R-14-01

Evolution of pH in SFR 1

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May 2014

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ISSN 1402-3091
SKB R-14-01
ID 1394973

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1 Background and objective

The final repository for radioactive operational waste, SFR 1, is located in Forsmark in northern Uppland in the immediate vicinity of the Forsmark nuclear power plant, see Figure 1-1.

SFR 1 is built to receive, and after closure serve as a passive repository for low- and intermediate-level radioactive waste. The disposal chambers are situated in rock beneath the sea floor.

The low- and intermediate-level waste in SFR 1 consists of operational waste from the Swedish nuclear power plants and from the interim storage facility for spent nuclear fuel, Clab, as well as similar radioactive waste from other industry, research institutions and medical care. Decommissioning waste is planned to be deposited in the extended SFR.

The various parts of the repository are designed to accommodate different types of containers and materials and to provide adequate protection depending on the activity levels present in different type of waste, see Figure 1-2. A more detailed description of the structure of SFR is given in SKB (2008).

One common material in SFR 1 is concrete either found in construction parts of the repository or as stabilisation matrix for some waste types in the 1 BTF, 1 BMA and the Silo repository parts. Radionuclides, as well as other elements, might sorb upon minerals included in the concrete hence the migration of these element will be affected by the availability of sorption sites. The speciation and sorption of radionuclides are strongly influenced by the pH. The purpose of the report is to evaluate the overall pH evolution in the repository parts in SFR 1 from a simplified thermodynamic model, where the water transport through the repository mainly occurs through an advective flow.

Within the long term safety assessment for SFR K_d-values are selected for different concrete degradation stages, represented as different pH-values that affect the speciation and sorption of the analyzed radionuclides.

***Figure 1-1.** Overview of the surface part of the facility at the harbour in Forsmark.*

Figure 1-2. *The different waste containers used to encapsulate the waste in SFR 1.*

2 Methodology

2.1 Scope of analysis

The water flow through the different parts of the repository is conceptualized as pore water exchanges of a mixed tank representation of the part. The advective flow infiltrates an averaged waste volume and all the solid material assumes thereby to be in contact and in equilibrium with the infiltrating water. Hence, each flow step results in a complete pore water exchange for the repository part. No kinetic constraints are assumed concerning the dissolution of evaporator concentrate or cementitous minerals, hence the pH evolution is assumed to be entirely governed by thermodynamics and the flow rates.

For 1 BLA, 1 BTF, 2 BTF one single combined waste and wall volume will be assumed, whereas for the Silo and 1 BMA two separate cells representing the wall and waste volume will be employed. Because of the strong physical separation between compartments in 1 BMA and the significant variation in waste content, two different models will be applied for 1 BMA; one generic compartment containing ion exchange resins stabilized with cement and one compartment where the ion exchange resin are stabilized with bitumen. The geometrical resolution of the repository is intentionally extremely coarse in order to provide conservative global averages of each repository part. The variation of input data will be confined to the composition of the infiltrating water and the waste composition in terms of the state of the ion exchange resins and the influence from degradation products from cellulose (iso-saccharinic acid, ISA). Other parameters with a presumed strong influence on the pH evolution, such as flow rates, content of cement have not been varied.

2.2 Computer program and thermodynamic database

All reactive-transport simulations were performed with PHREEQC 2.17 (Parkhurst and Appelo 1999) and BRGMs (Bureau de Recherches Géologiques et Minières) thermodynamic database Thermoddem (Blanc et al. 2007). The pH evolution has been evaluated at the same temperature as the thermodynamic properties in the database, *i.e.* 25°C.

3 Input data

3.1 Void volumes

The available void volume in each repository part determines the time required for completing a full pore water exchange given a fixed inflow of water. In addition to the larger intra- and inter-package void volumes, cement and concrete used as backfill or as construction concrete will contribute with void volumes in terms of the materials fine pore structure.

3.1.1 Silo

The total void volume for the Silo is evaluated from

- the void volume of the waste matrixes,
- pore volume from packaging, *i.e.* pores of the concrete,
- pore volume from backfill, *i.e.* pores of the concrete,
- pore volume from the walls of the Silo, *i.e.* pores of the construction concrete.

Values for the void and pore volumes have been assessed according to Keith-Roach et al. (2014), see Table 3-1.

Thus, the total void volume for the Silo is assumed to be 9.2E+3 m^3.

3.1.2 1 BMA

The total void volume for 1 BMA is evaluated from

- the void volume of the waste matrixes,
- pore volume from packaging, *i.e.* pores of the concrete,
- void volume between packages,
- pore volume from the walls of the 1 BMA compartment, *i.e.* pores of the construction concrete.

Thus, the total volumes for the compartment 1 and 3 are evaluated to 5.4E+3 m^3 and 4.8E+2 m^3 respectively, see Table 3-2.

Table 3-1. Void and pore volumes inside the Silo according to Keith-Roach et al. (2014).

In all waste packages, conditioning and packaging (m^3)	In the construction concrete (m^3)	In the backfill or void around the packages (m^3)	Total void volume (m^3)
5.3E+3	1.4E+3	2.5E+3	9.2E+3

Table 3-2. Void and pore volumes in compartment 1 and 3 of the 1 BMA (Keith-Roach et al. 2014).

Compartment	In all waste packages, conditioning and packaging (m^3)	In the construction concrete (m^3)	In the backfill or void around the packages (m^3)	Total void volume (m^3)
1	4.3E+2	4.4E+1	7.0E+1	5.4E+2
3	2.1E+2	4.4E+1	2.2E+2	4.8E+2

3.1.3 1 BTF

The total void for 1 BTF is evaluated from

- the void volume of the waste matrixes,
- pore volume from packaging, *i.e.* pores of the concrete,
- void volume between packages.

Thus, the total void volume for the 1 BTF is assumed to be 2.7E+3 m^3, see Table 3-3.

3.1.4 2 BTF

The total void for 2 BTF is evaluated from

- the void volume of the waste matrixes,
- pore volume from packaging, *i.e.* pores of the concrete,
- void volume between packages.

Thus, the total void volume for the 2 BTF is assumed to be 9.6E+3 m^3, see Table 3-4.

3.1.5 1 BLA

The total void for 1 BLA is evaluated from

- the void volume of the waste matrixes,
- void volume between packages, i.e. difference between the excavated volume and the storage capacity.

The void volumes in waste packages have been assessed by SKB 2013a[1] to 4.0E+3 m^3. The void between the waste packages have been evaluated as the difference between the excavated volume and the storage capacity as given in SKB (2001), *i.e.* 27E+3 m^3–15.1E+3 m^3 = 11.9E+3 m^3.

Thus, the total void volume for the 1 BLA is assumed to be 15.9E+3 m^3, see Table 3-5.

3.1.6 Summary of assumed void volumes

The assumed void and pore volumes is summarized in Table 3-6 along with total volumes as evaluated from Keith-Roach et al. (2014).

Table 3-3. Void and pore volumes inside 1 BTF.

In all waste packages, conditioning and packaging (m^3)	In the backfill or void around the packages (m^3)	Total void volume (m^3)
1.2E+3	1.5E+3	2.7E+3

Table 3-4. Void and pore volumes inside 2 BTF according to Keith-Roach et al. (2014).

In all waste packages, conditioning and packaging (m^3)	In the backfill or void around the packages (m^3)	Total void volume (m^3)
4.7E+3	4.9E+3	9.6E+3

Table 3-5. Void and pore volumes of 1 BLA (from SKB 2013a[2] and Keith-Roach et al. (2014)).

In all waste packages (m^3)	In the backfill or void around the packages (m^3)	Total void volume (m^3)
4.0E+3	11.9E+3	15.9E+3

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[1] Values taken from an earlier version of SKB 2013a. In this report the values from the earlier version has been used. The conclusions drawn are judged not to be affected.

[2] Values taken from an earlier version of SKB 2013a. In this report the values from the earlier version has been used. The conclusions drawn are judged not to be affected.

Table 3-6. The amount of concrete and cement, the associated void volume, the total void volume and the corresponding global porosity. Total volumes evaluated from Keith-Roach et al. (2014).

	Silo	1 BMA compartment 3 (Bitumen)	1 BMA compartment 1 (Cement)	1 BTF	2 BTF	1 BLA
In all waste packages (m^3)	5.3E+3	2.1E+2	4.3E+2	1.5E+3	4.7E+3	4.0E+3
Backfill or around the packages (m^3)	2.5E+3	2.2E+2	7.0E+1	1.2E+3	4.9E+3	11.9E+3
Construction concrete (m^3)	1.4E+3	4.8E+2	5.4E+2	–	–	–
Total void volume (m^3)	9.2E+3	4.4E+1	4.4E+1	2.7E+3	9.6E+3	15.9E+3
Total volume (m^3)	47.5E+03	1.07E+03	1.07E+03	2.00E+04	20.0E+03	27.0E+03
Global porosity	0.19	0.45	0.51	0.14	0.48	0.59

3.2 Flow data

The flow rates through different parts of the repository, the global voids and the corresponding years for completing a pore water exchange are summarized in Table 3-7. The number of years for completing a pore water exchange is evaluated as the time required filling the available pore volume (see Table 3-6) considering the assumed flow rate. As seen in Table 3-7, there is a substantial difference in terms of the number of pore water exchanges completed within the postulated 100,000 years between different repository parts, from 74 for the Silo to approximately 3,300 for 1 BLA.

The time scale associated with each pore water exchange is derived from the number of years to complete one pore water exchange in Table 3-7. For an example (see also Table 3-8), for 1 BLA no complete pore water exchange is performed during the interval 0–2,000 post closure, whereas during the subsequent 1,000 years a pore water exchange is completed every 264th year. For the remaining period of time each pore water exchange takes 117 years.

Table 3-7. Flow rates for the first 5,000 years after closure (SKB 2013b). The subsequent flow rates from year 5,000 are assumed to be the same as during the period 3,000–5,000 post closure. The notaion C1 and C3 denotes the compartment 1 and 3 respectively.

		0–2,000	2,000–3,000	3,000–5,000	0–100,000
1 BMA	Flow rate (m^3/y)	7.83E–03	1.41E+00	3.62E+00	
C1	Flow rate/compartment (m^3/y)	6.02E–04	1.08E–01	2.79E–01	
	Void/compartment (m^3)	5.4E+02	5.4E+02	5.4E+02	
	No. years for a complete pore exchange	8.97E+05	5.00E+03	1.94E+03	
	No. pore exchanges within the specified time interval	0.0	0.2	1.03	50.3
1 BMA	Flow rate (m^3/y)	7.83E–03	1.41E+00	3.62E+00	
C3	Flow rate/compartment (m^3/y)	6.02E–04	1.08E–01	2.79E–01	
	Void/compartment (m^3)	4.8E+02	4.8E+02	4.8E+02	
	No. years for a complete pore exchange	7.97E+05	4.44E+03	1.72E+03	
	No. pore exchanges within the specified time interval	0.0	0.2	1.2	56.5
1 BLA	Flow rate (m^3/y)	1.20E–01	6.02E+01	1.36E+02	
	Void (m^3)	1.59E+04	1.59E+04	1.59E+04	
	No. years for a complete pore exchange	1.32E+05	2.64E+02	1.17E+02	
	No. pore exchanges within the specified time interval	0.02	3.8	17.18	834.0
1 BTF	Flow rate (m^3/y)	9.67E–03	1.84E+00	3.80E+00	
	Void (m^3)	2.70E+03	2.70E+03	2.70E+03	
	No. years for a complete pore exchange	2.79E+05	1.46E+03	7.11E+02	
	No. pore exchanges within the specified time interval	0.01	0.68	2.81	137.1
2 BTF	Flow rate (m^3/y)	9.44E–03	3.19E+00	6.18E+00	
	Void (m^3)	9.60E+03	9.60E+03	9.60E+03	
	No. years for a complete pore exchange	1.02E+06	3.01E+03	1.55E+03	
	No. pore exchanges within the specified time interval	0.00	0.3	1.3	62.7
Silo	Flow rate (m^3/y)	4.68E–03	7.11E–01	1.41E+00	
	Void (m^3)	9.20E+03	9.20E+03	9.20E+03	
	No. years for a complete pore exchange	1.96E+06	1.29E+04	6.52E+03	
	No. pore exchanges within the specified time interval	0.00	0.08	0.3	15.0

Table 3-8. Example of the derivation of the time scale for 1 BLA.

No. of pore water exchanges	Time (years)
0	0
1	2,264
2	2,528
3	2,792
4	3,056
5	3,173
6	3,407
7	3,758
...	...

3.3 Composition of infiltrating water

The composition of the infiltrating water will evolve due to land lift. In terms of salinity, the saline water and the glacial derived water in Table 3-9, represents two extreme water types and the pH determined with these waters is expected to embrace the possible variations derived from other intermediate water compositions. The temperate-periglacial water represents the most probable water composition during the postulated period of time (100,000 years).

3.4 Waste categories

The composition between the different waste categories are summarized in Table 3-10 from SKB 2013a[3]. The thermodynamic representation of each waste category is further described in Section 3-4 to 3-8.

The waste categories which are assumed to dissolve or affect the pH evolution through ion exchange are;

- Aluminium/zinc.
- Ashes.
- Cellulose.
- Cement.
- Concrete.
- Evaporator concentrate.
- Ion exchange resin.
- Iron/Steel.

Table 3-9. Compositions of the waters assumed to infiltrate the repositories (Auqué et al. 2013).

Element	Saline groundwater (mol/kgw)	Temperate-periglacial water (mol/kgw)	Glacial derived water (mol/kgw)
C	1.48E–3	4.92E–3	6.40E–4
Ca	1.50E–2	1.25E–3	2.96E–4
Cl	9.87E–2	5.36E–3	8.19E–6
K	5.12E–4	1.28E–4	1.65E–5
Mg	6.17E–3	4.94E–4	1.04E–6
Na	6.53E–2	7.83E–3	4.35E–6
S	3.64E–3	5.21E–4	1.25E–5
Si	1.83E–4	2.00E–4	2.13E–4

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[3] Values taken from an earlier version of SKB 2013a. In this report the values from the earlier version has been used. The conclusions drawn are judged not to be affected.

Table 3-10. Content of various components identified as having a potential impact in the pH evolution in the different parts of SFR data taken from SKB 2013a[4].

	Silo	1 BMA	1 BTF	2 BTF	1 BLA
Aluminium/Zinc (kg)	9.17E+03	9.20E+03	5.56E+04	0.00E+00	6.06E+04
Aluminium/Zinc (m^2)	1.36E+03	1.14E+03	1.54E+04	0.00E+00	8.59E+03
Asphalt, gravel, soil (kg)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Ashes (kg)	0.00E+00	0.00E+00	5.43E+05	0.00E+00	0.00E+00
Concrete (kg)	1.21E+07	1.02E+07	6.74E+06	8.04E+06	9.59E+04
Bitumen (kg)	9.33E+05	1.48E+06	0.00E+00	0.00E+00	1.18E+05
Cellulose (kg)	2.43E+04	1.22E+05	1.62E+03	0.00E+00	2.89E+05
Cement (kg)	1.15E+07	4.81E+06	2.37E+05	0.00E+00	2.22E+05
Evaporator concentrate (kg)	0.00E+00	3.40E+05	0.00E+00	0.00E+00	2.70E+02
Ion exchange resin (kg)	3.02E+06	1.73E+06	4.50E+05	8.31E+05	9.74E+04
Iron/steel (kg)	4.59E+06	3.08E+06	1.36E+06	1.82E+06	3.49E+06
Iron/steel (m^2)	2.19E+05	1.35E+05	1.08E+05	1.20E+05	2.09E+05
Sand (kg)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Filter supplies (kg)	1.01E+04	5.07E+04	7.28E+04	1.31E+05	0.00E+00
Sludge (kg)	3.53E+04	2.01E+05	2.59E+04	4.46E+04	7.25E+02
Misc. Inorganic (kg)	8.48E+05	6.63E+04	0.00E+00	0.00E+00	1.79E+05
Misc.organic (kg)	5.09E+04	2.69E+05	4.90E+04	8.63E+04	1.40E+06

The distribution between aforementioned waste categories varies between repository parts. From Figure 3-1 it is evident that cement and concrete has the major impact on the pH evolution for all repository parts, except for 1 BLA, due to its abundance and highly alkaline character. In particular for the Silo and 1 BMA the additional buffering effect from the substantial amount of cement ensures a long – term buffering capacity.

The amount of cement and concrete (in wt. %) for each repository part is given in Table 3-11.

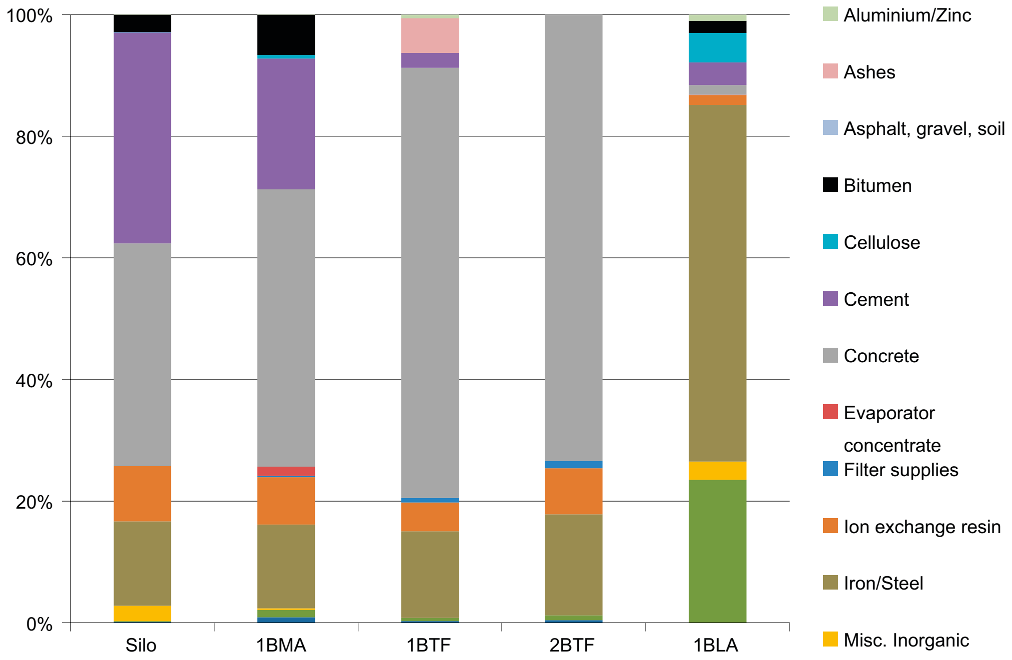

Figure 3-1. *The distribution (mass %) between waste categories for each repository part. Waste categories with an assumed impact on the pH evolution marked with bold text.*

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[4] Values taken from an earlier version of SKB 2013a. In this report the values from the earlier version has been used. The conclusions drawn are judged not to be affected.

Table 3-11. The fraction of cement and concrete in each repository part relative the total amount of deposited waste.

	Silo	1 BMA	1 BTF	2 BTF	1 BLA
Wt. % cement and concrete	71	67	73	73	5

Table 3-12. The cement and concrete content in different compartments in 1 BMA and the Silo.

Repository part	In all waste conditioning	In all waste packaging	In all construction concrete	Total
1 BMA compartment 1 (kg)	8.1E+05	2.50E+04	1.50E+05	1.20E+06
1 BMA compartment 3 (kg)	2.00E+05	6.40E+04	1.50E+05	4.10E+05
Silo (kg)	1.30E+07	2.60E+06	4.70E+06	2.90E+07

For 1 BMA the content of cement and concrete will vary between the compartments. According to Keith-Roach et al. (2014) the compartment 1 and 3 represent typical compartments containing cement- and bitumen stabilized waste. The corresponding masses of cement for compartment 1 and 3 and the Silo considered as a mixed tank are summarized in Table 3-12.

3.5 Cement and concrete

The chemical representation of cement and concrete is in principle the same as in Cronstrand (2007) and based on the available mineral phases in the selected database, see Table 3-13. The Calcium Silica Hydrate (CSH) have been represented by three distinct mineral phases, CSH_1.6, CSH_1.2 and CSH_0.8, with decreasing Ca/Si ratios in order to reflect the well documented incongruent dissolution (Berner 1988, Gartner and Jennings 1987). Although a solid solution representation will result in a less discontinuous and stepwise dissolution curve, the actual pH evolution will be fairly invariant to the selected representation. The deviation between results obtained with different representations of CSH is further assessed in Appendix 2.

In contrast to cement, concrete contains ballast, which reduces its buffer capacity. The ballast is represented by quartz which is assumed to dissolve according to the rate equations in Rimstidt and Barnes (1980). The assumed mineral distribution for 1 kg concrete and 1 kg cement respectively is given in Table 3-14 and Table 3-15.

Table 3-13. Initial mineral phases representing cement and concrete.

Phase	Formula	M (g/mol)
CSH	$Ca_{1.60}SiO_{3.6}$:$2.58H_2O$	196.3
Portlandite	$Ca(OH)_2$	74.1
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}$:$26H_2O$	1,255.1
C3AH6	$Ca_3Al_2(OH)_{12}$	378.3
Hydrotalcite	$Mg_4Al_2O_7$:$10H_2O$	453.4
Magnetite	Fe_3O_4	231.5
Quartz	SiO_2	60.1

Table 3-14. Mineral phases representing 1 kg of concrete.

Phase	n (mol)	(g)
CSH	0.446	87.5
Portlandite	0.431	32.0
Ettringite	0.010	12.6
C3AH6	0.028	10.5
Hydrotalcite	0.004	1.8
Magnetite	0.021	4.9
Ballast (Quartz)	16.642	850.7

Table 3-15. Mineral phases representing 1 kg of cement.

Phase	n (mol)	(g)
CSH	2.986	586.1
Portlandite	2.890	214.1
Ettringite	0.067	84.3
C3AH6	0.186	70.3
Hydrotalcite	0.027	12.1
Magnetite	0.143	33.1

The typical mineral evolution and the corresponding pH evolution for cement are depicted in Figure 3-2. The distinction between different discrete CSH phases is clearly artificial, but will still give an approximate value for the Ca/Si ratio corresponding to the stated pH.

The pH controlling mineral phase for each pH plateau is summarized in Table 3-16. Portlandite controls the pH at 12.5, whereas during the decalcification of CSH pH typically is decreasing in the interval 12-11. After the dissolution of CSH, pH drops to levels below 10, supported by remaining cement specific minerals such as hydrotalcite or precipitated hydroxides as Gibbsite.

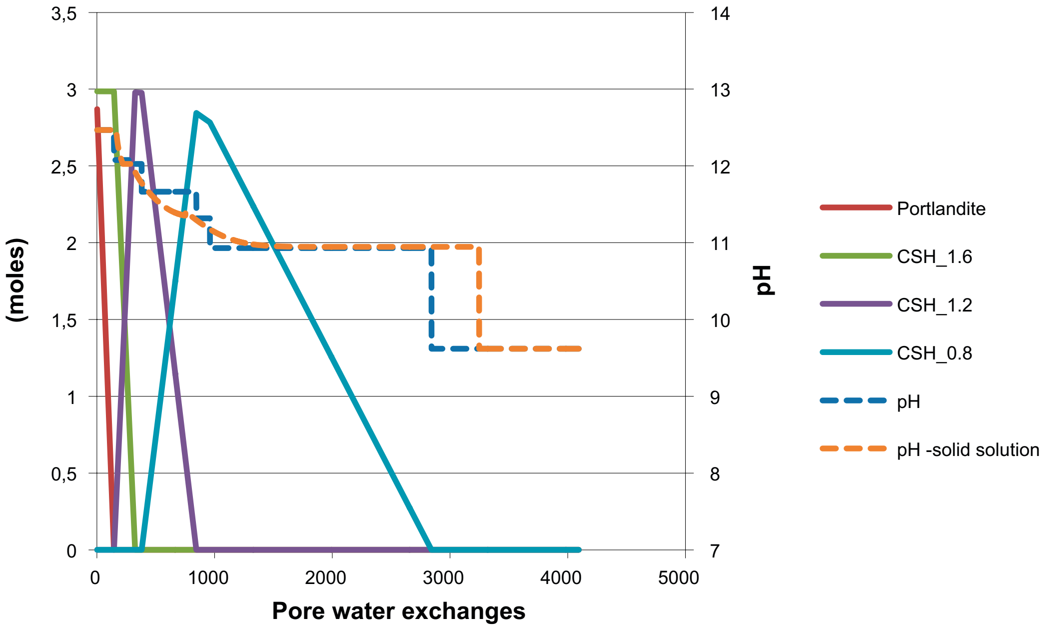

Figure 3-2. The mineral and pH evolution of 1 kg cement when equilibrated with 1kg water. Pore water exchanges here denote the number of exchanges of 1 kg demineralised water.

Table 3-16. The pH and corresponding pH regulating mineral phase.

pH	pH regulating mineral phase
12.5	Portlandite
12.0	CSH_1.6
11.7	CSH_1.2
11.0	CSH_0.8

3.6 Ashes

The ashes deposited in SFR 1 refer primarily to the waste type S.13, which is not further specified in a mineralogical point of view. In the context of estimating the pH stabilizing effect of ashes however it is sufficient to assume general mineralogical distribution, see Table 3-17, since the total amounts are significantly lower than concrete and cement.

The oxides in the ashes will hydrate when in contact with water in a similar manner as cement and result in a high pH solution. However, the distribution between primarily CaO and SiO_2 is different from the distribution in cement and will result in a quite different distribution between the mineral phases in the hydrated solid material.

Ashes only occur in repository part 1 BTF.

Table 3-17. Mineral phases representing 1 kg of ashes (evaluated from Misra et al. 1993).

Phase	n (mol)	m (g)
CaO	7.50	420
SiO_2	5.83	350
Al_2O_3	1.18	120
Na_2O	0.081	5
K_2O	0.053	5
MgO	2.48	100

3.7 Evaporator

The dominating elements in evaporator concentrate are Na and Cl, with some additional K, sulphates and carbonates. Evaporator concentrate is assumed to be represented by the mineral phases given in Table 3-18. No kinetic constraints are associated with their dissolution. Additional components expected in evaporator concentrate, as iron/rust, sand and oils have not been included.

Table 3-18. Mineral phases representing 1 kg evaporator concentrate.

Phase	Formula	n (mol)	m (g)
Halite	NaCl	10.27	600
Sylvite	KCl	0.54	40
Thenardite	Na_2SO_4	1.13	160
Na_2CO_3	Na_2CO_3	1.89	200

3.8 Ion exchange resins

Ion exchange resins occur in cementitious (as in R.01/02) or bitumenized wasteforms (as in F.17/18), but also in drained ion exchange resins as in B.07. The stabilization method will itself have an impact on the degradation of the resin and the residual ion exchange capacity and thereby also on the potential influence on pH evolution. The initial fraction of ion exchange resin with preserved ion exchange capacity is in principle an unknown property. Thus, in the assessment three extreme modeling cases will be assumed: one without any ion exchange resin at all and two where all deposited ion exchange resin have maintained its initial exchange capacity and loaded with either (Na^+, Cl^-) or (H^+, OH^-). The distribution between cationic and anionic exchange resin have been assumed to according to the ratio 2:1. If initially loaded with (Na^+, Cl^-) the initial pore water exchange will increase the pH due to the exchange between Na^+ and H^+. Conversely, an ion exchange resin initially loaded with (H^+, OH^-) will decrease the pH, due to the release of H^+ when exchanging with Na^+. In general, after a couple of exchanges the ion exchange resin will have the same composition, independent of initial loading and the impact on the pH evolution will be identical.

The cation exchange resin is represented by DOW 4% DVB and the anionic exchange resin by DOW Type I. The corresponding thermodynamic descriptions in terms of log k values are given in Appendix 1.

3.9 Metals

The corrosion of metals will release cations, which during their speciation and precipitation will influence the pH. The process will in general be kinetically controlled and often accelerated at low pH, decelerated at high pH. However, from a thermodynamic point of view, the corrosion process occurs instantaneously and can potentially increase the pH. In particular for repository parts with a low content of cement and high content of steel the pH may rise above realistic levels if steel is dissolved instantaneously. The general assumption concerning corrosion rate for steel in SFR is 0.05 µm/year (Rance et al. 2003), which implies that a 5 mm slab will completely corrode within 50,000 years when corroded from both sides. Thus, most compartments (see Table 3-7), will undergo several pore water exchanges before all available steel has been completely dissolved (assuming an average thickness of 5 mm). The linear corrosion rate of 0.05 µm/year has been transferred to first order rate constants according to Table 3-19.

The corresponding corrosion rate for aluminum is 1 mm/year, which implies that any goods with thickness below 5 mm, will be completely dissolved within 25 years, *i.e.* before any pore water exchange have been completed. Thus, for the corrosion of aluminum no kinetic constraints have been applied and the dissolution is assumed to follow the thermodynamic equilibrium.

Table 3-19. Steel content in repository parts and corresponding corrosion rate constants.

	BMA	BLA	1 BTF	2 BTF	Silo
Steel content (kg)	2.37E+05	3.49E+06	1.36E+06	1.82E+06	4.59E+06
Steel content (mol)	4.24E+06	6.25E+07	2.44E+07	3.26E+07	8.22E+07
Rate constant (1/s)	2.69E–06	3.96E–05	1.54E–05	2.07E–05	5.21E–05

3.10 Cellulose

The major end product of the degradation of cellulose in an alkaline environment is ISA isomers along with a fraction of small chain organic acids, such as formic, acetic, glycolic, pyruvic, glyceric, lactic, propionic (Van Loon and Glaus 1997, Glaus and Van Loon 2008 and Glaus et al. 1999).

The rate and mechanisms for alkaline degradation of cellulose have been the focus of numerous studies, see Van Loon and Glaus (1997) and Knill and Kennedy (2003) for a thorough review. A common observation is two separate reaction phases with distinct time scales. The primary peeling-off mechanism, resulting in the production of ISA and dissolved organic carbon (DOC), is well-characterized where the established rate constants have been elucidated by Glaus and Van Loon (2008).

The initial reaction phase typically reaches a plateau of stagnation within 2 years. The subsequent reaction phase is less well defined, both in terms of reaction mechanism as well as rate constants. Proposed candidates are mid-chain scission or decelerated peeling all of which feature a much slower progression than the initial peeling-off mechanism. Irrespective the chemical characterization of the actual mechanism, the two reaction phases can be combined in one single equation, see Equation 3-2, governing the degradation (Glaus and Van Loon 2008)

$$f = 1 + e^{-k_h t}\left[\frac{k_1}{k_t} G_r\left(1 - e^{-k_t t}\right) - 1\right] \qquad (3\text{-}2)$$

where *f* denotes the fraction degraded cellulose as a function of time and k_h k_1 and k_t are the reaction rate constants The proposed values for k_h k_1 and k_t according to Glaus and van Loon 2008 are summarized in Table 3-20.

The degradation rate according to Equation 3-1 and the kinetic parameters given in Table 3-9 is depicted in Figure 3-3.

Table 3-20. Kinetic parameters for cellulose.

Cellulose type	G_r	k_1 (h^{-1})	K_t (h^{-1})	K_h (h^{-1})
Tissue	9.0E–4	(1.0±0.1)×10–2	(2.9±0.5)×10–4	(1.0±0.2)×10–7
Cotton	5.6E–4	(2.0±0.3)×10–3	(3.3±0.5)×10–4	(2.9±0.3)×10–8
Paper	3.5E–3	(4.3±1.3)×10–3	(4.3±1.5)×10–4	(1.6±0.5)×10–7

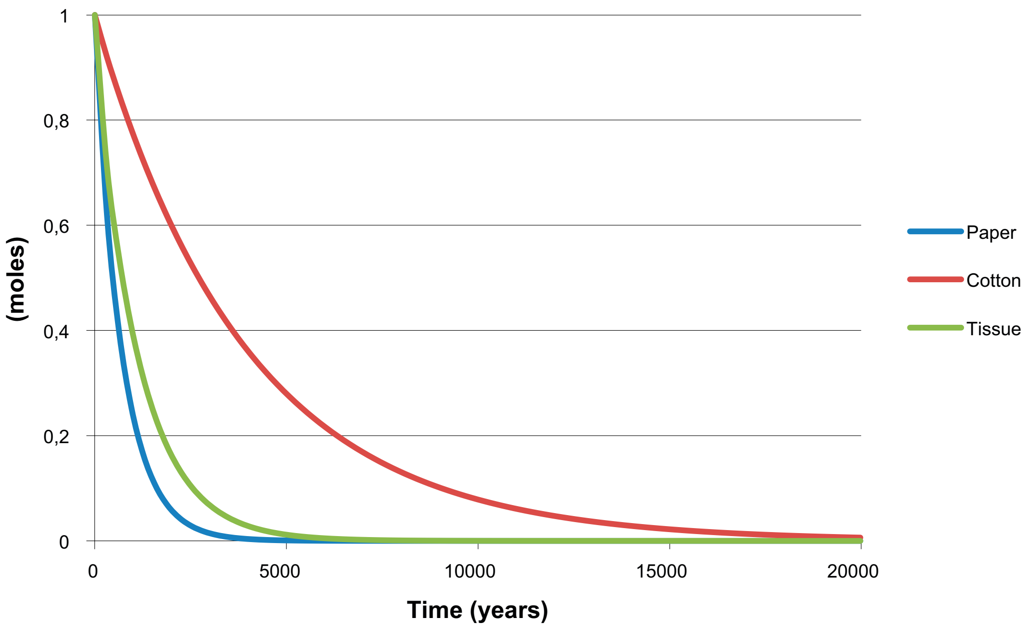

Figure 3-3. *Degradation rate for cotton and paper according to Equation 3-1.*

The deprotonation of ISA have been assumed according to the PCHatches database as:

$$H_4IsaH = H^+ + H_4Isa^-$$

with the corresponding log_k value of –10.

Estimations of the times for complete degradation of the cellulose present in SFR 1, here interpreted as 99.9%, based on reaction rate constants in Table 3-9, are displayed in Table 3-21.

All cellulose in the repository is in this report assumed to consist of paper in order to achieve the lowest pH as early as possible, which is deemed the most pessimistic approach.

The buffer capacity of the repository parts will prevail as long as the pH regulating phases (portlandite, CSH...) are not completely dissolved. Since ISA will dissolve and follow the pore water exchange, the contribution of H^+ from ISA will decrease exponentially with time. Thus, the pH impact from cellulose will be confined to the initial 5,000 years.

3.11 Initial composition of pore water

The initial composition of the pore water is assumed to be a mixture between pure concrete pore water (Jacques et al. 2010) and the infiltrating temperate-preglacial water (see Table 3-9) scaled to the fractional content of cement and concrete, *i.e.* for 1 BMA, 1 BTF, 2 BTF and the Silo the pore water is assumed to consist of 70% concrete pore water and 30% temperate-glacial water, whereas for 1 BLA the pore water is assumed to consist of 5% concrete pore water and 95% temperate-preglacial water (see Table 3-22).

3.12 Modeling cases

Except for 1 BMA and the Silo all modeling cases assumes one single volume representing the deposited waste and the surrounding walls together. For 1 BMA a compartment is addressed as two adjacent cells representing the concrete wall and the waste. The base cases do not include any pH effect from the degradation of cellulose or from exchange resins. The modeling base cases are summarized in Table 3-23.

Table 3-21. Estimated time for complete (99.9%) degradation.

	Paper	Cotton	Tissue
Time for complete degradation (years)	5,000	27,400	7,700

Table 3-22. The assumed initial composition of the pore water.

Element	Concrete pore water (M)	1 BMA, 1 BTF, 2 BTF, Silo (M)	1 BLA (M)
Al	1.38E–05	9.66E–06	6.90E–07
C	8.25E–05	1.53E–03	4.68E–03
Ca	1.58E–03	1.48E–03	1.27E–03
Cl		1.61E–03	5.09E–03
K	1.60E–01	1.12E–01	8.12E–03
Mg	1.93E–09	1.48E–04	4.69E–04
Na	6.82E–02	5.01E–02	1.09E–02
S	2.81E–04	3.53E–04	5.09E–04
Si	3.40E–05	8.38E–05	1.92E–04
pH	13.71	13.06	11.67
pH	13.71	13.06	11.67

Table 3-23. The models for the repository parts 1 BMA, 1 BLA, 1 BTF, 2 BTF and the Silo.

Modeling case	Comment	No. of cells
1 BMA – cement	Concrete wall + generic compartment with cementitious waste	2
1 BMA – bitumen	Concrete wall + generic compartment with bitumenized waste	2
1 BLA	Mixed tank	1
BTFs	Mixed tank	1
Silo	Concrete wall + Mixed tank	2

For each repository part a model parameter variation according to Table 3-24 were applied.

Table 3-24. The parameter variation within each repository part model.

Modeling case	Waste variation	Water composition
A	No cellulose or ion exchange resin	Temperate-periglacial
B	Cellulose degradation (ISA)	Temperate-periglacial
C	Corrosion of steel	Temperate-periglacial
D	Ion exchange resin (Na^+, Cl^-)	Temperate-periglacial
E	Ion exchange resin (H^+, OH^-)	Temperate-periglacial
F	No cellulose, steel or ion exchange resin	Glacial water
G	No cellulose, steel or ion exchange resin	Saline water

4 Summary of results

4.1 1 BLA

The pH evolution for the short term (0–10,000 years) and long term (0–100,000 years) evolution in 1 BLA are shown in Figure 4-1 and Figure 4-2. The pH starts to drop below 12 already at year 5,000 and within 10,000 years it is close to 9 for the base case, irrespective of the initial loading of the ion exchange resin (D and E). Apparently, the ion exchange resin does not have any significant influence on the pH evolution in 1 BLA.

The corrosion of steel seems to maintain the pH around 11.5 throughout the considered period of time. The inclusion of ISA on the other hand slightly lowers the pH compared to the base case. For the long term evolution the only parameters with the any significant influence on the pH evolution are the compositions of the infiltrating water and the corrosion of steel.

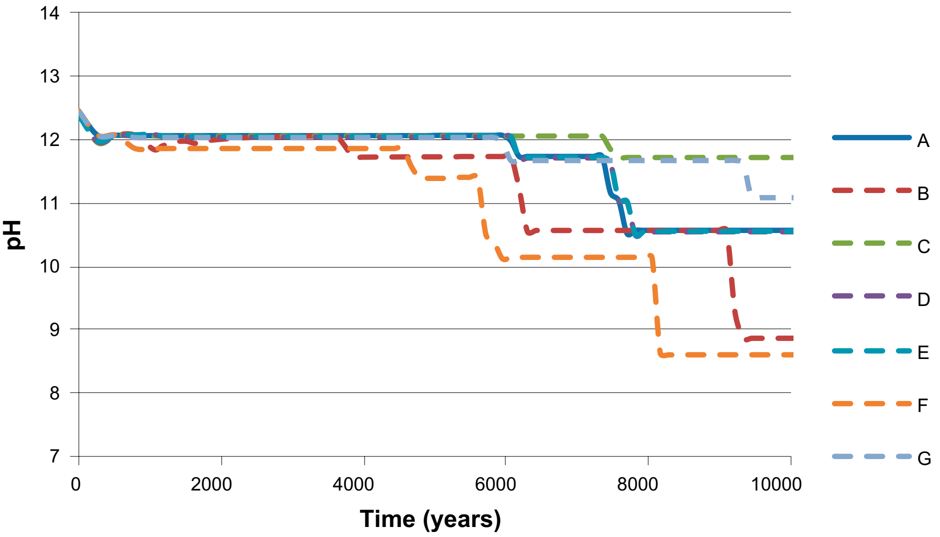

Figure 4-1. *The short term pH evolution of 1 BLA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

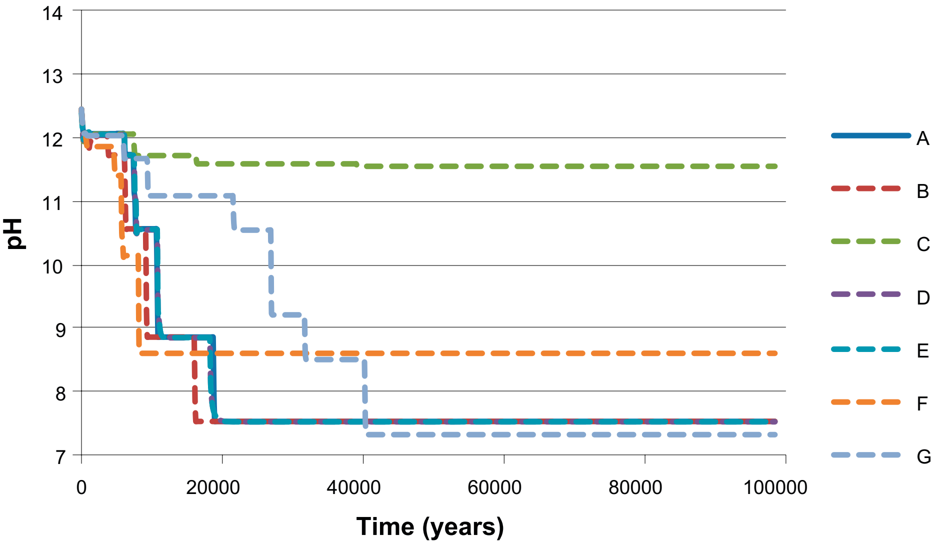

Figure 4-2. *The long term pH evolution of 1 BLA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

4.2 1 BTF

The pH evolution for the short term (0–10,000 years) and long term (0–100,000 years) evolution in 1 BTF are shown in Figure 4-3 and Figure 4-4. The pH is predicted to be constant throughout the considered period of time. The inclusion of ion exchange resin lowers the initial pH with at maximum a half pH unit for an initial loading with H and OH. After the first pore water exchange the ion exchange resin will have the almost same loading as the ion exchange resin initially loaded with Na and Cl, and the subsequent evolution of pH will be identical for the two modelling cases. In general, the modelling cases with ion exchange resin can be expected to converge within a handful of pore water exchanges.

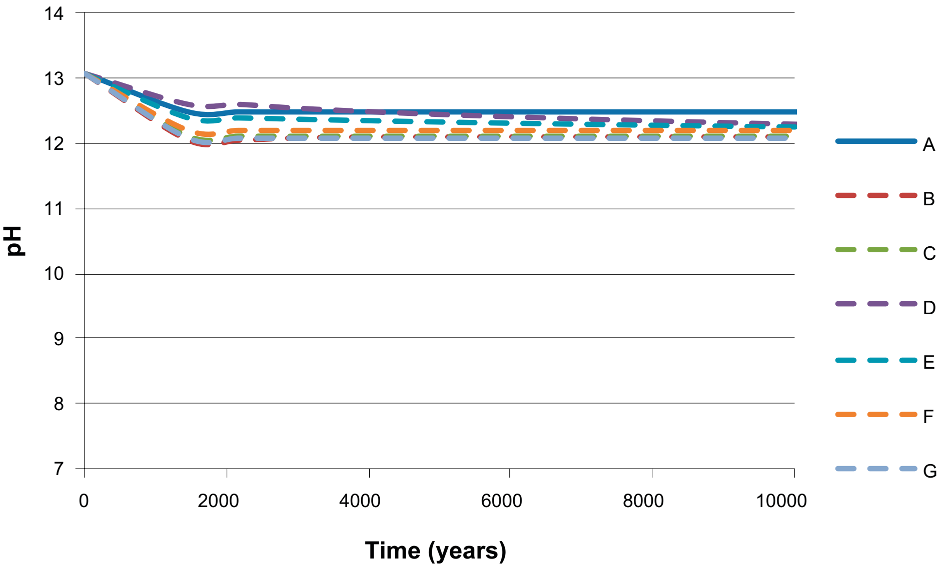

Figure 4-3. *The short term pH evolution of 1 BTF (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

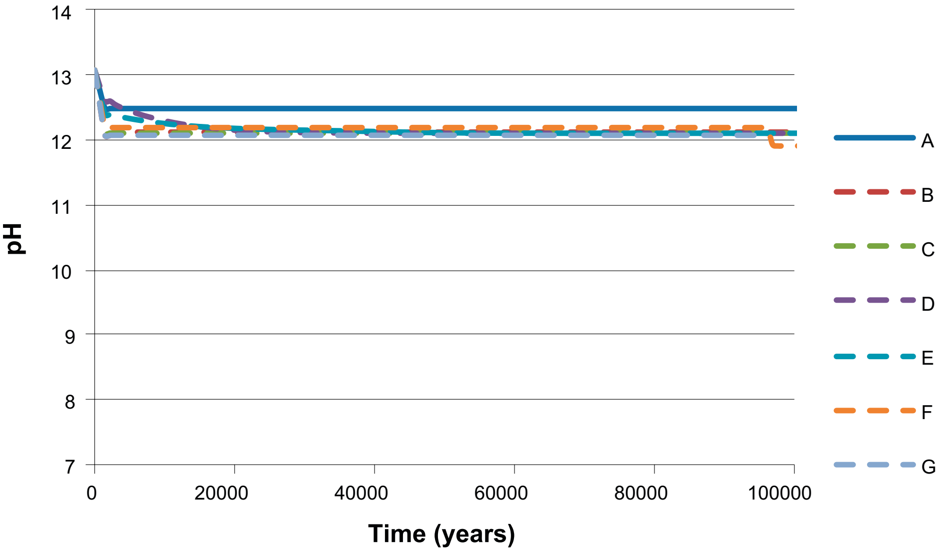

Figure 4-4. *The long term pH evolution of 1 BTF (A = base case, B = cellulose degradation, C = ion exchange resin loaded with Na and Cl, D = ion exchange loaded with H, OH, E = glacial water, F = saline water).*

4.3 2 BTF

The pH evolution for the short term (0–10,000 years) and long term (0–100,000 years) evolution in 2 BTF are shown in Figure 4-1 and Figure 4-2. The pH is predicted to constant throughout the considered period of time.

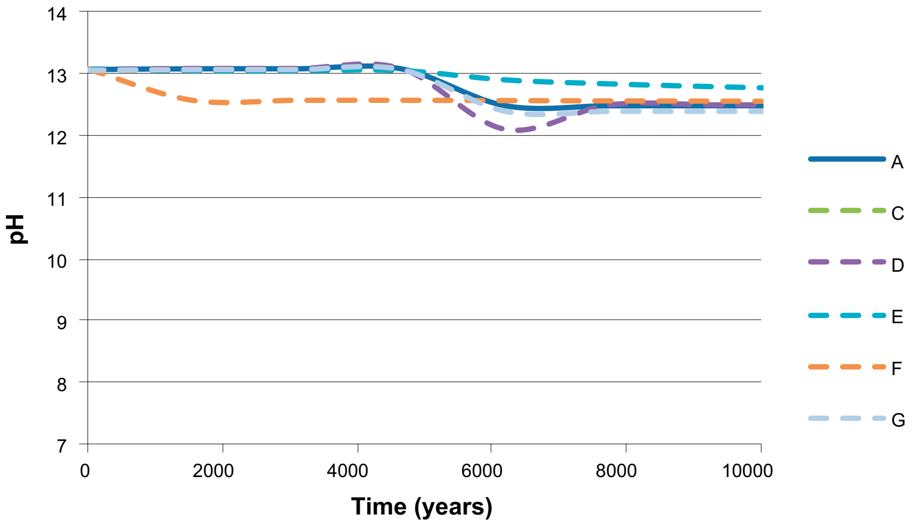

Figure 4-5. *The short term pH evolution of 2 BTF (A = base case, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

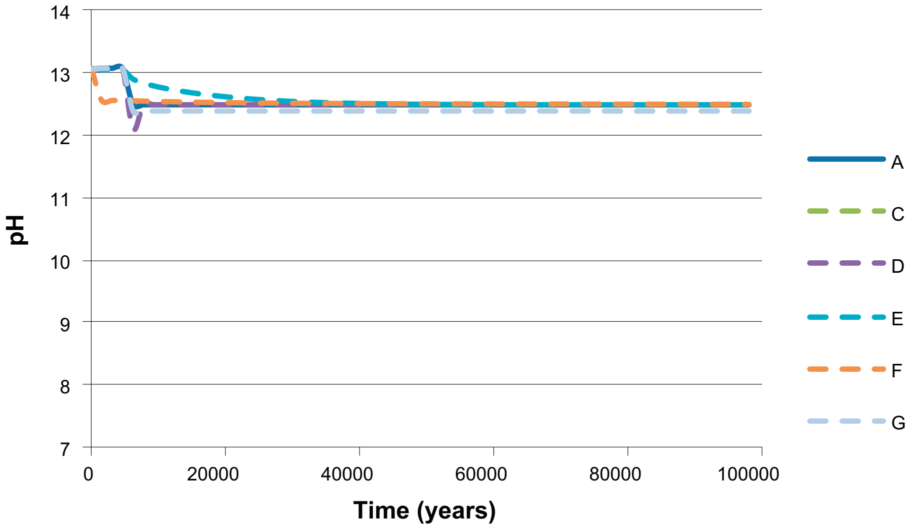

Figure 4-6. *The long term pH evolution of 2 BTF (A = base case, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

4.4 Silo

The pH evolution for the short term (0–10,000 years) and long term (0–100,000 years) evolution in the Silo are shown in Figure 4-7 to Figure 4-10. The pH is predicted to be stable throughout the considered period of time for all modelling cases. The modelling cases with ion exchange resin will approach each other within a couple of pore water exchanges.

Also for the Silo wall, the pH will be controlled by portlandite and stabilized around 12.5.

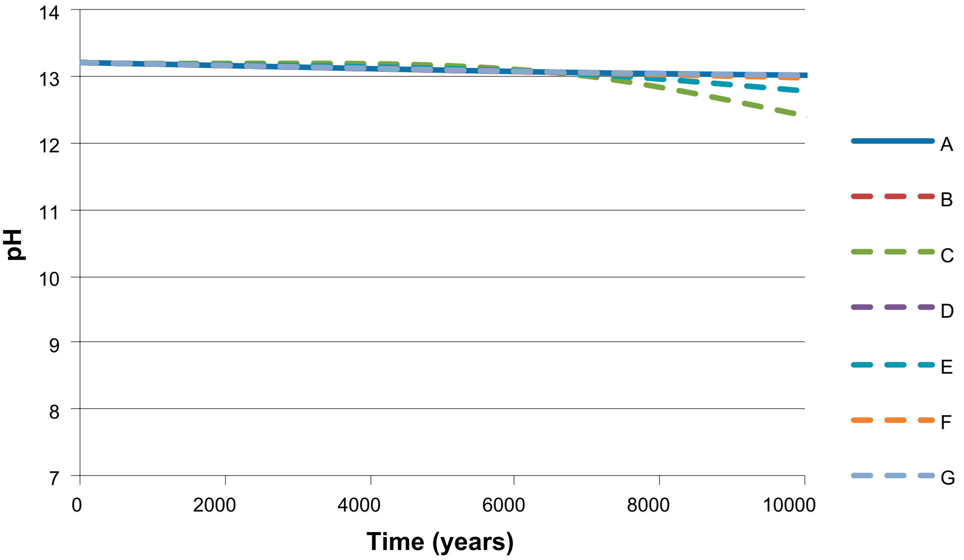

Figure 4-7. *The short term pH evolution of the waste in the Silo (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

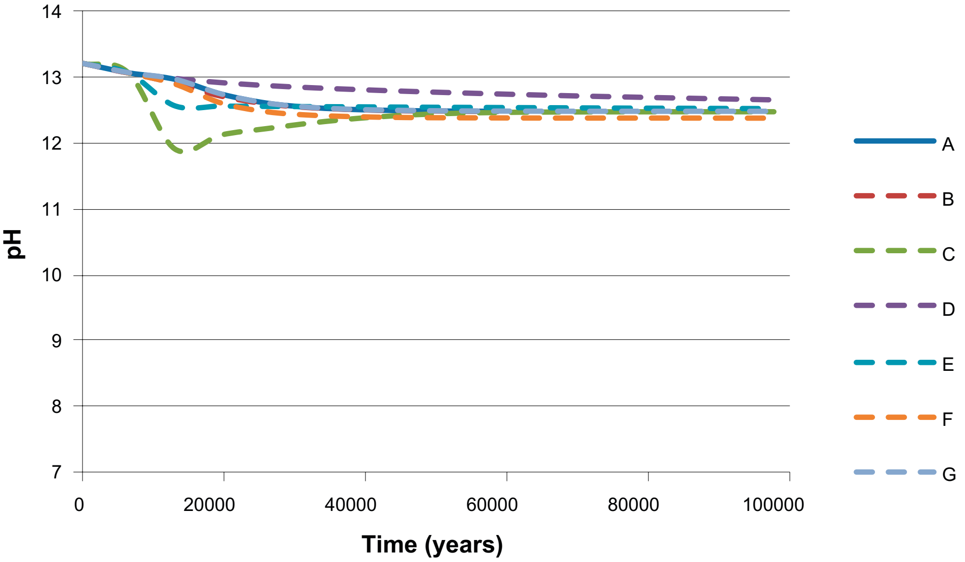

Figure 4-8. *The long term pH evolution of waste in the Silo (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

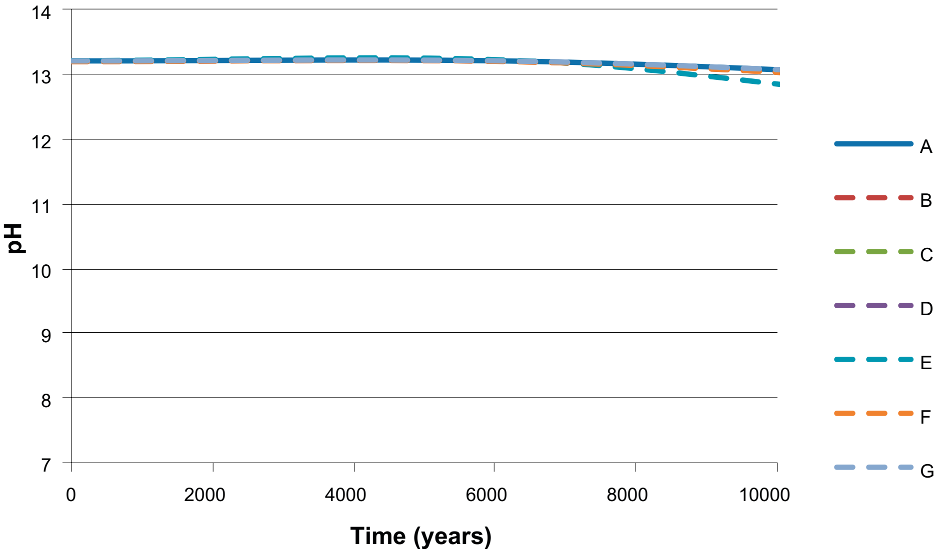

Figure 4-9. *The short term pH evolution of walls of the Silo (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

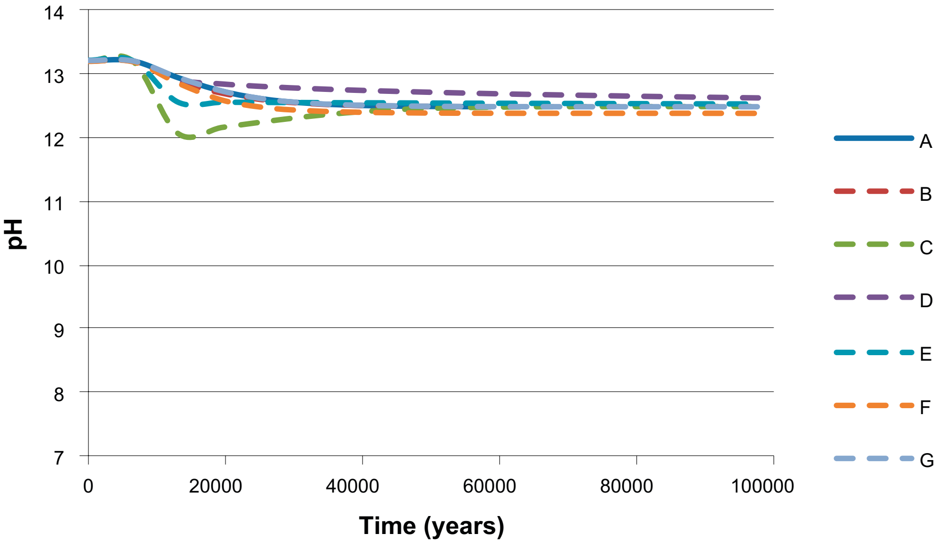

Figure 4-10. *The long term pH evolution of walls of the Silo (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

4.5 1 BMA – Compartment with cement stabilized waste

The pH evolution for the short term (0–10,000 years) and long term (0–100,000 years) evolution for 1 BMA compartment containing cement stabilized waste are shown in Figure 4-11 to Figure 4-14. Similar to the Silo, the pH of the pore water in the waste domain is stabilized around 12.5 due to remaining portlandite.

For the 1 BMA wall on the other hand the pH stepwise decreases down to a level slightly below 12 at year 50,000 indicating that CSH will remain throughout the considered period of time.

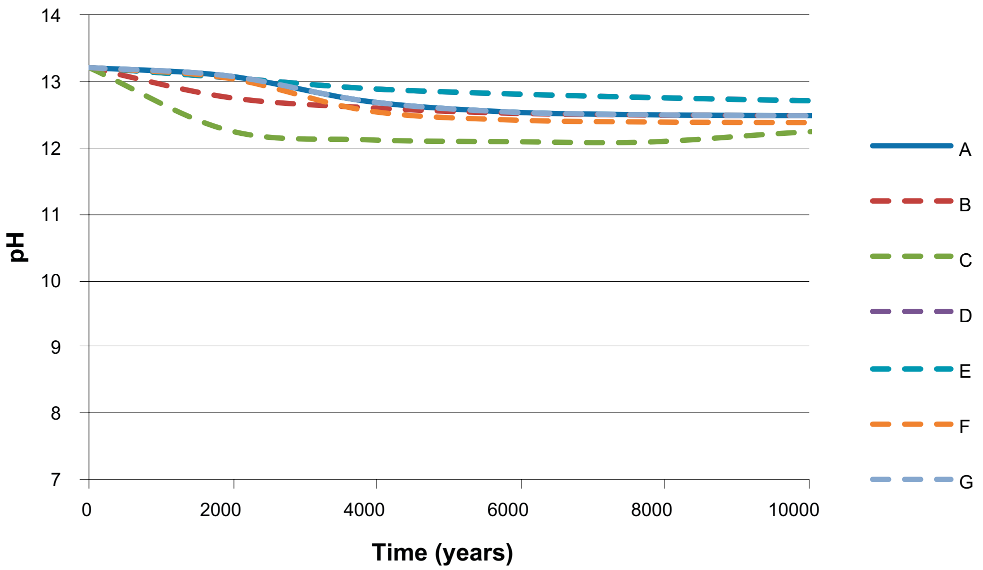

__Figure 4-11.__ The short term pH evolution of the waste in 1 BMA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).

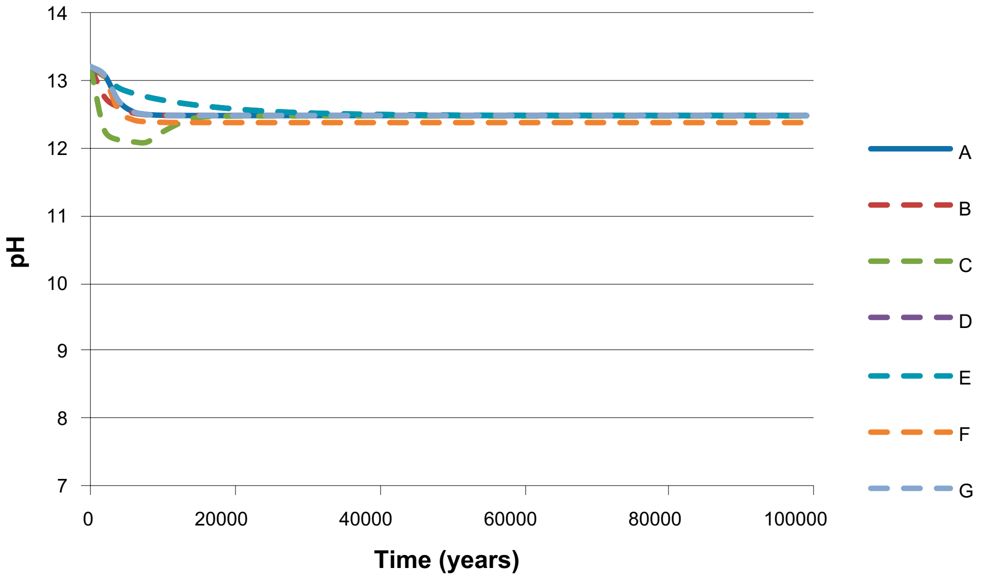

__Figure 4-12.__ The short term pH evolution of the waste in 1 BMA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).

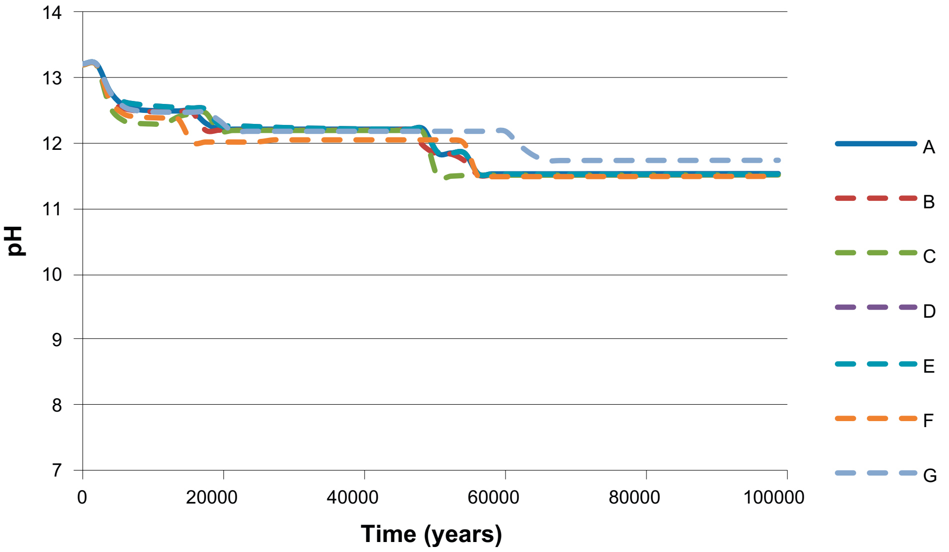

Figure 4-13. *The short term pH evolution of the walls of 1 BMA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

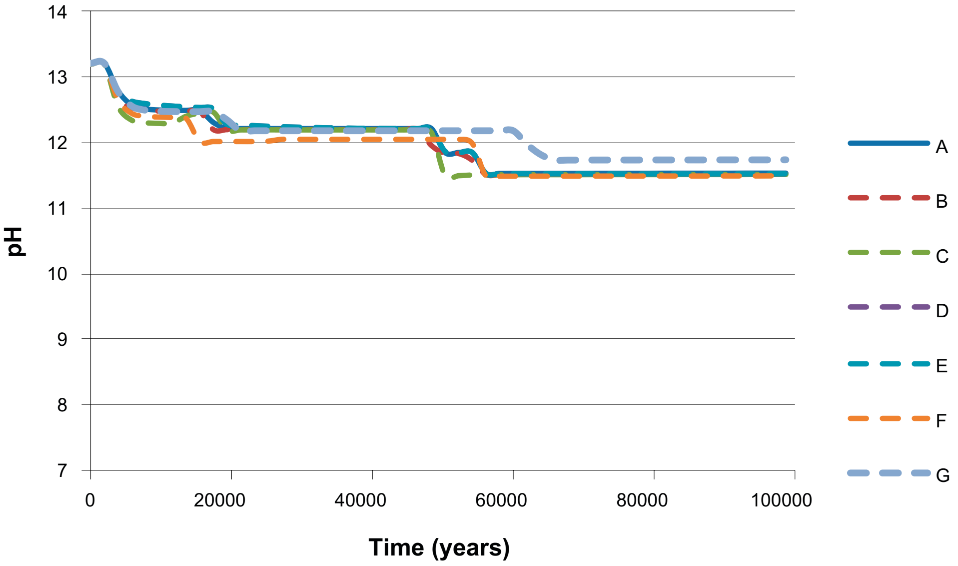

Figure 4-14. *The long term pH evolution of the walls of 1 BMA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

4.6 1 BMA – Compartment with bitumenized waste

The pH evolution for the short term (0–10,000 years) and long term (0–100,000 years) evolution for 1 BMA compartment containing bitumenized waste is shown in Figure 4-11 to Figure 4-14. Similar to compartment containing cement solidified waste, the pH stays above 12.0, indicating a significant amount of remaining portlandite.

The concrete walls surrounding the compartment containing bitumenized waste follows the pH evolution of the cement stabilized waste, maintained slightly below 12 throughout the considered period of time.

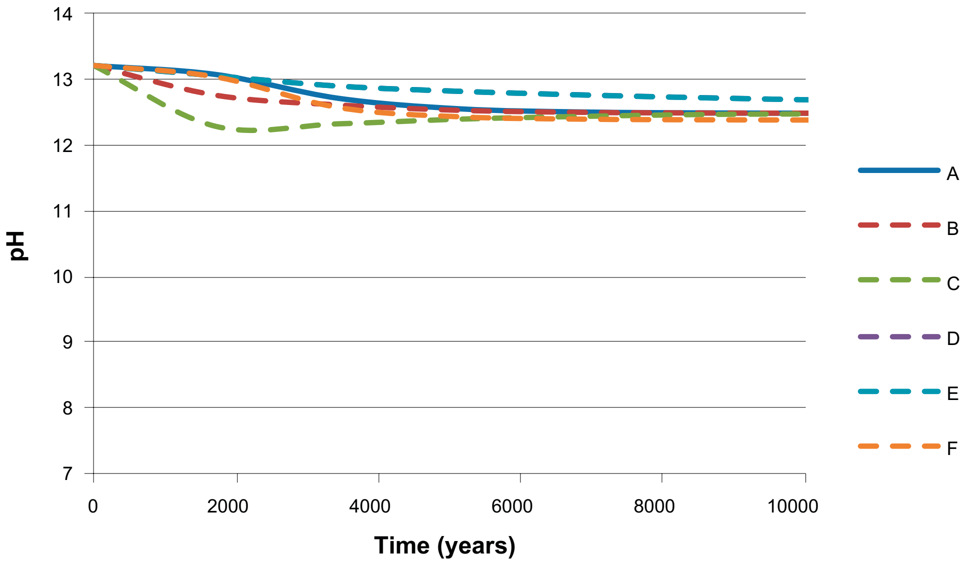

Figure 4-15. *The short term pH evolution of the waste of 1 BMA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

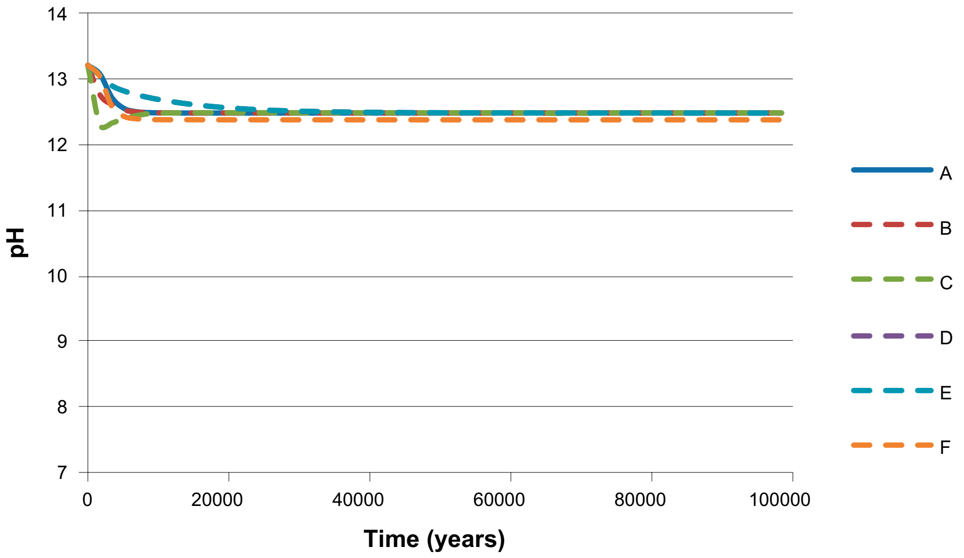

Figure 4-16. *The long term pH evolution of the waste of 1 BMA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).*

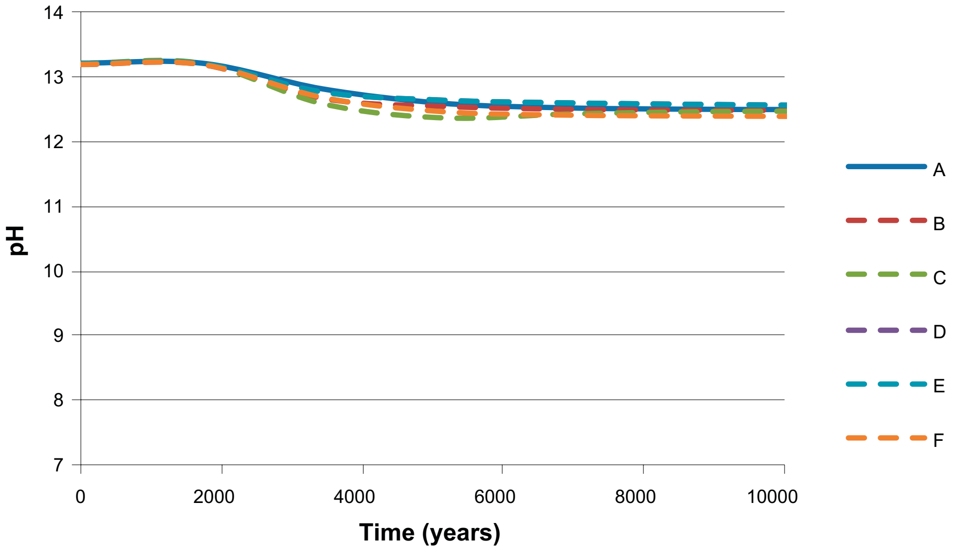

Figure 4-17. The short term pH evolution of the walls of 1 BMA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).

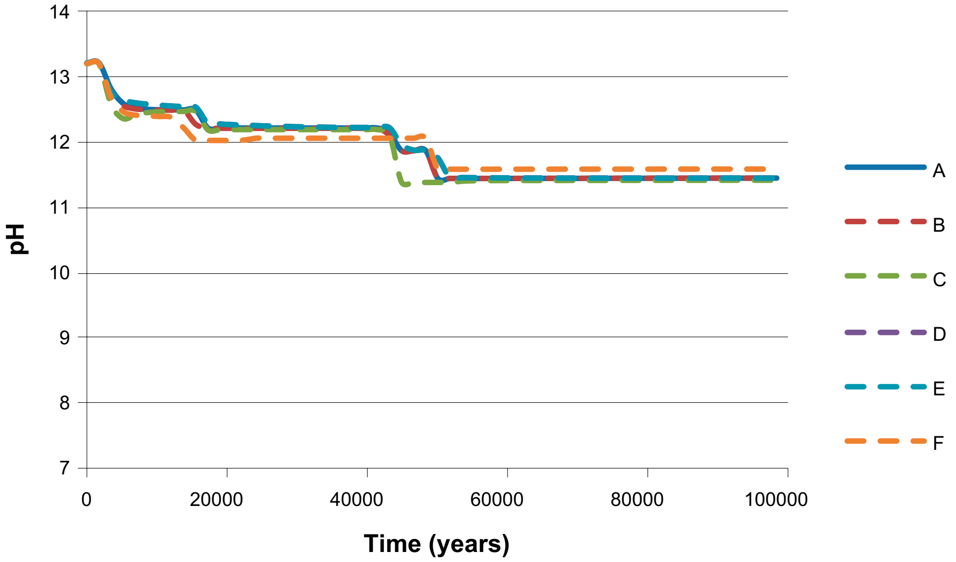

Figure 4-18. The long term pH evolution of the walls of 1 BMA (A = base case, B = cellulose degradation, C = steel corrosion, D = ion exchange resin loaded with Na and Cl, E = ion exchange loaded with H, OH, F = glacial water, G = saline water).

5 Conclusions

The overall conclusion is that for parts of the repository characterized by a high content of cement and concrete in combination with low flow rates, the pH is fairly constant throughout the considered period of time. The pH evolutions for the base case scenario for all repository parts are summarized in Figure 5-1 and Figure 5-2. With the exception of 1 BLA, the pH is predicted to maintain above 12 throughout the initial 10,000 years. The combination of higher flow rates and low content of cement and concrete leads to a more dramatic pH evolution for BLA than the other repository parts.

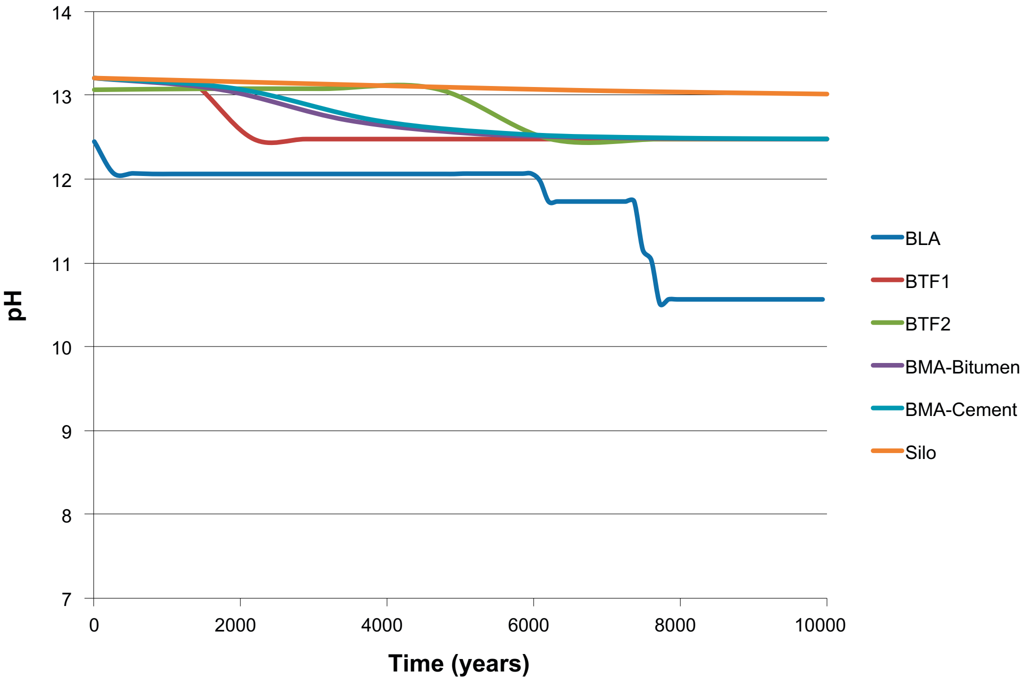

Figure 5-1. *The short term pH evolution in different parts of the repository.*

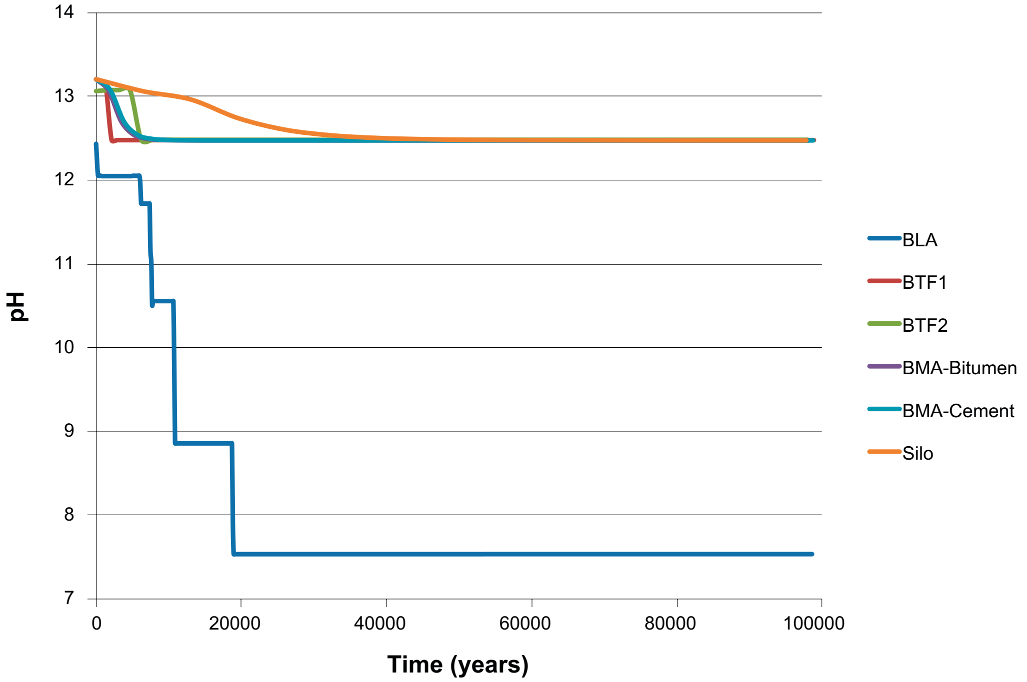

Figure 5-2. *The long term pH evolution in different parts of the repository.*

Even in the long term, the pH is maintained above 12 for all repository part, except 1 BLA. The initial differences before reaching the stable pH regulated by portlandite are results from differences in exchange times (due to differences in inflow and pore volumes), but also consequences of the influence of the adjacent concrete wall (for Silo and 1 BMA). Another reason for deviations in start values is the impact from corrosion of metals, which is difficult to predict. However, each repository part appears insensitive to any of the variations applied within the modelling cases. With the exception of BLA, the only variation with any significant impact on the predicted long term pH evolution is the composition of the infiltrating water.

The essential pH drops in each repository part are summarized in Table 5-1.

The Table 5-1, should be interpreted as follows. For 1 BMA compartment containing cement solidified waste the pH is initially (year 0) 13.0, drops to 12.5 at year 5,000 followed by additional pH drops at year 20,000 and 60,000. For 1 BLA, the pH is initially 12.5, drops to 12 at year 6,000, drops further down to 11.5 at year 7,000, drops down to 10.5 at year 7,200, pH 9 at year 9,000 and finally to 7.5 at year 19,000.

It is emphasized the method is a coarse and conservative method exclusively applied to provide the global average pH evolution. Substantial local deviations are expected due to the inhomogeneous character of the waste compartments, flow path restrictions etc. Nevertheless, in spite of the uncertainties associated with each set of input data, the results show a significant stability with respect to the variation of the input data as long as portlandire and CSH stabilizes the pH.

5.1 Uncertainties

5.1.1 Conceptual uncertainties

The most significant uncertainty is inherent to the method and the assumption of uniform flow patterns able to put all available solid material in equilibrium with the infiltrating water. Thus, the modeling approach assumes a global averaged repository part in complete equilibrium with the infiltrating water in each pore water exchange step. In reality, only a minor fraction of the waste will be equilibrated with the infiltrating water, due to flow path restrictions. Moreover, the waste domains will be inhomogeneous, with substantial pH variation within the repository parts. The mineralogical representation of the waste and the repository walls in terms of a confined set of mineral phases infers additional uncertainty, both from the selection of phases and the choice of database. The material with the major impact on the pH evolution, cement and concrete, are however well characterized in terms of thermodynamic stability. The uncertainties increase significantly once the mineral phase portlandite and CSH have dissolved.

5.1.2 Uncertainties of input data

Uncertainties of the input data relates primarily to the compositions of the initial pore water and infiltrating water, the waste categorization and the flow rates through the repository parts. The uncertainty of these parameters has however not been quantified in terms of numerical uncertainty intervals and no attempt to assess the uncertainty intervals have therefore been made.

Table 5-1. Summary of pH regimes for each repository parts. Cells shaded with grey indicates that no further changes are predicted during this time interval.

pH	Time (years)								
	1 BMA – cement		1 BMA – Bitumen		1 BLA	1 BTF	2 BTF	Silo	
	Waste	Wall	Waste	Wall				Waste	Wall
13.0	0	0	0	0		0	0	0	0
12.5	5,000	4,000	5,000	6,000	0	2,000	5,000	24,000	32,000
12.0		20,000		20,000	6,000				
11.5		56,000		48,000	7,000				
10.5					7,200				
9.0					9,000				
7.5					19,000				

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Log k values for ion exchange resins

Table A1-1. Log k values for cation exchange resin (DOW 4% DVB) referring to the reaction;. HX + M + = MX + H^+ (where X denotes the exchange site and M denotes an arbitrary cation) (Dow n d).

Counter Ion	Log k
H^+	0.000
Li^+	–0.119
H^+	0.000
Na^+	0.079
NH_4^+	0.158
K^+	0.236
Rb^+	0.270
Cs^+	0.305
Ag^+	0.554
Tl^+	0.706
UO_2^{2+}	0.253
Mg2+	0.348
Zn^{2+}	0.375
Co^{2+}	0.389
Cu^{2+}	0.396
Cd^{2+}	0.407
Ni^{2+}	0.417
Ca^{2+}	0.497
Sr^{2+}	0.551
Pb^{2+}	0.696
Ba^{2+}	0.753

Table A1-2. Log k values for anion exchange resin (Type I) referring to the reaction;. OHX + A– = AX + OH– (where X denotes the exchange site and A denotes an arbitrary anion)(DOW Tech Facts).

Anion	Log k
OH^-	0.000
Benzene sulphonate	2.699
Salicylate	2.653
Citrate	2.342
I^-	2.243
Phenate	2.041
HSO_4^-	1.929
ClO_3^-	1.869
NO_3^-	1.813
Br^-	1.699
CN^-	1.447
HSO_3^-	1.431
BrO_3^-	1.431
NO_2^-	1.380
Cl^-	1.342
HCO_3^-	0.778
IO_3^-	0.740
Formate	0.663
Acetate	0.505
Propionate	0.415
F^-	0.204

Appendix 2

Representation of CSH

There are several representations available for the CSH-gel in order to describe the incongruent dissolution with decreasing Ca/Si ratio. The most straight forward approach, *i.e.* assuming a selection of distinct mineral phases with stepwise decreasing log k values (see Table A2-1), has been compared with various solid solution approaches (see Figure A2-1). The mutual deviations in terms of pH evolution are limited to at maximum 200 years and/or 0.3 pH units.

Table A2-1. The distinct mineral phases representing CSH in the Thermoddem database.

Mineral phase	Formula	Log k
CSH_1.6	$Ca_{1.60}SiO_{3.6}:2.58H_2O$	28.000
CSH_1.2	$Ca_{1.2}SiO_{3.2}:2.06H_2O$	19.300
CSH_0.8	$Ca_{0.8}SiO_{2.8}:1.54H_2O$	11.050

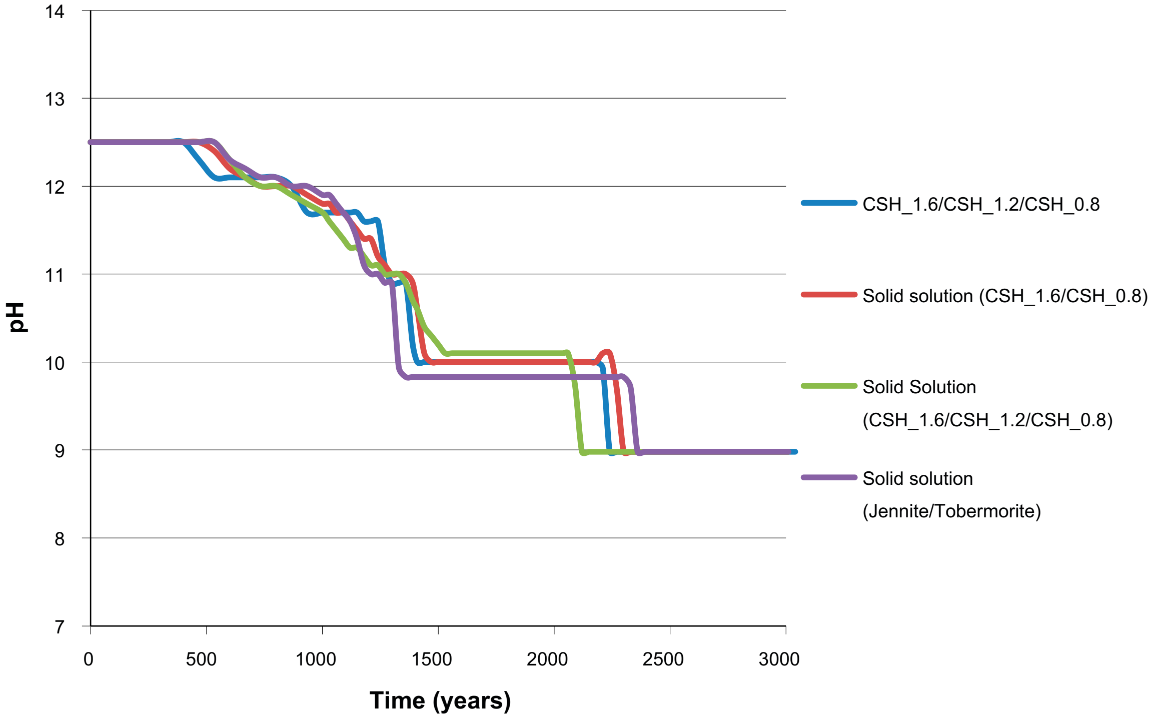

Figure A2-1. *The pH evolution for 1 BLA as predicted for the base case with different representation of the CSH (all thermodynamic parameters from the Thermoddem database).*

Appendix 3

Input files

Input file 1 BLA

```
TITLE BLA
PRINT
-species false
#-saturation_indices false

SOLUTION_MASTER_SPECIES
Isa           H4Isa-            0.0           Isa       179.147

SOLUTION_SPECIES
#To improve convergence
H2O + 0.01e-  = H2O-0.01;      log_k -9.0

# From PCHatches 18.1
H4Isa-        = H4Isa-;        log_k 0;      delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;        log_k 4;      delta_h 0 kcal
Ca+2 + H4Isa- = CaH3Isa + H+;  log_k -10.4;  delta_h 0 kcal
Ca+2 + H4Isa- = CaH4Isa+1;     log_k 1.7;    delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;        log_k 4;      delta_h 0 kcal

H4SiO4 = H3SiO4- + H+
log_k -9.810
-analytical_expression -7.168562E+2 -1.244851E-1 3.629892E+4
2.617007E+2 -2.235415E+6

PHASES
# From PCHatches 18.1
Ca(H4Isa)2
              Ca(H4Isa)2 = Ca+2 + 2H4Isa-
              log_k -6.4
              delta_h  0 kcal

H4IsaH
              H4IsaH = H+ + H4Isa-
              log_k -10

EXCHANGE_MASTER_SPECIES
# Cationic (X) and anionic (Xa) ion exchangers
X             X-
Xa            Xa+
```

```
EXCHANGE_SPECIES
# DOW cation exchange 4% DVB
X-              =   X-                      ; log_k   0.0
X- + H+        =  HX              ; log_k       0.0
HX + Li+       =  LiX   + H+      ; log_k       -0.119
HX + Na+       =  NaX   + H+      ; log_k       0.079
HX + NH4+      =  NH4X  + H+      ; log_k       0.158
HX + K+        =  KX    + H+      ; log_k       0.236
HX + Rb+       =  RbX   + H+      ; log_k       0.270
HX + Cs+       =  CsX   + H+      ; log_k       0.305
HX + Ag+       =  AgX   + H+      ; log_k       0.554
HX + Tl+       =  TlX   + H+      ; log_k       0.706
2HX + UO2++    =  UO2X2 + 2H+     ; log_k       0.253
2HX + Mg++     =  MgX2  + 2H+     ; log_k       0.348
2HX + Zn++     =  ZnX2  + 2H+     ; log_k       0.375
2HX + Co++     =  CoX2  + 2H+     ; log_k       0.389
2HX + Cu++     =  CuX2  + 2H+     ; log_k       0.396
2HX + Cd++     =  CdX2  + 2H+     ; log_k       0.407
2HX + Ni++     =  NiX2  + 2H+     ; log_k       0.417
2HX + Ca++     =  CaX2  + 2H+     ; log_k       0.497
2HX + Sr++     =  SrX2  + 2H+     ; log_k       0.551
2HX + Pb++     =  PbX2  + 2H+     ; log_k       0.696
2HX + Ba++     =  BaX2  + 2H+     ; log_k       0.753
# DOW Anion exchange Type 1
Xa+            = Xa+              ; log_k 0.0
Xa+  + OH-     =  OHXa            ; log_k 0.0
#OHXa + OH-    =  OHXa  + OH-;    log_k         0.000
OHXa + I-      =  IXa   + OH-;    log_k         2.243
OHXa + HSO4-   =  HSO4Xa + OH-;   log_k         1.929
OHXa + ClO3-   =  ClO3Xa + OH-;   log_k         1.869
OHXa + NO3-    =  NO3Xa  + OH-;   log_k         1.813
OHXa + Br-     =  BrXa   + OH-;   log_k         1.699
OHXa + CN-     =  CNXa   + OH-;   log_k         1.447
OHXa + HSO3-   =  HSO3Xa + OH-;   log_k         1.431
OHXa + BrO3-   =  BrO3Xa + OH-;   log_k         1.431
OHXa + NO2-    =  NO2Xa  + OH-;   log_k         1.380
OHXa + Cl-     =  ClXa   + OH-;   log_k         1.342
OHXa + HCO3-   =  HCO3Xa + OH-;   log_k         0.778
OHXa + IO3-    =  IO3Xa  + OH-;   log_k         0.740
OHXa + F-      =  FXa    + OH-;   log_k         0.204

RATES
H4IsaH
#Degradation rate for paper according to Glaus (2008)
-start
20 if (m <= 0) then goto 200
35 k1 = 4.3E-3/3600
```

```
44 kt = 4.3E-4/3600
55 kh = 1.6E-7/3600
65 Gr = 3.5E-3
100 rate = (exp(-kh*sim_time)*kt*kt*exp(-kt*sim_time)*Gr*k1)/kt^2-kh*-
exp(-kh*sim_time)*(((1-exp(-kt*sim_time))*Gr*k1)/kt-1)
180 moles = rate*time*m
190 REM moles = rate*time*m
200 SAVE moles
-end

Fe,element
#Corrosion of carbon steel
-start
20 if (m <= 0) then goto 200
30 R = 0.001250/365/24/3600
100 rate = R
180 moles = rate*time
190 REM moles = rate*time
200 SAVE moles
-end

Quartz,alpha
-start
10 dif_temp = 1/TK - 1/298
20 pk_w = 13.7 + 4700.4 * dif_temp
40 moles = (m/m0)^0.67 * 10^-pk_w *(1 - SR(“Quartz,alpha”))
50 save moles * time
-end

SOLUTION 0
pH 7.0 charge
-water  4.02
units mol/kgw
#Saline groundwater
#C   1.48E-03
#Ca  1.50E-02
#Cl  9.87E-02
#K   5.12E-04
#Mg  6.17E-03
#Na  6.53E-02
#S   3.64E-03
#Si  1.83E-04

#Temperate-preglacial
C             4.92E-3
Ca            1.25E-3
Cl            5.36E-3
```

```
K             1.28E-4
Mg            4.94E-4
Na            7.83E-3
S             5.21E-4
Si            2.00E-4

#Glacial derived water
#C   6.40E-04
#Ca  2.96E-04
#Cl  8.19E-06
#K   1.65E-05
#Mg  1.04E-06
#Na  4.35E-06
#S   1.25E-05
#Si  2.13E-04

EQUILIBRIUM_PHASES 1
#Cement + concrete
csh_1.6       0      7.05663E-01
portlandite   0      6.82913E-01
ettringite    0      1.58330E-02
C3AH6         0      4.39772E-02
hydrotalcite  0      6.37760E-03
Hematite      0      3.37599E-02
#SiO2         0      1.59597E+00
#Metals
Al,element    0      2.245941739
#Fe,element   0      62.49440415
#Evaporator concentrate
Halite        0      2.77193E-03
Sylvite       0      1.44867E-04
Thenardite    0      3.04135E-04
Na2CO3        0      5.09492E-04
#
# Secondary phases
Boehmite      0.0    0.0
Calcite       0.0    0.0
Chalcedony    0.0    0.0
csh_1.2              0.0       0.0
csh_0.8              0.0       0.0
Gibbsite      0.0    0.0
Gismondine    0.0    0.0
Goethite      0.0    0.0
Gyrolite      0.0    0.0
Kaolinite     0.0    0.0
Laumontite    0.0    0.0
magnetite     0.0    0.0
Prehnite      0.0    0.0
```

```
Straetlingite 0.0     0.0
# Corrosion off gas
O2,g          0.0     0.0
H2,g          0.0     0.0

SOLUTION 1
-pH 7.0 charge
-water 4.02
units mol/kgw
Al   6.90E-07
C    4.68E-03
Ca   1.27E-03
Cl   5.09E-03
K    8.12E-03
Mg   4.69E-04
Na   1.09E-02
S    5.09E-04
Si   1.92E-04

KINETICS 1
#H4ISAH
#-m 1.6132
#-m0 1.6132

#Fe,element
#-m  62.49440415
#-m0 62.49440415

Quartz,alpha
-m 1.59597E+00
-m0 1.59597E+00

EXCHANGE 1
#NaX   0.064933333
#ClXa  0.032466667
#HX           0.064933333
#OHXa  0.032466667

USER_GRAPH
-headings Time sim_no step_no pH  H4IsaH Steel Portlandite CSH_1.6
CSH_1.2 CSH_0.8
-initial_solutions true
-connect_simulations true
-plot_concentration_vs time
-axis_scale y_axis 7 14 1
-start
10 graph_x sim_time/3600/24/365
```

```
20 REM graph_y time/3600/24/365
30 graph_y sim_no
40 graph_y step_no
50 graph_y -la("H+")
60 graph_sy KIN("H4IsaH")
65 graph_sy KIN("Fe,element")
70 graph_sy equi("Portlandite")
80 graph_sy equi("CSH_1.6")
90 graph_sy equi("CSH_1.2")
100 graph_sy equi("CSH_0.8")
-end

TRANSPORT     # 0- 2000 AD
-cells 1
-length 10
-dispersivity 0.002
-shifts 0              # 0 pore water exchanges during 0-2000 AD
-flow_direction forward
-time_step 4.1644E+12
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT     # 2000- 3000 AD
-cells 1
-length 10
-dispersivity   0.002
-shifts 4              # 4 pore water exchanges during 2000-3000 AD
-flow_direction forward
-time_step 8.3237E+09
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT     # > 3000 AD
-cells  1
-length 10
-dispersivity 0.002
-shifts 834            # 834 pore water exchanges during 3000-100000 AD
-flow_direction forward
-time_step 3.6853E+09

END
```

Input file 2 BTF1

```
TITLE BTF1
SOLUTION_MASTER_SPECIES
Isa           H4Isa-            0.0           Isa       179.147

SOLUTION_SPECIES
#To improve convergence
H2O + 0.01e- = H2O-0.01;        log_k         -9.0

# From PCHatches 18.1
H4Isa-         = H4Isa-;         log_k 0;      delta_h 0 kcal
H+ + H4Isa-    = H4IsaH;         log_k 4;      delta_h 0 kcal
Ca+2 + H4Isa- = CaH3Isa + H+;   log_k -10.4;delta_h 0 kcal
Ca+2 + H4Isa- = CaH4Isa+1;      log_k 1.7;    delta_h 0 kcal
H+ + H4Isa-    = H4IsaH;         log_k 4;      delta_h 0 kcal

PHASES
# From PCHatches 18.1
Ca(H4Isa)2
          Ca(H4Isa)2 = Ca+2 + 2H4Isa-
          log_k -6.4
          delta_h  0 kcal

H4IsaH
          H4IsaH = H+ + H4Isa-
          log_k -10

EXCHANGE_MASTER_SPECIES
# Cationic (X) and anionic (Xa) ion exchangers
X         X-
Xa        Xa+

EXCHANGE_SPECIES
# DOW cation exchange 4% DVB
X-               = X-                         ; log_k   0.0
X- + H+        =  HX                          ; log_k   0.0
HX + Li+       =  LiX   + H+                  ; log_k   -0.119
HX + Na+       =  NaX   + H+                  ; log_k   0.079
HX + NH4+      =  NH4X  + H+                  ; log_k   0.158
HX + K+          = KX   + H+                  ; log_k   0.236
HX + Rb+       =  RbX   + H+                  ; log_k   0.270
HX + Cs+       =  CsX   + H+                  ; log_k   0.305
HX + Ag+       =  AgX   + H+                  ; log_k   0.554
HX + Tl+       =  TlX   + H+                  ; log_k   0.706
2HX + UO2++    =  UO2X2 + 2H+                 ; log_k   0.253
2HX + Mg++     =  MgX2  + 2H+                 ; log_k   0.348
2HX + Zn++     =  ZnX2  + 2H+                 ; log_k   0.375
```

```
2HX + Co++    =  CoX2  + 2H+                ; log_k   0.389
2HX + Cu++    =  CuX2  + 2H+                ; log_k   0.396
2HX + Cd++    =  CdX2  + 2H+                ; log_k   0.407
2HX + Ni++    =  NiX2  + 2H+                ; log_k   0.417
2HX + Ca++    =  CaX2  + 2H+                ; log_k   0.497
2HX + Sr++    =  SrX2  + 2H+                ; log_k   0.551
2HX + Pb++    =  PbX2  + 2H+                ; log_k   0.696
2HX + Ba++    =  BaX2  + 2H+                ; log_k   0.753
# DOW Anion exchange Type 1
Xa+             =   Xa+                               ; log_k 0.0
Xa+  +  OH-   =  OHXa                                 ; log_k 0.0
#OHXa +  OH-  =  OHXa   + OH-   ; log_k      0.000
OHXa + I-     =  IXa             + OH-      ; log_k   2.243
OHXa + HSO4-  =  HSO4Xa + OH-   ; log_k      1.929
OHXa + ClO3-  =  ClO3Xa + OH-   ; log_k      1.869
OHXa + NO3-   =  NO3Xa  + OH-   ; log_k      1.813
OHXa + Br-    =  BrXa   + OH-   ; log_k      1.699
OHXa + CN-    =  CNXa   + OH-   ; log_k      1.447
OHXa + HSO3-  =  HSO3Xa + OH-   ; log_k      1.431
OHXa + BrO3-  =  BrO3Xa + OH-   ; log_k      1.431
OHXa + NO2-   =  NO2Xa           + OH-      ; log_k   1.380
OHXa + Cl-    =  ClXa            + OH-      ; log_k   1.342
OHXa + HCO3-  =  HCO3Xa + OH-   ; log_k      0.778
OHXa + IO3-   =  IO3Xa           + OH-      ; log_k   0.740
OHXa + F-     =  FXa    + OH-   ; log_k      0.204

RATES
H4IsaH
#Degradation rate for paper according to Glaus 2008
-start
20  if (m <= 0) then goto 200
35  k1 = 4.3E-3/3600
44  kt = 4.3E-4/3600
55  kh = 1.6E-7/3600
65  Gr = 3.5E-3
100 rate = (exp(-kh*sim_time)*kt*kt*exp(-kt*sim_time)*Gr*k1)/kt^2-kh*-
exp(-kh*sim_time)*(((1-exp(-kt*sim_time))*Gr*k1)/kt-1)
190 moles = rate*time*m
200 SAVE moles
-end

Fe,element
#carbonsteel
#Corrosion of carbon steel
-start
20 if (m <= 0) then goto 200
30 R = 4.87E-04/365/24/3600
```

```
100 rate = R
180 moles = rate*time
190 REM moles = rate*time
200 SAVE moles
-end

Quartz,alpha
-start
10 dif_temp = 1/TK - 1/298
20 pk_w = 13.7 + 4700.4 * dif_temp
40 moles = (m/m0)^0.67 * 10^-pk_w *(1 - SR(“Quartz,alpha”))
50 save moles * time
-end

SOLUTION 0
pH 7.0 charge
#-water 5.09E5
-water  0.509
units mol/kgw
# Saline groundwater
#C             1.48E-03
#Ca            1.50E-02
#Cl            9.87E-02
#K             5.12E-04
#Mg            6.17E-03
#Na            6.53E-02
#S             3.64E-03
#Si            1.83E-04

#Temperate-periglacial
C              4.92E-3
Ca             1.25E-3
Cl             5.36E-3
K              1.28E-4
Mg             4.94E-4
Na             7.83E-3
S              5.21E-4
Si             2.00E-4

#Glacial derived water
#C             6.40E-04
#Ca            2.96E-04
#Cl            8.19E-06
#K             1.65E-05
#Mg            1.04E-06
#Na            4.35E-06
#S             1.25E-05
#Si            2.13E-04
```

```
EQUILIBRIUM_PHASES 1
#Cement + concrete
csh_1.6         0               3.71372E+00
portlandite     0               3.58987E+00
ettringite      0               8.32790E-02
C3AH6           0               2.32802E-01
hydrotalcite  0 3.33590E-02
Hematite        0               1.75431E-01
#SiO2           0               1.12167E+02
#Metals
Al,element                      0.0                    2.06E+00
#Fe,element                     0.0                    2.44E+01
#Ashes
Lime                            0.0                    4.07E+00
Amorphous_silica 0.0                         3.16E+00
Al2O3glass                      0.0                    6.39E-01
Na2O                            0.0                    4.38E-02
K2O                                          0.0            2.88E-02
Periclase                       0.0                    1.35E+00
# Secondary phases
Boehmite      0.0               0.0
Calcite       0.0               0.0
Chalcedony    0.0               0.0
csh_1.2                         0.0                    0.0
csh_0.8                         0.0                    0.0
Gibbsite      0.0               0.0
Gismondine    0.0               0.0
Goethite      0.0               0.0
Gyrolite      0.0               0.0
Kaolinite     0.0               0.0
Laumontite    0.0               0.0
magnetite     0.0               0.0
Prehnite      0.0               0.0
Straetlingite 0.0               0.0
# Corrosion off gas
O2,g          0.0               0.0
H2,g          0.0               0.0
CO2,g                           0.0          0.0

SOLUTION 1
-pH 7.0  charge
#-water 5.09E5
-water  0.509
units mol/kgw
#redox     O(-2)/O(0)
#O(0)    8.0 mg/kgw
Al   9.66E-06
```

```
C    1.53E-03
Ca   1.48E-03
Cl   1.61E-03
K    1.12E-01
Mg   1.48E-04
Na   5.01E-02
S    3.53E-04
Si   8.38E-05

EXCHANGE 1
#NaX 0.3
#ClXa  0.15
#HX  0.3
#OHXa  0.15

KINETICS  1
#H4ISAH
#-m  0.009042853
#-m0 0.009042853

#Fe,element
#-m  2.44E+01
#-m0 2.44E+01

Quartz,alpha
-m   1.12167E+02
-m0  1.12167E+02

USER_GRAPH
-headings Time sim_no step_no pH  H4IsaH Steel Portlandite CSH_1.6 CSH_1.2 CSH_0.8
-initial_solutions true
-connect_simulations true
-plot_concentration_vs time
-axis_scale y_axis 7 14 1
-start
10 graph_x sim_time/3600/24/365
20 REM graph_y time/3600/24/365
30 graph_y sim_no
40 graph_y step_no
50 graph_y -la(“H+”)
60 graph_sy KIN(“H4IsaH”)
65 graph_sy KIN(“Fe,element”)
70 graph_sy equi(“Portlandite”)
80 graph_sy equi(“CSH_1.6”)
90 graph_sy equi(“CSH_1.2”)
100 graph_sy equi(“CSH_0.8”)
-end
```

```
TRANSPORT     # 0- 2000 AD
-cells  1
-lengths 10
-dispersivities  0.002
-shifts 0          # 0 pore water exchanges during 0 - 2 000 AD
-flow_direction forward
-time_step 8.8020E+12
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT     # 2000- 3000 AD
-cells  1
-lengths 10
-dispersivities   0.002
-shifts 1          # 1 pore water exchanges during 2 000 - 3 000 AD
-flow_direction forward
-time_step 4.6186E+10
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT     # 3000- 100000 AD
-cells  1
-shifts 138        # 138 pore water exchanges during 3 000 - 100 000 AD
-flow_direction forward
-time_step 2.2421E+10

END
```

Input file 3 BTF2

```
TITLE BTF2
PRINT
-species false
-saturation_indices false

SOLUTION_MASTER_SPECIES
Isa           H4Isa-           0.0           Isa       179.147

SOLUTION_SPECIES
#To improve convergence
H2O + 0.01e- = H2O-0.01;        log_k         -9.0

# From PCHatches 18.1
H4Isa-        = H4Isa-;         log_k 0;      delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;         log_k 4;      delta_h 0 kcal
Ca+2 + H4Isa- = CaH3Isa + H+;   log_k -10.4;  delta_h 0 kcal
Ca+2 + H4Isa- = CaH4Isa+1;      log_k  1.7;   delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;         log_k  4;     delta_h 0 kcal

PHASES
# From PCHatches 18.1
Ca(H4Isa)2
              Ca(H4Isa)2 = Ca+2 + 2H4Isa-
              log_k -6.4
              delta_h  0 kcal


H4IsaH
              H4IsaH = H+ + H4Isa-
              log_k -10

EXCHANGE_MASTER_SPECIES
# Cationic (X) and anionic (Xa) ion exchangers
X             X-
Xa            Xa+

EXCHANGE_SPECIES
# DOW cation exchange 4% DVB
X-              =              X-                           ; log_k
0.0
X- + H+       =  HX                                    ; log_k 0.0
HX + Li+      =  LiX   + H+                  ; log_k   -0.119
HX + Na+      =  NaX   + H+                  ; log_k   0.079
HX + NH4+     =  NH4X  + H+                  ; log_k   0.158
HX + K+       =  KX    + H+                  ; log_k   0.236
HX + Rb+      =  RbX   + H+                  ; log_k   0.270
HX + Cs+      =  CsX   + H+                  ; log_k   0.305
```

```
HX + Ag+      = AgX   + H+                   ; log_k   0.554
HX + Tl+      = TlX   + H+                   ; log_k   0.706
2HX + UO2++   = UO2X2 + 2H+                  ; log_k   0.253
2HX + Mg++    = MgX2  + 2H+                  ; log_k   0.348
2HX + Zn++    = ZnX2  + 2H+                  ; log_k   0.375
2HX + Co++    = CoX2  + 2H+                  ; log_k   0.389
2HX + Cu++    = CuX2  + 2H+                  ; log_k   0.396
2HX + Cd++    = CdX2  + 2H+                  ; log_k   0.407
2HX + Ni++    = NiX2  + 2H+                  ; log_k   0.417
2HX + Ca++    = CaX2  + 2H+                  ; log_k   0.497
2HX + Sr++    = SrX2  + 2H+                  ; log_k   0.551
2HX + Pb++    = PbX2  + 2H+                  ; log_k   0.696
2HX + Ba++    = BaX2  + 2H+                  ; log_k   0.753
# DOW Anion exchange Type 1
Xa+             = Xa+                                  ; log_k 0.0
Xa+  +  OH-   = OHXa                                   ; log_k 0.0
#OHXa +  OH-  = OHXa + OH-                   ; log_k   0.000
OHXa + I-       = IXa            + OH-       ; log_k   2.243
OHXa + HSO4-    = HSO4Xa + OH-               ; log_k   1.929
OHXa + ClO3-  = ClO3Xa + OH-                 ; log_k   1.869
OHXa + NO3-   = NO3Xa + OH-                  ; log_k   1.813
OHXa + Br-    = BrXa + OH-                   ; log_k   1.699
OHXa + CN-    = CNXa + OH-                   ; log_k   1.447
OHXa + HSO3-  = HSO3Xa + OH-                 ; log_k   1.431
OHXa + BrO3-  = BrO3Xa + OH-                 ; log_k   1.431
OHXa + NO2-   = NO2Xa + OH-                  ; log_k   1.380
OHXa + Cl-    = ClXa + OH-                   ; log_k   1.342
OHXa + HCO3-  = HCO3Xa + OH-                 ; log_k   0.778
OHXa + IO3-   = IO3Xa            + OH-       ; log_k   0.740
OHXa + F-     = FXa + OH-                    ; log_k   0.204

RATES
H4IsaH
#Degradation rate for paper according to Glaus 2008
-start
20 if (m <= 0) then goto 200
35 k1 = 4.3E-3/3600
44 kt = 4.3E-4/3600
55 kh = 1.6E-7/3600
65 Gr = 3.5E-3
100 rate = (exp(-kh*sim_time)*kt*kt*exp(-kt*sim_time)*Gr*k1)/kt^2-kh*-
exp(-kh*sim_time)*(((1-exp(-kt*sim_time))*Gr*k1)/kt-1)
190 moles = rate*time*m
200 SAVE moles
-end
```

```
Fe,element
#carbonsteel
#Corrosion of carbon steel
-start
20 if (m <= 0) then goto 200
30 R = 6.52E-04/365/24/3600
100 rate = R
180 moles = rate*time
190 REM moles = rate*time
200 SAVE moles
-end

Quartz,alpha
-start
10 dif_temp = 1/TK - 1/298
20 pk_w = 13.7 + 4700.4 * dif_temp
40 moles = (m/m0)^0.67 * 10^-pk_w *(1 - SR(“Quartz,alpha”))
50 save moles * time
-end

SOLUTION 0
pH 7.0 charge
-water  0.641
units mol/kgw
# Saline groundwater
#C           1.48E-03
#Ca          1.50E-02
#Cl          9.87E-02
#K           5.12E-04
#Mg          6.17E-03
#Na          6.53E-02
#S           3.64E-03
#Si          1.83E-04

#Temperate-periglacial water
C            4.92E-3
Ca           1.25E-3
Cl           5.36E-3
K            1.28E-4
Mg           4.94E-4
Na           7.83E-3
S            5.21E-4
Si           2.00E-4
```

```
#Glacial derived water
#C            6.40E-04
#Ca           2.96E-04
#Cl           8.19E-06
#K            1.65E-05
#Mg           1.04E-06
#Na           4.35E-06
#S            1.25E-05
#Si           2.13E-04

EQUILIBRIUM_PHASES 1
#Concrete
csh_1.6         0               3.58584      # dissolve_only
portlandite     0               3.46524
ettringite      0               0.0804
C3AH6           0               0.22512
hydrotalcite  0 0.03216
Hematite        0               0.16884
#SiO2           0               133.80168
#Metals
#Fe,element                     0.0          32.590205
# Ion exchange resin, see EXCHANGE
# Secondary phases
Boehmite      0.0               0.0
Calcite       0.0               0.0
Chalcedony    0.0               0.0
csh_1.2                         0.0                    0.0
csh_0.8                         0.0          0.0
Gibbsite      0.0               0.0
Gismondine    0.0                            0.0
Goethite      0.0               0.0
Gyrolite      0.0               0.0
Kaolinite     0.0               0.0
Laumontite    0.0               0.0
magnetite     0.0               0.0
Prehnite      0.0               0.0
Straetlingite 0.0               0.0
# Corrosion off gas
O2,g          0.0               0.0
H2,g          0.0               0.0

SOLUTION 1
-pH 7.0  charge
-water  0.641
units mol/kgw
Al   9.66E-06
C    1.53E-03
```

```
Ca   1.48E-03
Cl   1.61E-03
K    1.12E-01
Mg   1.48E-04
Na   5.01E-02
S    3.53E-04
Si   8.38E-05

EXCHANGE 1
#NaX   0.554
#ClXa 0.277
#HX    0.554
#OHXa 0.277

KINETICS  1
#H4ISAH
#-m   0
#-m0  0
#Fe,element
#-m  32.590205
#-m0 32.590205

Quartz,alpha
-m 133.80168
-m0 133.80168

USER_GRAPH
-headings Time sim_no step_no pH  H4IsaH Steel Portlandite CSH_1.6
CSH_1.2 CSH_0.8
-initial_solutions true
-connect_simulations true
-plot_concentration_vs time
-axis_scale y_axis 7 14 1
-start
10 graph_x sim_time/3600/24/365
20 REM graph_y time/3600/24/365
30 graph_y sim_no
40 graph_y step_no
50 graph_y -la(“H+”)
60 graph_sy KIN(“H4IsaH”)
65 graph_sy KIN(“Fe,element”)
70 graph_sy equi(“Portlandite”)
80 graph_sy equi(“CSH_1.6”)
90 graph_sy equi(“CSH_1.2”)
100 graph_sy equi(“CSH_0.8”)
-end
```

```
TRANSPORT
-cells  1
-lengths 10
-dispersivities   0.002
-shifts 0                # 0 pore water changes during 0 - 2 000 AD
-flow_direction forward
-time_step 3.2054E+13
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT
-cells  1
-lengths 10
-dispersivities   0.002
-shifts 0                # 0 pore water changes during 2 000 - 3 000 AD
-flow_direction forward
-time_step 9.4811E+10
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT
-cells  1
-lengths 10
-dispersivities   0.002
-shifts 63            # 63 pore water changes during 3 000 - 100 000 AD
-flow_direction forward
-time_step 4.9024E+10
-boundary_conditions flux flux

END
```

Input file 4 BMA – Bitumen

```
TITLE BMA Bitumen Fack 3
PRINT
-species false
-saturation_indices false

SOLUTION_MASTER_SPECIES
Isa           H4Isa-            0.0           Isa       179.147

SOLUTION_SPECIES
# From PCHatches 18.1
H4Isa-        = H4Isa-;         log_k 0;      delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;                       log_k 4;  delta_h 0 kcal
Ca+2 + H4Isa- = CaH3Isa + H+;   log_k -10.4;delta_h 0 kcal
Ca+2 + H4Isa- = CaH4Isa+1;      log_k  1.7;   delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;         log_k  4;     delta_h 0 kcal

PHASES
# From PCHatches 18.1
Ca(H4Isa)2
       Ca(H4Isa)2 = Ca+2 + 2H4Isa-
       log_k -6.4
       delta_h  0 kcal

H4IsaH
       H4IsaH = H+ + H4Isa-
       log_k -10

SOLUTION_SPECIES
#To improve convergence
H2O + 0.01e- = H2O-0.01;        log_k        -9.0

EXCHANGE_MASTER_SPECIES
# Cationic (X) and anionic (Xa) ion exchangers
X             X-
Xa            Xa+

EXCHANGE_SPECIES
# DOW cation exchange 4% DVB
X-                              = X-         ; log_k   0.0
X- + H+       = HX                           ; log_k   0.0
HX + Li+      =  LiX   + H+                  ; log_k   -0.119
HX + Na+      =  NaX   + H+                  ; log_k   0.079
HX + NH4+     =  NH4X  + H+                  ; log_k   0.158
HX + K+       =  KX    + H+                  ; log_k   0.236
HX + Rb+      =  RbX   + H+                  ; log_k   0.270
HX + Cs+      =  CsX   + H+                  ; log_k   0.305
```

```
HX + Ag+      = AgX   + H+                    ; log_k   0.554
HX + Tl+      = TlX   + H+                    ; log_k   0.706
2HX + UO2++   = UO2X2 + 2H+                   ; log_k   0.253
2HX + Mg++    = MgX2  + 2H+                   ; log_k   0.348
2HX + Zn++    = ZnX2  + 2H+                   ; log_k   0.375
2HX + Co++    = CoX2  + 2H+                   ; log_k   0.389
2HX + Cu++    = CuX2  + 2H+                   ; log_k   0.396
2HX + Cd++    = CdX2  + 2H+                   ; log_k   0.407
2HX + Ni++    = NiX2  + 2H+                   ; log_k   0.417
2HX + Ca++    = CaX2  + 2H+                   ; log_k   0.497
2HX + Sr++    = SrX2  + 2H+                   ; log_k   0.551
2HX + Pb++    = PbX2  + 2H+                   ; log_k   0.696
2HX + Ba++    = BaX2  + 2H+                   ; log_k   0.753
# DOW Anion exchange Type 1
Xa+                               = Xa+       ; log_k 0.0
Xa+ + OH-     = OHXa                          ; log_k 0.0
#OHXa + OH-   = OHXa   + OH-                  ; log_k   0.000
OHXa + I-     = IXa  + OH-                    ; log_k   2.243
OHXa + HSO4-  = HSO4Xa + OH-                  ; log_k   1.929
OHXa + ClO3-  = ClO3Xa + OH-                  ; log_k   1.869
OHXa + NO3-   = NO3Xa  + OH-                  ; log_k   1.813
OHXa + Br-    = BrXa   + OH-                  ; log_k   1.699
OHXa + CN-    = CNXa   + OH-                  ; log_k   1.447
OHXa + HSO3-  = HSO3Xa + OH-                  ; log_k   1.431
OHXa + BrO3-  = BrO3Xa + OH-                  ; log_k   1.431
OHXa + NO2-   = NO2Xa  + OH-                  ; log_k   1.380
OHXa + Cl-    = ClXa  + OH-                   ; log_k   1.342
OHXa + HCO3-  = HCO3Xa + OH-                  ; log_k   0.778
OHXa + IO3-   = IO3Xa  + OH-                  ; log_k   0.740
OHXa + F-       = FXa    + OH-                ; log_k   0.204

RATES
H4IsaH
#Degradation rate for paper according to Glaus 2008
-start
20  if (m <= 0) then goto 200
35  k1 = 4.3E-3/3600
44  kt = 4.3E-4/3600
55  kh = 1.6E-7/3600
65  Gr = 3.5E-3
100 rate = (exp(-kh*sim_time)*kt*kt*exp(-kt*sim_time)*Gr*k1)/kt^2-kh*-
exp(-kh*sim_time)*(((1-exp(-kt*sim_time))*Gr*k1)/kt-1)
190 moles = rate*time*m
200 SAVE moles
-end
```

```
Fe,element
#carbonsteel
#Corrosion of carbon steel
-start
20 if (m <= 0) then goto 200
30 R = 8.49E-05/365/24/3600
100 rate = R
180 moles = rate*time
190 REM moles = rate*time
200 SAVE moles
-end

Quartz,alpha
-start
10 dif_temp = 1/TK - 1/298
20 pk_w = 13.7 + 4700.4 * dif_temp
40 moles = (m/m0)^0.67 * 10^-pk_w *(1 - SR("Quartz,alpha"))
50 save moles * time
-end

SOLUTION 0
pH 7.0 charge
-water  0.15538
units mol/kgw
# Saline groundwater
#C            1.48E-03
#Ca           1.50E-02
#Cl           9.87E-02
#K            5.12E-04
#Mg           6.17E-03
#Na           6.53E-02
#S            3.64E-03
#Si           1.83E-04

#Temperate-periglacial
C             4.92E-3
Ca            1.25E-3
Cl            5.36E-3
K             1.28E-4
Mg            4.94E-4
Na            7.83E-3
S             5.21E-4
Si            2.00E-4

##Glacial derived water
#C            6.40E-04
#Ca           2.96E-04
```

```
#Cl           8.19E-06
#K            1.65E-05
#Mg           1.04E-06
#Na           4.35E-06
#S            1.25E-05
#Si           2.13E-04

######################### WALL #############################

EQUILIBRIUM_PHASES 1
#Concrete wall
csh_1.6         0              3.34500E-02
portlandite     0              3.23250E-02
ettringite      0              7.50000E-04
C3AH6           0              2.10000E-03
hydrotalcite  0 3.00000E-04
Hematite        0              1.57500E-03
#SiO2           0              1.24815E+00
# Secondary phases
Boehmite      0.0              0.0
Calcite       0.0              0.0
Chalcedony    0.0              0.0
csh_1.2                        0.0                    0.0
csh_0.8                        0.0           0.0
Gibbsite      0.0              0.0
Gismondine    0.0              0.0
Goethite      0.0              0.0
Gyrolite      0.0              0.0
Kaolinite     0.0              0.0
Laumontite    0.0              0.0
magnetite     0.0              0.0
Prehnite      0.0              0.0
Straetlingite 0.0              0.0

SOLUTION 1
-pH 7.0  charge
-water  0.15538
units mol/kgw
Al   1.38E-05
C    8.25E-05
Ca   1.58E-03
Cl   0.00E+00
K    1.60E-01
Mg   1.93E-09
Na   6.82E-02
S    2.81E-04
Si   3.40E-05
```

```
KINETICS 1
Quartz,alpha
-m   1.24815E+00
-m0  1.24815E+00

######################### WASTE #############################

EQUILIBRIUM_PHASES 2
#LLW/ILW
#Cement + concrete
csh_1.6         0               7.88E-01
portlandite     0               7.63E-01
ettringite      0               1.77E-02
C3AH6           0               4.91E-02
hydrotalcite    0               7.13E-03
Hematite        0               3.78E-02
#SiO2           0               0.00E+00
#####
# Evaporator concentrate
Halite          0.0                          2.68506E-01
Sylvite         0.0                          1.40327E-02
Thenardite      0.0                          2.94604E-02
Na2CO3          0.0                          4.93525E-02
#Metals
Al,element      0.0                          2.62283E-02
#Fe,element     0.0                          4.24251E+00
# Secondary phases
Boehmite      0.0               0.0
Calcite       0.0               0.0
Chalcedony    0.0               0.0
csh_1.2                         0.0                   0.0
csh_0.8                         0.0          0.0
Gibbsite      0.0               0.0
Gismondine    0.0               0.0
Goethite      0.0               0.0
Gyrolite      0.0               0.0
Kaolinite     0.0               0.0
Laumontite    0.0               0.0
magnetite     0.0               0.0
Prehnite      0.0               0.0
Straetlingite 0.0               0.0
# Corrosion gas
O2,g          0.0               0.0
H2,g          0.0               0.0
```

```
SOLUTION 2
-pH 7.0  charge
-water  0.15538
units mol/kgw
Al   9.66E-06
C    1.53E-03
Ca   1.48E-03
Cl   1.61E-03
K    1.12E-01
Mg   1.48E-04
Na   5.01E-02
S    3.53E-04
Si   8.38E-05

EXCHANGE 2
#NaX  0.088717949
#ClXa 0.044358974
#HX       0.088717949
#OHXa 0.044358974

KINETICS  2
#H4ISAH
#-m  0.052384999
#-m0  0.052384999
#Fe,element
#-m   4.24251E+00
#-m0  4.24251E+00

USER_GRAPH
-headings Time sim_no step_no pH  H4IsaH Steel Portlandite CSH_1.6
CSH_1.2 CSH_0.8  Fe Al
-initial_solutions true
-connect_simulations true
-plot_concentration_vs time
-axis_scale y_axis 7 14 1
-start
10 graph_x sim_time/3600/24/365
20 REM graph_y time/3600/24/365
30 graph_y sim_no
40 graph_y step_no
50 graph_y -la(“H+”)
60 graph_sy KIN(“H4IsaH”)
65 graph_sy KIN(“Fe,element”)
70 graph_sy equi(“Portlandite”)
80 graph_sy equi(“CSH_1.6”)
90 graph_sy equi(“CSH_1.2”)
100 graph_sy equi(“CSH_0.8”)
```

```
120 graph_sy equi("Fe,element")
130 graph_sy equi("Al,element")
-end

TRANSPORT     # 0-2000 AD
-cells  2
-lengths 0.5 10
-dispersivities  0.002
-shifts 0              # 0 pore water exchanges during 0-2000 AD
-punch_cells 2         # 1 = Wall, 2 = Waste
-flow_direction forward
-time_step 2.5145E+13
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT     # 2000 - 3000 AD
-cells  2
-shifts 0              # 0 pore water exchanges during 2000-3000 AD
-punch_cells 2         # 1 = Wall, 2 = Waste
-flow_direction forward
-time_step 1.4006E+11

END

TRANSPORT     # > 3000 AD
-cells  2
-shifts 57             # 57 pore water exchanges during > 3000 AD
-punch_cells 2         # 1 = Wall, 2 = Waste
-flow_direction forward
-time_step 5.4317E+10

END
```

Input file 5 BMA – Cement

```
TITLE BMA Cement fack 1
PRINT
-species false
-saturation_indices false

SOLUTION_MASTER_SPECIES
Isa           H4Isa-            0.0          Isa       179.147

SOLUTION_SPECIES
# From PCHatches 18.1
H4Isa-        = H4Isa-;         log_k 0;     delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;         log_k 4;     delta_h 0 kcal
Ca+2 + H4Isa- = CaH3Isa + H+;   log_k -10.4; delta_h 0 kcal
Ca+2 + H4Isa- = CaH4Isa+1;      log_k  1.7;  delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;         log_k  4;    delta_h 0 kcal

PHASES
# From PCHatches 18.1
Ca(H4Isa)2
              Ca(H4Isa)2 = Ca+2 + 2H4Isa-
              log_k -6.4
              delta_h  0 kcal

H4IsaH
              H4IsaH = H+ + H4Isa-
              log_k -10

SOLUTION_SPECIES
#To improve convergence
H2O + 0.01e- = H2O-0.01;        log_k        -9.0

EXCHANGE_MASTER_SPECIES
# Cationic (X) and anionic (Xa) ion exchangers
X      X-
Xa     Xa+

EXCHANGE_SPECIES
# DOW cation exchange 4% DVB
X-              = X-                                 ; log_k    0.0
X- + H+ = HX                                ; log_k   0.0
HX + Li+      =  LiX   + H+                 ; log_k   -0.119
HX + Na+      =  NaX   + H+                 ; log_k   0.079
HX + NH4+     =  NH4X  + H+                 ; log_k   0.158
HX + K+         =               KX    + H+  ; log_k   0.236
HX + Rb+      =  RbX   + H+                 ; log_k   0.270
HX + Cs+      =  CsX   + H+                 ; log_k   0.305
```

```
HX + Ag+      = AgX   + H+                    ; log_k   0.554
HX + Tl+      = TlX   + H+                    ; log_k   0.706
2HX + UO2++   = UO2X2 + 2H+                   ; log_k   0.253
2HX + Mg++    = MgX2  + 2H+                   ; log_k   0.348
2HX + Zn++    = ZnX2  + 2H+                   ; log_k   0.375
2HX + Co++    = CoX2  + 2H+                   ; log_k   0.389
2HX + Cu++    = CuX2  + 2H+                   ; log_k   0.396
2HX + Cd++    = CdX2  + 2H+                   ; log_k   0.407
2HX + Ni++    = NiX2  + 2H+                   ; log_k   0.417
2HX + Ca++    = CaX2  + 2H+                   ; log_k   0.497
2HX + Sr++    = SrX2  + 2H+                   ; log_k   0.551
2HX + Pb++    = PbX2  + 2H+                   ; log_k   0.696
2HX + Ba++    = BaX2  + 2H+                   ; log_k   0.753
# DOW Anion exchange Type 1
Xa+             = Xa+                                   ; log_k 0.0
Xa+  +  OH-   = OHXa                                    ; log_k 0.0
#OHXa +  OH-  = OHXa   + OH-                  ; log_k   0.000
OHXa + I-        = IXa           + OH-        ; log_k   2.243
OHXa + HSO4-     = HSO4Xa + OH-               ; log_k   1.929
OHXa + ClO3-  = ClO3Xa + OH-                  ; log_k   1.869
OHXa + NO3-   = NO3Xa  + OH-                  ; log_k   1.813
OHXa + Br-    = BrXa   + OH-                  ; log_k   1.699
OHXa + CN-    = CNXa   + OH-                  ; log_k   1.447
OHXa + HSO3-  = HSO3Xa + OH-                  ; log_k   1.431
OHXa + BrO3-  = BrO3Xa + OH-                  ; log_k   1.431
OHXa + NO2-   = NO2Xa            + OH-        ; log_k   1.380
OHXa + Cl-    = ClXa             + OH-        ; log_k   1.342
OHXa + HCO3-  = HCO3Xa + OH-                  ; log_k   0.778
OHXa + IO3-   = IO3Xa            + OH-        ; log_k   0.740
OHXa + F-        = FXa    + OH-               ; log_k   0.204

RATES
H4IsaH
#Degradation rate for paper according to Glaus 2008
-start
20  if (m <= 0) then goto 200
35  k1 = 4.3E-3/3600
44  kt = 4.3E-4/3600
55  kh = 1.6E-7/3600
65  Gr = 3.5E-3
100 rate = (exp(-kh*sim_time)*kt*kt*exp(-kt*sim_time)*Gr*k1)/kt^2-kh*-
exp(-kh*sim_time)*(((1-exp(-kt*sim_time))*Gr*k1)/kt-1)
190 moles = rate*time*m
200 SAVE moles
-end
```

```
Fe,element
#carbonsteel
#Corrosion of carbon steel
-start
20 if (m <= 0) then goto 200
30 R = 8.49E-05/365/24/3600
100 rate = R
180 moles = rate*time
190 REM moles = rate*time
200 SAVE moles
-end

Quartz,alpha
-start
10 dif_temp = 1/TK - 1/298
20 pk_w = 13.7 + 4700.4 * dif_temp
40 moles = (m/m0)^0.67 * 10^-pk_w *(1 - SR(“Quartz,alpha”))
50 save moles * time
-end

SOLUTION 0
pH 7.0 charge
-water  0.15538
units mol/kgw
# Saline groundwater
#C            1.48E-03
#Ca           1.50E-02
#Cl           9.87E-02
#K            5.12E-04
#Mg           6.17E-03
#Na           6.53E-02
#S            3.64E-03
#Si           1.83E-04

#Temperate-periglacial
C             4.92E-3
Ca            1.25E-3
Cl            5.36E-3
K             1.28E-4
Mg            4.94E-4
Na            7.83E-3
S             5.21E-4
Si            2.00E-4

#Glacial derived water
#C            6.40E-04
#Ca           2.96E-04
```

```
#Cl           8.19E-06
#K            1.65E-05
#Mg           1.04E-06
#Na           4.35E-06
#S            1.25E-05
#Si           2.13E-04

######################### WALL #############################

EQUILIBRIUM_PHASES 1
#Concrete wall
csh_1.6          0              3.34500E-02
portlandite      0              3.23250E-02
ettringite       0              7.50000E-04
C3AH6            0              2.10000E-03
hydrotalcite  0  3.00000E-04
Hematite         0              1.57500E-03
#SiO2            0              1.24815E+00
#Secondary phases
Boehmite         0.0            0.0
Calcite          0.0            0.0
Chalcedony       0.0            0.0
csh_1.2                         0.0                    0.0
csh_0.8                         0.0           0.0
Gibbsite         0.0            0.0
Gismondine       0.0            0.0
Goethite         0.0            0.0
Gyrolite         0.0            0.0
Kaolinite        0.0            0.0
Laumontite       0.0            0.0
magnetite        0.0            0.0
Prehnite         0.0            0.0
Straetlingite    0.0            0.0
# Corrosion off gas
O2,g             0.0            0.0
H2,g             0.0            0.0

SOLUTION 1
-pH 7.0  charge
-water  0.15538
units mol/kgw
Al   1.38E-05
C    8.25E-05
Ca   1.58E-03
Cl   0.00E+00
K    1.60E-01
Mg   1.93E-09
```

```
Na   6.82E-02
S    2.81E-04
Si   3.40E-05

KINETICS 1
Quartz,alpha
-m   1.24815E+00
-m0  1.24815E+00

######################### WASTE #############################

EQUILIBRIUM_PHASES 2
# LLW/ILW
#Cement + concrete
csh_1.6         0              3.17E+00
portlandite     0              3.06E+00
ettringite      0              7.10E-02
C3AH6           0              1.97E-01
hydrotalcite  0 2.86E-02
Hematite        0              1.52E-01
#SiO2           0              0.00E+00
# Evaporator concentrate
Halite          0.0                          2.68506E-01
Sylvite         0.0                          1.40327E-02
Thenardite      0.0                          2.94604E-02
Na2CO3          0.0                          4.93525E-02
#Metals
Al,element      0.0                          2.62283E-02
#Fe,element     0.0                          4.24251E+00
# Secondary phases
Boehmite        0.0            0.0
Calcite         0.0            0.0
Chalcedony      0.0            0.0
csh_1.2                        0.0                     0.0
csh_0.8                        0.0           0.0
Gibbsite        0.0            0.0
Gismondine      0.0            0.0
Goethite        0.0            0.0
Gyrolite        0.0            0.0
Kaolinite       0.0            0.0
Laumontite      0.0            0.0
magnetite       0.0            0.0
Prehnite        0.0            0.0
Straetlingite   0.0            0.0
# Corrosion off gas
O2,g            0.0            0.0
H2,g            0.0            0.0
```

```
SOLUTION 2
-pH 7.0  charge
-water  0.15538
units mol/kgw
Al   9.66E-06
C    1.53E-03
Ca   1.48E-03
Cl   1.61E-03
K    1.12E-01
Mg   1.48E-04
Na   5.01E-02
S    3.53E-04
Si   8.38E-05

#EXCHANGE 2
#NaX  0.088717949
#ClXa 0.044358974
#HX       0.088717949
#OHXa 0.044358974

KINETICS  2
#H4ISAH
#-m  0.052384999
#-m0 0.052384999
#Fe,element
#-m  4.24251E+00
#-m0 4.24251E+00

USER_GRAPH
-headings Time sim_no step_no pH  H4IsaH Steel Portlandite CSH_1.6
CSH_1.2 CSH_0.8
-initial_solutions true
-connect_simulations true
-plot_concentration_vs time
-axis_scale y_axis 7 14 1
-start
10 graph_x sim_time/3600/24/365
20 REM graph_y time/3600/24/365
30 graph_y sim_no
40 graph_y step_no
50 graph_y -la("H+")
60 graph_sy KIN("H4IsaH")
65 graph_sy KIN("Fe,element")
70 graph_sy equi("Portlandite")
80 graph_sy equi("CSH_1.6")
90 graph_sy equi("CSH_1.2")
100 graph_sy equi("CSH_0.8")
-end
```

```
TRANSPORT     # 0- 2000 AD
-cells  2
-lengths 0.5 10
-dispersivities     0.002
-shifts 0          # 0 pore water exchanges during 0-2000 AD
-punch_cells 1
-flow_direction forward
-time_step 2.8288E+13
-boundary_conditions flux flux
-diffusion_coefficient   0.3e-9

END

TRANSPORT     #  2000-3000 AD
-cells  2
-shifts 0          # 0 pore water exchanges during 2 000 -  3 000 AD
-punch_cells 1
-flow_direction forward
-time_step 1.5756E+11

END

TRANSPORT     # > 3000 AD
-cells  2
-shifts 51         # 51 pore water exchanges during 3 000 -  100 000 AD
-punch_cells 1
-flow_direction forward
-time_step 6.1107E+10

END
```

Input file 6 Silo

```
TITLE Silo
PRINT
-species false
-saturation_indices false

SOLUTION_MASTER_SPECIES
Isa           H4Isa-            0.0           Isa       179.147

SOLUTION_SPECIES
#To improve convergence
H2O + 0.01e- = H2O-0.01;     log_k   -9.0

# From PCHatches 18.1
H4Isa-        = H4Isa-;         log_k 0;     delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;         log_k 4;     delta_h 0 kcal
Ca+2 + H4Isa- = CaH3Isa + H+;   log_k -10.4; delta_h 0 kcal
Ca+2 + H4Isa- = CaH4Isa+1;      log_k  1.7;  delta_h 0 kcal
H+ + H4Isa-   = H4IsaH;         log_k  4;    delta_h 0 kcal

PHASES
# From PCHatches 18.1
Ca(H4Isa)2
              Ca(H4Isa)2 = Ca+2 + 2H4Isa-
              log_k -6.4
              delta_h  0 kcal


H4IsaH
              H4IsaH = H+ + H4Isa-
              log_k -10

EXCHANGE_MASTER_SPECIES
# Cationic (X) and anionic (Xa) ion exchangers
X             X-
Xa            Xa+

EXCHANGE_SPECIES
# DOW cation exchange 4% DVB
X-               =   X-                               ; log_k 0.0
X- + H+          =   HX                               ; log_k 0.0
HX + Li+      =  LiX   + H+                  ; log_k   -0.119
HX + Na+      =  NaX   + H+                  ; log_k   0.079
HX + NH4+     =  NH4X  + H+                  ; log_k   0.158
HX + K+            = KX    + H+                ; log_k   0.236
HX + Rb+      =  RbX   + H+                  ; log_k   0.270
HX + Cs+      =  CsX   + H+                  ; log_k   0.305
HX + Ag+      =  AgX   + H+                  ; log_k   0.554
```

```
HX + Tl+      = TlX   + H+                ; log_k   0.706
2HX + UO2++   = UO2X2 + 2H+               ; log_k   0.253
2HX + Mg++    = MgX2  + 2H+               ; log_k   0.348
2HX + Zn++    = ZnX2  + 2H+               ; log_k   0.375
2HX + Co++    = CoX2  + 2H+               ; log_k   0.389
2HX + Cu++    = CuX2  + 2H+               ; log_k   0.396
2HX + Cd++    = CdX2  + 2H+               ; log_k   0.407
2HX + Ni++    = NiX2  + 2H+               ; log_k   0.417
2HX + Ca++    = CaX2  + 2H+               ; log_k   0.497
2HX + Sr++    = SrX2  + 2H+               ; log_k   0.551
2HX + Pb++    = PbX2  + 2H+               ; log_k   0.696
2HX + Ba++    = BaX2  + 2H+               ; log_k   0.753
# DOW Anion exchange Type 1
Xa+             = Xa+                               ; log_k 0.0
Xa+  +  OH-   = OHXa                                ; log_k 0.0
#OHXa +  OH-  = OHXa   + OH-              ; log_k   0.000
OHXa + I-       = IXa          + OH-      ; log_k   2.243
OHXa + HSO4-    = HSO4Xa + OH-            ; log_k   1.929
OHXa + ClO3-  = ClO3Xa + OH-              ; log_k   1.869
OHXa + NO3-   = NO3Xa  + OH-              ; log_k   1.813
OHXa + Br-    = BrXa   + OH-              ; log_k   1.699
OHXa + CN-    = CNXa   + OH-              ; log_k   1.447
OHXa + HSO3-  = HSO3Xa + OH-              ; log_k   1.431
OHXa + BrO3-  = BrO3Xa + OH-              ; log_k   1.431
OHXa + NO2-   = NO2Xa          + OH-      ; log_k   1.380
OHXa + Cl-    = ClXa           + OH-      ; log_k   1.342
OHXa + HCO3-  = HCO3Xa + OH-              ; log_k   0.778
OHXa + IO3-   = IO3Xa          + OH-      ; log_k   0.740
OHXa + F-       = FXa    + OH-            ; log_k   0.204

RATES
H4IsaH
#Degradation rate for paper according to Glaus 2008
-start
20  if (m <= 0) then goto 200
35  k1 = 4.3E-3/3600
44  kt = 4.3E-4/3600
55  kh = 1.6E-7/3600
65  Gr = 3.5E-3
100 rate = (exp(-kh*sim_time)*kt*kt*exp(-kt*sim_time)*Gr*k1)/kt^2-kh*-
exp(-kh*sim_time)*(((1-exp(-kt*sim_time))*Gr*k1)/kt-1)
190 moles = rate*time*m
200 SAVE moles
-end
```

```
Fe,element
#carbonsteel
#Corrosion of carbon steel
-start
20 if (m <= 0) then goto 200
30 R = 1.64E-03/365/24/3600
100 rate = R
180 moles = rate*time
190 REM moles = rate*time
200 SAVE moles
-end

Quartz,alpha
-start
10 dif_temp = 1/TK - 1/298
20 pk_w = 13.7 + 4700.4 * dif_temp
40 moles = (m/m0)^0.67 * 10^-pk_w *(1 - SR("Quartz,alpha"))
50 save moles * time
-end

SOLUTION 0
pH 7.0 charge
-water  1.85
units mol/kgw
# Saline groundwater
#C            1.48E-03
#Ca           1.50E-02
#Cl           9.87E-02
#K            5.12E-04
#Mg           6.17E-03
#Na           6.53E-02
#S            3.64E-03
#Si           1.83E-04

#Temperate-periglacial
C             4.92E-3
Ca            1.25E-3
Cl            5.36E-3
K             1.28E-4
Mg            4.94E-4
Na            7.83E-3
S             5.21E-4
Si            2.00E-4
```

```
#Glacial derived water
#C            6.40E-04
#Ca           2.96E-04
#Cl           8.19E-06
#K            1.65E-05
#Mg           1.04E-06
#Na           4.35E-06
#S            1.25E-05
#Si           2.13E-04

########### WALL ##############

EQUILIBRIUM_PHASES 1
csh_1.6         0              4.178860782
portlandite     0              4.038316137
ettringite      0              0.09369643
C3AH6           0              0.262350004
hydrotalcite  0 0.037478572
Hematite        0              0.196762503
#SiO2           0              155.929599
# Secondary phases
Boehmite      0.0              0.0
Calcite       0.0              0.0
Chalcedony    0.0              0.0
csh_1.2                        0.0                   0.0
csh_0.8                        0.0         0.0
Gibbsite      0.0              0.0
Gismondine    0.0              0.0
Goethite      0.0              0.0
Gyrolite      0.0              0.0
Kaolinite     0.0              0.0
Laumontite    0.0              0.0
magnetite     0.0              0.0
Prehnite      0.0              0.0
Straetlingite 0.0              0.0
# Corrosion off gas
O2,g          0.0              0.0
H2,g          0.0              0.0

SOLUTION 1
-pH 7.0  charge
-water  1.85
units mol/kgw
Al   1.38E-05
C    8.25E-05
Ca   1.58E-03
Cl   0.00E+00
```

```
K    1.60E-01
Mg   1.93E-09
Na   6.82E-02
S    2.81E-04
Si   3.40E-05

KINETICS 1
Quartz,alpha
-m   155.929599
-m0  155.929599

####### WASTE ##############

EQUILIBRIUM_PHASES 2
#Concrete
csh_1.6          0              5.20E+01
portlandite      0              5.03E+01
ettringite       0              1.17E+00
C3AH6            0              3.24E+00
hydrotalcite  0  4.70E-01
Hematite         0              2.48E+00
#SiO2            0              2.01E+02
#Metals
Al,element       0.0                          3.40E-01
#Fe,element      0.0                          8.22E+01
# Ion exchange resin, see EXCHANGE
# Secondary phases
Boehmite         0.0            0.0
Calcite          0.0            0.0
Chalcedony       0.0            0.0
csh_1.2                         0.0                     0.0
csh_0.8                         0.0           0.0
Gibbsite         0.0            0.0
Gismondine       0.0            0.0
Goethite         0.0            0.0
Gyrolite         0.0            0.0
Kaolinite        0.0            0.0
Laumontite       0.0            0.0
magnetite        0.0            0.0
Prehnite         0.0            0.0
Straetlingite    0.0            0.0
# Corrosion off gas
O2,g             0.0            0.0
H2,g             0.0            0.0
```

```
SOLUTION 2
-pH 7.0  charge
-water  1.85
units mol/kgw
Al   9.66E-06
C    1.53E-03
Ca   1.48E-03
Cl   1.61E-03
K    1.12E-01
Mg   1.48E-04
Na   5.01E-02
S    3.53E-04
Si   8.38E-05

EXCHANGE 2
#NaX     2.88E+00
#ClXa 1.44E+00
#HX      2.88E+00
#OHXa 1.44E+00

KINETICS  2
#H4ISAH
#-m          0.135642796
#-m0         0.135642796
#Fe,element
#-m          8.22E+01
#-m0 8.22E+01
Quartz,alpha
-m 2.01E+02
-m0 2.01E+02

USER_GRAPH
-headings Time sim_no step_no pH  H4IsaH Steel Portlandite CSH_1.6
CSH_1.2 CSH_0.8
-initial_solutions true
-connect_simulations true
-plot_concentration_vs time
-axis_scale y_axis 7 14 1
-start
10 graph_x sim_time/3600/24/365
20 REM graph_y time/3600/24/365
30 graph_y sim_no
40 graph_y step_no
50 graph_y -la("H+")
60 graph_sy KIN("H4IsaH")
65 graph_sy KIN("Fe,element")
70 graph_sy equi("Portlandite")
```

```
80 graph_sy equi(“CSH_1.6”)
90 graph_sy equi(“CSH_1.2”)
100 graph_sy equi(“CSH_0.8”)
-end

TRANSPORT     # 0- 2000 AD
-cells  2
-punch_cells 1                  # 1 = Wall, 2 = Waste
-lengths 1.0 10.0
-dispersivities   0.00
-shifts 0          # 0 pore water exchanges during 0 - 2 000 AD
-flow_direction forward
-time_step 6.1932E+13
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT     # 2000- 3000 AD
-cells  2
-punch_cells 1     # 1 = Wall, 2 = Waste
-lengths 1.0 10.0
-dispersivities   0.00 # 0.002
-shifts 0          # 0 pore water exchanges during 2 000 - 3 000 AD
-flow_direction forward
-time_step 4.0814E+11
-boundary_conditions flux flux
-diffusion_coefficient 0.3e-9

END

TRANSPORT     # > 3000 AD
-cells  2
-punch_cells 1     # 1 = Wall, 2 = Waste
-shifts 15         # 15 pore water exchanges during 3 000 - 100 000 AD
-flow_direction forward
-time_step 2.0557E+11

END
```