kilometres from the Hanford Site, the former alternative to the Yucca Mountain repository.

This comes at a time when the approach to nuclear waste disposal has undergone fundamental changes. The geologists no longer postulate that there exists a geological formation that can isolate the nuclear waste for a million years. Only a technical barrier in concert with the host rock is considered to be capable of completing this task. The waste container should be chemically compatible with the host rock. In the ideal case, the waste container is in thermodynamic equilibrium with the host-rock's groundwater regime. The essay examines how this can be achieved.

Looking back, the CRB at Hanford was the only serious competitor left when eventually Yucca Mountain was designated by the Nuclear Waste Policy Act (US Department of Energy 2004) in 1987 to be the deep geological repository for high-level nuclear waste in the USA. As a consequence, the work on a deep repository in the CRB at Hanford was suspended; however, the CRB with its low-salinity groundwater regime offers what Yucca Mountain certainly has not: a geochemical environment in which metallic waste containers can survive without serious damage by corrosion.

The Yucca Mountain repository is unique because it is conceived for waste storage above the water table (Farmer et al. 2003). In other parts of the world, potential repositories are located below the water table (Schwartz 1996, 2008). The unsaturated zone precludes the protection of the metallic waste container by bentonite because the clay minerals would dehydrate and lose their isolating properties; thus, an entirely metallic barrier system has to be used. Evaporation of water from the metal barrier's surface has been found to produce salinities up to 4 mol/L Cl in the water remaining on the barrier's surface under the strongly oxidising conditions in the arid climate zone. Any kind of metallic barrier system is bound to fail in such an environment, long before the radioactive interior becomes harmless. In this respect, the Yucca Mountain project is similar to the salt-dome project at

✉ Michael O. Schwartz
mathgeol@yahoo.de

¹ MathGeol, Postfach 101204, 30833 Langenhagen, Germany

Fig. 1 Extent of the Columbia River Basalt (CRB) and location of the Hanford, Wallula and Yucca Mountain sites (USA). WA Washington, OR Oregon, ID Idaho, NV Nevada

Gorleben, Germany (Schwartz 2012a), started in 1977 and ended in 2013 (German Federal Government 2013).

Worldwide, there are only two approved high-level waste repositories under construction—both the Forsmark project in Sweden (Schwartz 2012b) and the Olkiluoto project, Finland, are in a granite-dominated low-salinity environment and envisage the storage of copper-shielded waste containers. Compared with basalt, granite has lower concentrations of sulphur and higher Fe-III/Fe-II ratios, which is favourable when it comes to corrosion resistance of the copper shield, and low concentrations of copper (unfavourable with respect to resistance). Within a subaerially erupted basalt sequence (e.g. CRB), the top of an individual basalt flow has lower concentrations of sulphur and higher Fe-III/Fe-II ratios than the interior of the flow. Degassing at the top of the flow reduces sulphur concentrations and the reaction with atmospheric oxygen increases the iron-III/iron-II ratio.

The high-porosity tops of basalt flows are attractive targets for underground storage projects, not only for nuclear waste but also for natural gas (Reidel et al. 2002) and carbon dioxide (McGrail et al. 2011, 2014; McGrail and Schaef 2015; Matter et al. 2016). The reasons for the attractiveness, of course, are different. The top of a subaerially extruded sequence not only has low sulphur concentrations and high Fe-III/Fe-II ratios but also a high proportion of glassy phases containing calcium, magnesium and iron silicates that quickly react with wet CO₂ to form stable carbonate minerals and amorphous SiO₂; however, this is only one side of the story. Carbon-dioxide injection is like a large-scale hydrology experiment at its extreme. The huge volume of injected fluid causes high-speed groundwater movements, which are conveniently monitored at the surface by geophysical methods. The prediction of groundwater movement during the envisaged life of a nuclear waste repository, on the other hand, is one of the major tasks of a security analysis. Consider that a carbon-dioxide injection project in the CRB can be seen as a hydrology data collection event with a built-in time accelerator, which is convenient for projections concerning groundwater and nuclear waste disposal. The case of the deep CRB groundwater is especially interesting because it is very old: >30,000 years or even >100,000 years according to ¹⁴C or helium data, respectively (Reidel et al. 2002). Chemically, the old groundwaters are characterised by high pH as well as high sodium and fluoride concentrations, whereas calcium and magnesium concentrations are low. Both the Hanford Reference Repository and the Wallula CO₂ injection zone (Table 1) are in typical deep CRB groundwater (Reidel et al. 2002; McGrail et al. 2009; Lavalleur 2012), where formation temperature ranges from 37 to 54 °C.

Among the various candidate materials for nuclear waste packages, copper has unique oxidation characteristics. The

Table 1 Simplified stratigraphy of the CRB Group (Reidel et al. 2002) and depth ranges of the Reference Repository (Rockwell Hanford Operations 1982) and Wallula CO₂ injection zone (McGrail et al. 2011)

Formation	Member	Age (ma)	Depth range (m)	
			Reference Repository	Wallula
Saddle Mountains	-	6–13	-	-
Basalt				
Wanapum Basalt	-	14.5–15.6	-	-
Grande Ronde	Sentinel Bluffs	15.6	910–980	-
Basalt	Slack Canyon	-	-	828–887
	Fields Spring	-	-	-
	Shumaker Creek	-	-	-
	Winter Water	-	-	-
	Umtanum	-	1,100–1,170	-
	Ortley through Teepee Butte	-	-	-
	Buckhorn Springs	16.5	-	-
Imnaha Basalt	-	17.5	-	-

conversion from native metal (Cu^0) to metal oxide (Cu_2O) occurs in a mildly oxidising to mildly reducing environment (positive Eh for pH < 7.7 at 25 °C; Fig. 2), whereas the conversion of steel, titanium or nickel-chromium alloy is not only possible under oxidising conditions but also under strongly reducing conditions, i.e., below the stability field of liquid water. The example of naturally occurring native copper in the Earth's crust must be taken into account in the disposal site design. The largest native copper deposits are located on the Keweenaw Peninsula of Michigan (mid-west USA), where they have been mined to a depth of 2.2 km (Butler and Burbank 1929; Broderick et al. 1946; White 1968). These deposits formed 1 billion years ago at temperatures of 100–200 °C. The mineralising fluids were slightly less reducing but had much higher copper concentrations than commonly present-day groundwater.

In low-salinity groundwater (0.0005–0.05 mol/L Cl^-), CuCl^0 is the dominant aqueous copper species. Accordingly, the thermodynamically relevant parameter is the $\Sigma\text{Cu}/\text{Cl}$ activity ratio, which refers to the sum of activities of all dissolved copper species divided by the Cl^- activity. Groundwater in the Deccan Basalt, India, has $\Sigma\text{Cu}/\text{Cl}$ ratios in the range from $10^{-3.5}$ to 10^{-5} (Muralidhar and Raju 1990). Similar conditions are achievable in the bentonite buffer around a copper container for non-basalt repositories if the bentonite contains artificial admixtures of fine-grained native copper. Thus thermodynamic equilibrium between the container and

the external fluid on the high-Eh side of the native-copper stability field is implemented in the repository-container system as an analogue to the natural counterparts.

The low-Eh and low-pH side of the native-copper stability field is the copper-sulphide phase boundary (CuS and CuS_2). The position of this boundary depends on the total activity of aqueous sulphur species (ΣS), which is $\leq 1.5 \times 10^{-3}$ in CRB groundwater (Grande Ronde Basalt Formation; Reidel et al. 2002). Provided the bentonite backfill contains no sulphur-bearing minerals, the corrosion of the copper container is constrained by the diffusion of aqueous sulphide from the igneous rock aquifer through the bentonite to the container surface. This situation is quite different from corrosion of other package materials such as steel, titanium or nickel-chromium alloy, which all corrode by reaction with omnipresent water. It is not possible to control corrosion of these materials by a diffusion barrier around the container.

In the case of a sulphur-free buffer, general corrosion of the copper container can be determined by a simple calculation. The experimentally derived diffusion coefficient of aqueous sulphide in bentonite is approximately $7 \times 10^{-8} \text{ cm}^2/\text{s}$ (King and Stroes-Gascoyne 1995; King et al. 2002). The CRB groundwater has an average sulphide concentration of $1.1 \times 10^{-4} \text{ mol/L}$. Assuming a 35-cm-thick bentonite buffer, $2 \times 10^{-16} \text{ mol}$ per second and per square centimetre are transported through the buffer to the container surface. This is equivalent to a general corrosion rate of 10^{-7} cm/a , when Cu^0 is transformed to Cu_2S ; thus, the corrosion depth is 0.1 cm within 1 million years and a service time for a 5–10-cm-thick copper shell beyond 1 million years is a realistic possibility.

The situation can be further improved if hematite is added to the bentonite buffer. Such a measure would expand the stability field of native copper to lower Eh in the presence of $\text{FeSO}_4(\text{c})$ or pyrite by 0.07 V or 0.05 V, respectively. The average CRB groundwater with Eh = −0.3 V and pH = 9.4 would be in the stability field of native copper, and corrosion would be nil. The scenario replicates the natural process: the precipitation of native copper is linked to the dissolution of hematite in the Keweenaw deposits.

Paradoxically, the old CRB project (1968–1987) lives up to modern scientific standards. The more recent Yucca Mountain project (1978–2011) with its extremely high corrosion rates does not even come near those.

Fig. 2 Eh-pH diagram for the system Cu-(Fe)-S-Cl-O-H at 25 °C and 0.1 MPa. The thermodynamic data are calculated with the SUPCRT92 program (Johnson et al. 1992) except for CuCl^0 (Xiao et al. 1998) and $\text{FeSO}_4(\text{c})$ (Hemingway et al. 2002). Two types of Cu^0 - Cu_2S boundaries are shown: the black lines refer to the Fe-free system with ΣS of 10^{-2} and 10^{-5} ; the red interrupted line shows the limit of the Cu^0 stability field for $\Sigma\text{S} = 10^{-5}$ in the presence of hematite and $\text{FeSO}_4(\text{c})$. Note that the position of the Cu^0 - CuCl^0 boundaries (for $\Sigma\text{Cu}/\text{Cl}$ of $10^{-3.5}$ and 10^{-5}) slightly varies with total salinity; this is not explicitly shown in the diagram but the thickness of the boundary lines is designed in such a way that it is wider than required for the salinity range of 0.005–0.05 mol/L Cl^-

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Broderick TM, Hohl CD, Eidemiller HN (1946) Recent contributions to the geology of the Michigan copper district. *Econ Geol* 41:675–725
- Butler BS, Burbank WS (1929) The copper deposits of Michigan. *US Geol Surv Prof Pap* 144:1–234
- Farmer J et al. (2003) Technical basis document no. 6: waste package and drip shield corrosion. LLNL report UCRL-LR-155288, Lawrence Livermore National Laboratory, Livermore, CA
- German Federal Government (2013) Standortauswahlgesetz vom 23. July 2013. *Bundesgesetzblatt I-S-2553*, German Federal Government, Berlin
- Hemingway BS, Seal RR, Chou IM (2002) Thermodynamic data for modeling acid mine drainage problems: compilation and estimation for selected soluble iron-sulfate minerals. *US Geol Surv Open File Rep* 02-161
- Johnson JW, Oelkers EH, Helgeson HC (1992) SUPCRT92: a software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species and reactions from 1 to 5000 bar and 0 to 1000°C. *Comput Geosci* 18:899–947
- King F, Stroes-Gascoyne S (1995) Microbially influenced corrosion of nuclear fuel waste disposal containers. *Proc. Int. Conf. on Microbially Influenced Corrosion*, NACE International, Houston, TX; and American Welding Society, Miami, FL, pp 35/1–35/14
- King F, Ahonen L, Taxen C, Vuorinen U, Werne L (2002) Copper corrosion under expected conditions in a deep geologic repository. *Posiva report* 2002–01, Posiva, Eurajoki, Finland
- Lavallaur HJ (2012) Microbiology of basalts targeted for deep geological carbon sequestration: field observations and laboratory experiments. MSc Thesis, Oregon State University, Corvallis, OR
- Matter JM et al (2016) Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science* 352: 1312–1314
- McGrail BP, Schaef HT (2015) Utilization of CO₂ in unconventional reservoirs. Carbon Storage R&D Project Review Meeting, August 18–21, 2015, National Energy Technology Laboratory, Pittsburgh, PA
- McGrail BP, Spane FA, Bacon DH, Hund G, Thorne PD, Thompson CJ, Reidel SP, Colwel FS (2009) Preliminary hydrogeologic characterization results from the Wallula basalt pilot study. PNWD-4129 Battelle Northwest Division, Richland, WA
- McGrail BP, Spane FA, Sullivan EC, Bacon DH, Hund G (2011) The Wallula basalt sequestration pilot project. *Energy Procedia* 4:5653–5660
- McGrail BP, Spane FA, Amonette JE, Thompson CR, Brown CF (2014) Injection and monitoring at the Wallula basalt pilot project. *Energy Procedia* 63:2939–2948
- Muralidhar M, Raju CS (1990) Comparative study of groundwater quality in Sadasivpet area, Andhra Pradesh, Bangalore, India. *Bangalore Univ Stud Earth Sci* 1990:93–100
- Reidel SP, Johnson VG, Spane FA (2002) Natural gas storage in basalt aquifers of the Columbia Basin, Pacific Northwest USA: a guide to site characterization. PNNL-13962, Pacific Northwest National Laboratory, Richland, WA
- Rockwell Hanford Operations (1982) Site characterization for the basalt waste isolation project. DOE/RL 82–3 volume II. US Department of Energy, Washington, DC
- Schwartz MO (1996) Native copper deposits and the disposal of high-level waste. *Int Geol Rev* 38:33–41
- Schwartz MO (2008) High-level waste disposal, ethics and thermodynamics. *Environ Geol* 54:1485–1488
- Schwartz MO (2012a) Modelling groundwater contamination above a nuclear waste repository at Gorleben, Germany. *Hydrogeol J* 20:533–546
- Schwartz MO (2012b) Modelling radionuclide transport in large fractured-media system: the example Forsmark, Sweden. *Hydrogeol J* 20:673–687
- US Department of Energy (2004) Nuclear waste policy as amended. US Department of Energy, Washington, DC. https://energy.gov/sites/prod/files/edg/media/nwpa_2004.pdf. Accessed 24 May 2017
- White WS (1968) The native-copper deposits of northern Michigan. In: Ridge JD (ed) *Ore deposits of the United States, 1933–1967*, vol 1. AIME, New York, pp 303–325
- Xiao X, Gammons CH, Williams-Jones AE (1998) Experimental study of copper(I) chloride complexing in hydrothermal solutions at 40 to 300°C and saturated vapor pressure. *Geochim Cosmochim Acta* 62:2949–2964