Corrosion of glass used for radioactive waste disposal influenced by iron corrosion products

Ali AL DABBAS¹, Katalin KOPECSKÓ²
Faculty of Civil Engineering,
Budapest University of Technology and Economics,
Műegyetemrkpart 3, Budapest 1111, Hungary

E-mail: ali.al.dabbas@epito.bme.hu and kopecsko.katalin@epito.bme.hu

Abstract. Iron corrosion products of the steel canister in the nuclear waste container are highly silica sorptive materials and very much expected to delay formation of the protective layer (gel) on the nuclear glass interface. This study is focusing on the role of the iron carbonates (ankerite), which is probably one of iron corrosion products and already exists in the clay structure of the disposal depth. Simulating nuclear borosilicate glass samples (alternative to the R7T7-type) samples are planned to leach in different series of experimental models with dissimilar quantities of ankerite. Batch experiments all will be cultivated in synthetic groundwater; where different pH (4-9) values and temperatures (35, 50, 90 °C) are considered. In this paper the state of the art of the radioactive waste glass corrosion in the circumstances of deep geological disposal will focus on the role of ankerite as one of the iron corrosion products and clarify how it is expected to show delay in achieving the Si saturation status and accelerate glass alterations.

1. Introduction
Disposal of the High Level radioactive Waste (HLW) in deep geological formation in multi-layer containers is internationally highly recommended. After evaporation of the volatile radionuclides it is immobilized and vitrified by incorporating into borosilicate glass matrix (R7T7 type glass) [1, 2]. The glass matrix is formed to pellet shape and poured into stainless steel containers to facilitate its handling, storage and disposal operations. Finally it is embedded in a buffer i.e. concrete isolation in the claystones [3]. Experiments will be conducted with small polished simulating nuclear borosilicate glass chips, involving accelerated ageing of glass due to environment provided by the microbial activity to figure out the convenient and optimum conditions of the maximum Si uptake by ankerite. Ankerite is expected to show noticeable Si uptake, Iron-silicates precipitation is highly predicted to happen. They both are very much expected to sharing the glass corrosion role with the other important parameters mentioned in the literature. The experiments will show if the ankerite ratio will increase due to the microbial activity.

1.1. High level waste
Nuclear spent fuel mainly consists of (96-97%) uranium plutonium and (3-4%) fission products. Spent fuel is reprocessed (uranium and plutonium are separated) to generate new nuclear fuel used in economic reactors. The remaining fission products (¹²⁹I, ⁹⁰Sr, ⁹⁹Tc, ⁷⁹Se, ³⁶Cl, and ¹³⁵Cs) and other actinides are considered as HLW. In particular, some radioactive isotopes such as ⁹⁹Tc, ⁷⁹Se, and ¹²⁹I are mobile in water, requiring special storage medium that reduces their ability to move into the groundwater [4, 5].
1.2. Immobilization of the HLW
One of the most recommended immobilization methods of the HLW is the vitrification. It is calcination of the HLW and then incorporation it into borosilicate glass to be as glass matrix material then it is poured into stainless steel canisters. Finally, non-recoverable fission products and actinides became locked in the glass matrix insoluble in water and stable for hundreds of thousands of years [6].

1.3. Storage and disposal of HLW
Disposal of the non-recyclable HLW is a long-term storage for hundreds of thousands of years in a deep geological disposal located between 450 and 500 m depth [7, 8] in a multi-layer container, where tectonic stability is great and natural barrier are effective to contain that kind of waste.

2. Glass corrosion
Formation of alteration layer on glass in the geological formation has been studied as well as experimentally evaluated and determined by several studies. The long-term storage was experimentally estimated by evaluating the effects of the physico-chemical parameters on the short-term alteration of glass such as pH, temperature, glass composition and redox potential [7, 9].

2.1. Glass dissolution
Water saturated surrounding dissolution of glass is a result of various processes; First: glass hydration by water diffusion into the glass network followed by ion exchange between positive protons in the groundwater and alkali metals in the glass formation, which leads to glass hydration and formation of amorphous alteration layer (gel) on the glass surface. Second: hydrolysis of the ionic-covalent bonds of the most soluble elements by attacking the glass network (Si-O-X; X: Si, Al, Fe, Zr) bonds by groundwater. Third: condensation mechanism where the silica is reversely reacts and dissolves in the groundwater and condensate as a gel layer influenced by pH and temperature. In the experiment, the leaching solution should be saturated by Si as a condition necessary for the formation of the gel layer [7, 10, 11 and 12].

2.2. Function of the gel layer
The gel layer is a natural phenomenon important to reduce the direct contact between the groundwater and the glass to protect the glass from dissolving in the groundwater and so prevent potential release of the radioactive substances back to the biosphere [13, 14 and 15]. The Iron Corrosion Products (ICPs) in the solution will provide surfaces for Si sorption. Reducing Si content in the surrounding formation is expected to delay the creation of gel layer in the insufficient Si saturated solution thus motivate glass dissolution [16].

2.3. Iron corrosion products
Steel alteration in presence of bacterial activities is highly responsible for accelerating exponentially rising ICPs in the anaerobic conditions [8, 17]. Sulphate Reducing Bacteria (SRB) are considered as the main reason of that [17, 18]. They produce H\textsubscript{2} in the process formation of iron sulfide, FeS [19]. SRB exist widely in deep geological repository and they influence iron corrosion by releasing free Fe ions in the solution surroundings the glass, which are expected to create different kinds of iron carbonate minerals [20].

3. Silica sorption
Experiments have been performed with simulating glass samples to determine the chemical durability of R7T7 to better understand the glass corrosion and performance under potential disposal conditions. Silica saturation was achieved in 91days at 90 °C. Glass corrosion rate was measured 1000 times lower after Si saturation [21]. Nuclear waste is providing the higher temperature and microbial influenced corrosion mechanism is enhancing the lower pH by producing acidic by-products which are providing appropriate medium conditions for Si sorption mechanism on the ICPs, which were experimented and showed enhancing and accelerating effect on the corrosion process of the borosilicate glass [22, 23].
3.1. Power of ICPs to uptake silicon

Bacterial activities on the different carbon steel applications in both aerobic and anaerobic mediums have shown ICPs whether iron carbonates (i.e. siderite, FeCO$_3$) or iron oxides (i.e. magnetite, Fe$_3$O$_4$; goethite, α-FeOOH) in the bulk medium [9, 20 and 24]. Experiment was conducted on SON68 glass and ancient ICPs [25] has shown strong influenced alteration of the glass by the ICPs formed precipitation which lowered the Si concentration in the solution. Magnetite and goethite were added to the solution and showed deleterious effect on the glass chemical durability [11] justified by the power of Si sorption on the outer surface of the ICPs which showed up 5 times more of glass corrosion [21]. However, zero glass dissolution-rate was obtained due to clogging of the external gel porosity at the gel/Si saturated solution after about one month of leaching under certain conditions [26, 27].

3.2. Formation and role of ankerite

Ankerite is present in the clayey matrix and its dissolution showed goethite FeOOH formation [28]. In the carbonatites in the past siderite has approved to be ankerite, Ca(Fe,Mg,Mn)(CO$_3$)$_2$ [29]. Ankerite (CaFe(CO$_3$)$_2$) has the same crystal structure as dolomite (CaMg(CO$_3$)$_2$) [30] and considered as a member of the dolomite group of minerals and it shares siderite many of similarities [31]. Siderite, ankerite and dolomite have shown up significant identified precipitation in the sandstone, when Fe(II) source provider was exist there [30, 32]. MIC mechanisms on the steel canister release Fe(II), which most likely sufficient to precipitate ankerite. This study is predicting ankerite precipitation as one of the ICPs. However, Natural ankerite is already taking part in mineralogical composition of the French Callovo-Oxfordian host-rock [33, 34] and it is one of the main chemical compositions of the carbonates in the nuclear waste repository formations [35].

4. Experimental Parameters influencing the alteration of HLW glass

Experimental parameters will be special in composition and prepared in a standard methods to demonstrate the deep underground reactions.

4.1. Glass

The study is conducted over small polished simulating nuclear borosilicate glass chips/coupons, involving accelerated ageing of glass due to model environment. SON68 type glass and International Simple Glass ISG are inactive analogs of the French high-level waste glass (R7T7-type) and they are approved by many researches in the literature for studying the durability of the R7T7 glass [1, 2, 7, 12, 16, 25, 26, 27 and 36]. The composition of the SON68 glass is shown in Table 1.

| Oxide  | Composition, wt.% | Oxide  | Composition, wt.% | Oxide  | Composition, wt.% |
|--------|--------------------|--------|--------------------|--------|--------------------|
| SiO$_2$ | 45.85              | ZnO   | 2.53               | Nd$_2$O$_3$ | 2.04               |
| B$_2$O$_3$ | 14.14         | P$_2$O$_5$ | 0.29             | Pr$_2$O$_3$ | 0.46               |
| Na$_2$O | 10.22             | SrO   | 0.35               | Ag$_2$O | 0.03               |
| Al$_2$O$_3$ | 5.00          | ZrO$_2$ | 2.75              | CdO    | 0.03               |
| CaO    | 4.07              | MoO$_3$ | 1.78              | SnO$_2$ | 0.02               |
| Li$_2$O | 1.99              | Cs$_2$O | 1.12              | TeO$_2$ | 0.23               |
| Fe$_2$O$_3$ | 3.03           | BaO   | 0.62               | Ce$_2$O$_3$ | 0.97               |
| NiO    | 0.43              | Y$_2$O$_3$ | 0.20            | Others | 0.39               |
| Cr$_2$O$_3$ | 0.53            | La$_2$O$_3$ | 0.93            |        |                    |

4.2. Synthetic Groundwater

To realize the groundwater in the nuclear waste repository formations; a synthetic groundwater is recommended. It is originally Ultra-Pure Water (UPW) under addition of some nutrients and organic carbon. Table 2 illustrates the components, which will be added experimentally to the UPW.
Table 2. Composition of the synthetic argillite water [8]

| Compound | Concentration, mole/l | Compound | Concentration, mole/l |
|----------|-----------------------|----------|-----------------------|
| Fe       | 3.40E-05              | Na       | 4.56E-02              |
| Sr       | 2.00E-04              | TIC      | 3.34E-03              |
| K        | 1.03E-03              | Si       | 1.80E-04              |
| Mg       | 6.67E-03              | Cl       | 4.10E-02              |
| Ca       | 7.36E-03              | NH₄      | 2.90E-04              |
| Al       | 4.70E-09              | Mn       | 4.70E-06              |
| SO₄      | 1.56E-02              | Lactate  | 8.00E-06              |

4.3. Clay

Scientific researchers are using drilled out clay from deep geological formation in selected countries where the HLW could be disposed. These include France (Callovo-Oxfordian Clayrock at Bure), Belgium (Boom Clay at Mol), Hungary (Boda Claystone at Mecsek), Switzerland (Opalinus Clay at Mont Terri and Benken, and Palfris Formation at Wellenberg), United Kingdom (Oxford Clay) and Canada (Queenston Formation) [28], [33], [37].

4.4. Synthetic Ankerite

In our ongoing experiments synthetic ankerite will be added to the samples by different concentrations, however it is not planned to be added to the blank (reference) sample to figure out how does the ankerite role would affect the Si concentrations in the aqueous solution in the different samples.

5. Conclusions

High level radioactive wastes are immobilized and vitrified by incorporating into borosilicate glass matrix. This glass matrix is poured then into stainless steel containers. Finally it is embedded in a buffer i.e. concrete isolation in the clay-stones of deep geological disposal. In this paper the state of the art of the corrosion of radioactive waste glass in the circumstances of deep geological disposal were extensively studied. Microbial influenced corrosion is highly expected to be happening on the carbon steel canister of the nuclear waste in the anaerobic conditions deep in the geological repository formation. Steel alteration in presence of bacterial activities is proved as a basic factor responsible to accelerate the formation the iron corrosion products. Ankerite should be considered as one of the important iron carbonates, which is suggested to take part in the iron corrosion products in addition to its ubiquitous in soils. Therefore; it is highly expected to be additional factor influencing the glass alteration in the disposal repository formation in addition to the factors already studied by the literature. Ankerite could have multifunctional (direct and indirect) effects on the alteration of glass, which hypothesis should be experimentally proved.

Acknowledgement

Stipendium Hungaricum Scholarship Programme is highly acknowledged for supporting the PhD study and research work. Authors are acknowledged having the opportunity to present the paper at the 5th international conference on competitive materials and technology processes, Miskolc-Lillafüred, Hungary.

References

[1] Minet Y, Bonin B, Gin S, Frugier P 2010 Journal of Nuclear Materials 404 (3) 178 https://doi.org/10.1016/j.jnucmat.2010.07.015
[2] Grambow B 2006 Elements 2 (6) 357 https://doi.org/10.2113/gselements.2.6.357
[3] Thompson L 2010 Coursework for Physics 240 Stanford University
[4] IAEA, Storage and disposal of spent fuel and high level radioactive waste. 2006 https://www.iaea.org/About/Policy/GC/GC50/.../English/ge50inf-3-att5_en.pdf (last visited 25/12/2017).

[5] Treatment and conditioning of nuclear waste *Word Nuclear Association* 2017

[6] Bouakaz R, Abdelouas A, El Mendili Y, Grambow B, Gin S 2016 *RSC Adv* 6 72616 https://doi.org/10.1039/C6RA12404F

[7] El Hajj H, Abdelouas A, Grambow B, Martin C, Dion M 2010 *Physics and Chemistry of the Earth Parts A/C* 35 (6-8) 248 https://doi.org/10.1016/j.pce.2010.04.007

[8] Damien Féron, Didier Crusset, Jean-Marie Gras 2008 *Journal of Nuclear Materials* 379 (1-3) 16 https://doi.org/10.1016/j.jnucmat.2008.06.023

[9] Gin S 2014 *Procedia Materials Science* 7 163 https://doi.org/10.1016/j.mspro.2014.10.022

[10] Philippini V, Naveau A, Catalette H, Leclercq S 2006 *Journal of Nuclear Materials* 348 (1-2) 60 https://doi.org/10.1016/j.jnucmat.2005.09.002

[11] Burger E, Rebiscoul D, Bruguier F, Jublot M, Lartigue J E, Gin S 2013 *Applied Geochemistry* 31 159 https://doi.org/10.1016/j.apgeochem.2012.12.016

[12] Rebiscoul D, Frugier P, Gin S, Ayral A 2005 *Journal of Nuclear Materials* 342 (1-3) 26 https://doi.org/10.1016/j.jnucmat.2005.03.018

[13] Vernaz E, Gin S, Jegou C, Ribet I 2001 *Journal Nuclear Materials* 298 (1-2) 27 https://doi.org/10.1016/S0022-3115(01)00643-2

[14] Gin S, Ribet I, Couillard M 2001 *Journal Nuclear Materials* 298 (1-2) 1 https://doi.org/10.1016/S0022-3115(01)00573-6

[15] Curti E 2003 *Technical Report No. PSI-03-18*, Paul Scherrer Institute, CH-5232 Villigen PSI (Switzerland) *INIS* 36 (3) 62.

[16] Kuang F, Wang J, Yan L, Zhang D 2007 *Electrochimica Acta* 52 (20) 6084 https://doi.org/10.1016/j.electacta.2007.03.041

[17] Sagues A A, Poor N D, Gaseres L, Akhoondam M 2009 *Final Report to Florida Department of Transportation* University of South Florida

[18] Beech I B 2003 *Microbiology Today* 30 (3) 115

[19] Little B J, Lee J S, Ray R I 2006 *Corrosion* 62 (11) 1006 https://doi.org/10.5006/1.3278228

[20] Bart G, Zwicky H U, Aerne E T, Graber T H, ZBerg D, Tokiwa M 1987 *Symposium L - Scientific Basis for Nuclear Waste Management* X 18 (22) 459 https://doi.org/10.1557/JMR-1990.1130

[21] Mitsui S, Aoki R 2001 *Journal of Nuclear Materials* 298 (1-2) 184 https://doi.org/10.1016/S0022-3115(01)00595-5

[22] Jordan N, Marmier N, Lomeanche C, Giffaut E, Ehrhardt J J 2007 *Journal of Colloid and Interface Science* 312 (2) 224 https://doi.org/10.1016/j.jcis.2007.03.053

[23] Dillmann P, Gin S, Neff D, Gentaz L, Rebiscoul D 2016 *Geochimica et Cosmochimica Acta* 172 287 https://doi.org/10.1016/j.gca.2015.09.033

[24] Jollivet P, Angeli F, Caillietou C, Devreux F, Frugier P, Gin S 2008 *Journal of Non-Crystalline Solids* 354 (45-46) 4952 https://doi.org/10.1016/j.jnoncrysol.2008.07.023

[25] Jonathan P Icenhower, Carl I Steefel 2013 *Journal of Nuclear Materials* 439 (1-3) 137 https://doi.org/10.1016/j.jnucmat.2013.04.008

[26] Breitenr D, Osán J, Fábián M, Zagyvai P, Szabó C, Dähn R, Fernandes M M, Sajó I, Máthé Z, Török S 2015 *Environmental Earth Sciences* 73 (1) 209 http://dx.doi.org/10.1007/s12665-014-3413-4

[27] Buckley H A, Woolley A R 1990 *Mineralogical Magazine* 54 413 https://doi.org/10.1180/minmag.1990.054.376.06

[28] Chai L, Navrotsky A 1996 *American Mineralogist* 81 (9-10) 1141 https://doi.org/10.2138/am.1996-9-1012

[29] Amethyst Galleries' Mineral Gallery, Ankerite. http://www.galleries.com/Ankerite (last visited on 24/12/17).

[30] Xu T, Apps J A, Pruess K 2005 *Chemical Geology* 217 (3-4) 295
[31] Gaucher E C, Tournassat C, Pearson F J, Blanc P, Crouzet C, Lerouge C, Altmann S 2009 Geochemistry et Cosmochimica Acta 73 (21) 6470 https://doi.org/10.1016/j.gca.2009.07.021

[32] Lerouge C, Vinsot A, Grangeon S, Wille G, Flehoc C, Gailhanou H, Gaucher E C, Madé B, Altmann S, Tournassat C 2013 Procedia Earth and Planetary Science 7 475 https://doi.org/10.1016/j.proeps.2013.03.133

[33] Tournassat C, Lerougea C, Blanc P, Brendlé J, Grenache J M, Touzelet S, Gaucher E C 2008 Applied Geochemistry 23 (4) 641 https://doi.org/10.1016/j.apgeochem.2007.11.002

[34] Collin M, Fournier M, Frugier P, Charpentier T, Moskura M, Deng L, Ren M, Du J, Gin S 2018 Materials Degradation 2 (4) https://doi.org/10.1038/s41529-017-0025-y

[35] Buocz I, Rozgonyi-Boissinot N, Török Á, Görög P 2014 Pollack Periodica 9 (3) 139 https://doi.org/10.1556/Pollack.9.2014.3.15