

**Thermo-Hydro-Geochemical Evolution Influences on the Concrete Cask in
Long-Term Storage Facility of Spent Fuel – 16171**

Wen-Sheng Lin*, Chen-Wuing Liu**, Ming-Hsu Li***

* Hydrotech Research Institute, National Taiwan University, Taiwan

** Department of Bioenvironmental Systems Engineering, National Taiwan
University, Taiwan

*** Institute of Hydrological and Oceanic Sciences, National Central University,
Taiwan

ABSTRACT

Due to humid environment and weather condition in Taiwan's island, as well as the acid rain environment resulting from sulfur dioxide emissions, the concrete cask might be damaged or degraded under the effect of humid, salt, acid rain, and sulfate attack on cementitious materials. These degradation factors could influence the safety design of the long-term spent fuel storage facility. Due to the long-term decay heat of spent fuel and severe environments to be encountered, the thermo-hydro-geochemical evolution could play an important role in the safety assessment of concrete-cask storage facility. The effects of humid, salt, acid rain, and sulfate attack on the degradation of cementitious materials of concrete-cask facility in thermo-hydro-geochemical evolution under rain water quality conditions have been investigated. The results show that the main processes responsible for concrete degradation are species induced from hydrogen ion, sulfate and chloride. For most storage and disposal casks and conditions, the American Concrete Institute nuclear safety code requirements (ACI-349 Appendix A [1]) specify a bulk-concrete shield temperature limit of 150°F (65.5°C). However, localized temperatures at the inner walls of the shielding casks could reach 200-300°F (93-149°C). Simulation of geochemical degradation reactions for 100 years of cask storage under two temperature scenarios was performed. The results indicate that the hydrogen ion, sulfate anion, and chloride do not result in the dissolution of portlandite, or formation of ettringite and Friedel's salt. Therefore, these results indicate the concrete cask may remain in a durable condition.

INTRODUCTION

There are three nuclear power plants with six existing nuclear power units which consist of four boiling water reactors (BWR) and two pressurized water reactors (PWR) in Taiwan. These nuclear power plants are operated by the government-owned utility of Taiwan Power Company (TPC) and provide a total installed capacity of 5.144 GWe

which contribute about 19% of the total electricity in Taiwan. Discharged spent fuels from the reactor must be continually cooled, due to the higher activity and heat of the spent fuels, they are first stored in the spent fuel pool of nuclear power plants to let the activity and heat decay and then continue follow-up management. Three nuclear power plants operating for 40 years and have produced 4,950 metric tons of spent nuclear fuel while the fourth nuclear power plant (Lungmen) will produce roughly 2,497 metric tons. The locations of nuclear power plants in Taiwan are depicted in Figure 1. The pool capacities and the spent nuclear fuel storage quantities for the first three nuclear power plants are shown in Table I.[2-3]

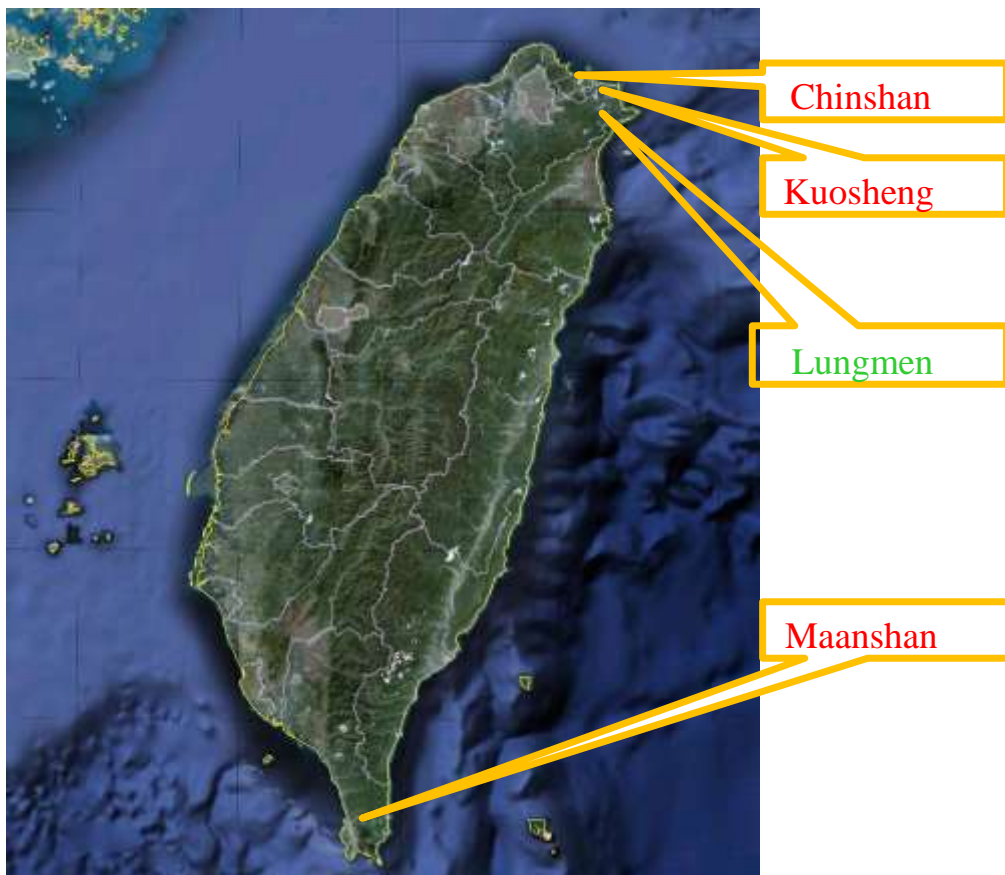


Fig. 1. Locations of Nuclear Power Plants in Taiwan

TABLE I. Pool Capacities and Spent fuel Storage Quantities in Nuclear power

Nuclear power plant	Commerical Date	Pool capacity (Assembly)	Quantity after 40-yr Operation	Current Inventory (As of 12/2012)	Time Reaches Full Pool Capacity
Chinshan1	12/6/1978	3,083	3,76	2,870	2,014
Chinshan2	7/16/1979	3,083	3,76	2,856	2,016
Kuosheng1	12/28/198	5,026	5,76	4,042	2,016
Kuosheng2	3/15/1983	5,026	5,76	3,872	2,016
Maanshan1	7/27/1984	2,151	1,92	1,251	2,025
Maanshan2	5/18/1985	2,159	1,92	1,214	2,026

The present spent fuel management policies and practices in Taiwan are “storage in spent fuel pools for the near term, onsite dry storage for the medium term, and final disposal for the long term”. After spent fuels are discharged from the reactor, because of the higher activity and heat, they are first stored in the spent fuel pool of nuclear power station to let the activity and heat decay prior to follow-up management. Taiwan’s Atomic Energy Council (AEC) and TPC have proposed the new Independent Spent Fuel Storage Installation (ISFSI) located at the Chinshan Nuclear Power Plant site near the coast in northern Taiwan to store 1400 spent nuclear fuel assemblies. [3-4]



Fig. 2. Schematic depiction of ISFSI Dry-Storage Facility at Chinshan

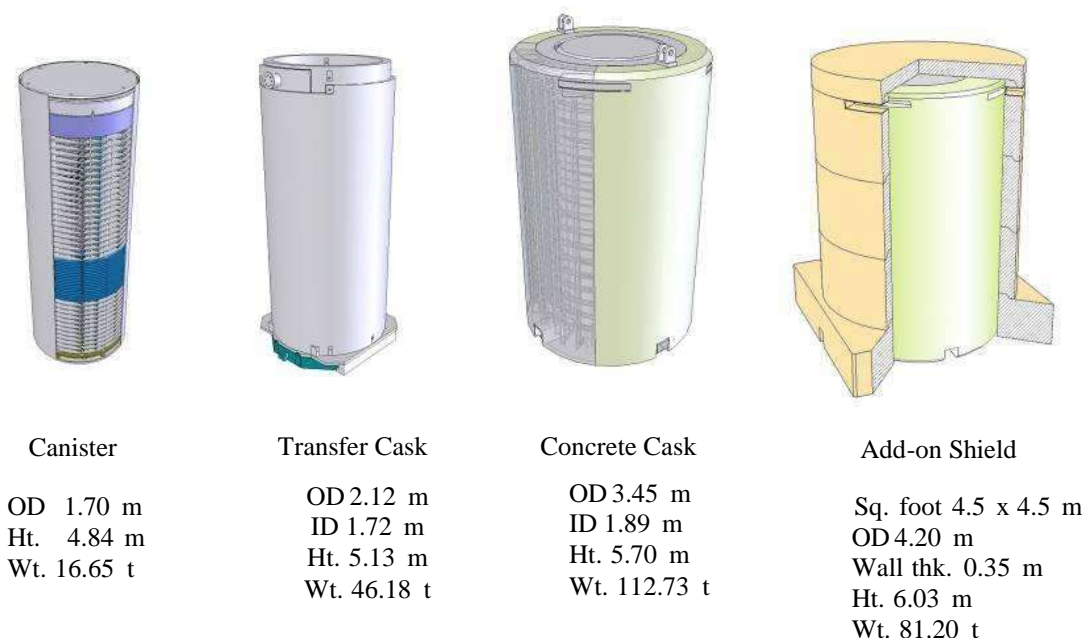


Fig. 3. The major components of canister, transfer cask, concrete cask and add-on shield.

The ISFSI technology transfer between Taiwan’s Institute of Energy Research (INER), and NAC International have recommended a type of vertical concrete cask design, the NAC-UMS storage system (Certificate no. 1015), which is an eligible system approved by the U.S. Nuclear regulatory Commission (USNRC). The storage capacity of the site contains 25 NAC UMS-56 concrete casks and stores 56 BWR spent nuclear fuel assemblies each cask, also is designed to store up to 30 casks, or 1680 assemblies.[2-4] The schematic depiction of ISFSI dry storage facility at Chinshan is shown in Figure 2. The major components which consist of the outer diameter (OD), inner diameter (ID), height (Ht.) and weight (Wt.) of canister, transfer cask, concrete cask and add-on shield are illustrated in Figure 3.

Due to humid environment and weather condition in Taiwan’s island, as well as the acid rain environment resulting from sulfur dioxide emissions, the concrete cask might be damaged or degraded under the effect of humid, salt, acid rain, and sulfate attack on cementitious materials. These degradation factors could influence the safety design of long-term storage facility of spent fuel. Due to the long-term decay heat of spent fuel and severe environments to be encountered, the thermo-hydro-geochemical evolution could play an important role in the safety assessment of concrete-cask storage facility. Degradation of spent fuel storage facilities for long-term storage (e.g. 100 years) under the aggressive situations of thermo-hydro-geochemical evolution should to be examined. HYDROGEOCHEM5.0

model was applied to simulate the effect of humid, salt, acid rain, and sulfate attack on the degradation of cementitious materials of concrete-cask facility under thermo-hydro-geochemical evolution under different rain water quality conditions.

To obtain further insights into these interactions and provide a detailed overview of the concrete degradation evolution in the thermo-hydro-geochemical environment of the concrete cask, a reactive chemical transport model of HYDROGEOCHEM 5.0 [5] was used to assess the thermo-hydro-geochemical influences on concrete cask degradation. The paper only discusses the degradation induced by geochemical reaction, and appears to be modeling those reactions without regard for the potential for fracturing that may induce additional pathways for infiltration and further surface area for internal degradation. The results of this study only offer a part performance information on the degradation evolution behavior of the concrete cask.

METHODOLOGY

Concrete is principally comprised of a mixture of cement, water, and aggregates. The mineral compounds in cement are calcium silicates (Ca_3SiO_5 and Ca_2SiO_4), aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$), and ferrite ($4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) abbreviated as C_3S , C_2S , C_3A and C_4AF . As these constituents mix with water, calcium-silicate-hydrate (C-S-H), portlandite ($\text{Ca}(\text{OH})_{2(s)}$), ettringite (Aft), monosulfate (AFm), hydrogarnet etc. will form in the cement hydration process. These hydration products also control the setting and hardening of concrete. These alterations have direct consequences on the engineering properties of the concrete cask.

A number of reactions may occur simultaneously between cement-based materials of cask and the rain water concentration (for example, the pH, and ionic composition of chloride, sulfate), including the dissolution of portlandite that is generated from the intrusion of hydrogen ion, increase of the concentration of calcium in the pore solution, formation of ettringite by sulfate attacking the cement, and dissolution of Calcium-Silicate-Hydrate (CSH) gel by chloride entering the cement, and the formation of Friedel's salt.

Due to the long-term decay heat of spent fuel and severe environments to be encountered, the thermo-hydro-geochemical evolution could play an important role in the safety assessment of concrete-cask storage facility. HYDROGEOCHEM 5.0 is the simulator of coupled fluid flow, hydrologic transport, heat transfer, and biogeochemical transport under variably saturated conditions in three dimensions. HYDROGEOCHEM 5.0 model has been validated against experimental data for effectiveness at thermo-hydro-geochemical evolution modeling[5]. To assess the thermo-hydro-geochemical evolution influences on the concrete cask in long-term

storage facility of spent fuel, a three-dimensional model of coupled fluid flow, thermal transport, and hydrogeochemical transport through variably saturated conditions model, HYDROGEOCHEM 5.0[5], was used to simulate the reactive chemical transport processes that are involved in the concrete degradation in the concrete cask.

The composition and phase development of hydration products as the chemical reaction of cement with rain water influences the lifetime performance of the concrete cask. The thermodynamic modeling of Portland cement in the cementitious media was formulated and applied to assess the performance of concrete cask. Blanc et al. [6-7] established the thermodynamic data of the chemical model for the phases of system CaO-SiO₂-H₂O, CaO-Al₂O₃-SiO₂-H₂O, CaO-Al₂O₃-SO₃-CO₂-Cl-H₂O in the water and cement-based materials. In addition, Galíndez [8] used the reactive transport model to simulate the degradation of cementitious materials. These thermodynamic data allow the reactive transport model to simulate the composition and concentration of chemical species under various thermos-hydro-geochemical environments. Table II shows the Enthalpy parameter of chemical species [6-7]. Table III lists the rain water quality [9] as the boundary condition of concrete cask in the HYDROGEOCHEM modeling. Table IV indicates the physical parameters of the concrete used in the study.

The PHREEQCI [10] was first used to calculate the concrete porewater composition that equilibrated with rainwater and cement mineral. Table V represents the porewater composition as the initial conditions of component concentration. Table VI expresses the precipitation-dissolution reactions of cement mineral that are associated with the described reactions of cementitious materials degradation in a water-solid system of this study. Table VII denotes aqueous complexation reactions considered in this study.

Table II Enthalpy parameters of chemical species used in this study.

No.	Chemical species	Enthalpy (KJ/mol)	No.	Chemical species	Enthalpy (KJ/mol)
1	Na+	-240.34	21	CaOH+	-751.62
2	K+	-252.14	22	CaSO ₄	-1448.05
3	Ca ⁺⁺	-543	23	CO ₃ ⁻⁻	-675.23
4	Al ⁺⁺⁺	-538.4	24	KCl	-415.04
5	H+	0	25	KOH	-471.53
6	HCO ₃ ⁻	-689.93	26	KSO ₄ ⁻	-1158.33
7	Cl ⁻	-167.08	27	NaCl	-405.42
8	SO ₄ ⁻⁻	-909.34	28	NaCO ₃ ⁻	-878.19

No.	Chemical species	Enthalpy (KJ/mol)	No.	Chemical species	Enthalpy (KJ/mol)
9	H4SiO4	-1461.1	29	NaOH	-472.78
		9			
10	OH-	-230.02	30	NaSO4-	-1152.49
11	AlH3SiO4++	-1922.2	31	HSO4-	-885.75
		1			
12	H2SiO4--	-1386.7	32	Calcite	-1207
		2			
13	Ca(H3SiO4)+	-1972.5	33	SiO2(s)	-919.64
		6			
14	H3(SiO4)-	-1431.8	34	GYPSUM	-2022.95
		3			
15	NaH3SiO4(aq)	-1693.8	35	Portlandite	-984.55
		1			
16	Al(OH)4-	-1500.8	36	Ettringite	-17544.5
		4			
17	KAl(OH)4	-1722.1	37	Hydrogarnet	-5548
		9			
18	NaAl(OH)4	-1731.7	38	Monocarboaluminate	-8175.75
		1			
19	CaCl+	-702.93	39	Friedelssalt	-7670.04
20	CaCO3	-1203.4	40	Thaumasite	-8682.04

Table III Rain water quality used in the thermodynamic equilibrium model.

Species	pH	Cl-	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Concentration (Units:umol/l)	3.48	660.9	475.2	674.6	31.4	157.6	118.6

Table IV Physical parameters used in this study.

Media	Porosity (%)	Diffusion coefficient (m ² /s)	Bulk density (kg/m ³)	Specific Heats (J/g K)	Thermal conductivity (W/m K)
Concrete	0.15	3.0×10 ⁻¹²	2030	1.023	0.663

Table V Initial conditions of component concentration (mole/l) used in this study.

Component	Na ⁺	K ⁺	Ca ²⁺	Al ³⁺	OH ⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	H ₄ SiO ₄
I.C	6.908×10 ⁻²	0.2665	29.906	2.628	21.1	1.394×10 ⁻¹¹	5.64×10 ⁻⁵	1.633×10 ⁻³	9.1984

Table VI Precipitation-dissolution reactions of cement mineral considered in this study.

Precipitation-dissolution reactions of cement mineral (25°C)				
No	Mineral	Reaction	log K	Molar volume (dm ³ /mole)
1	Calcite	HCO ₃ ⁻ + Ca ²⁺ + OH ⁻ = CaCO ₃ + H ₂ O	12.15	0.03693
2	Portlandite	Ca ²⁺ + 2OH ⁻ = Ca(OH) ₂	5.20	0.03300
3	Ettringite	2Al ³⁺ + 6Ca ²⁺ + 26H ₂ O + 3SO ₄ ²⁻ + 12OH ⁻ = Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O	111.0	0.71032
4	Quartz	H ₄ SiO ₄ = SiO ₂ + 2H ₂ O	3.98	0.02269
5	Gypsum	Ca ²⁺ + SO ₄ ²⁻ + 2H ₂ O = CaSO ₄ ·2H ₂ O	4.58	0.07470
6	Hydrogarnet	2Al ³⁺ + 3Ca ²⁺ + 12OH ⁻ = Ca ₃ Al ₂ (OH) ₁₂	87.68	0.14952
7	Friedel's salt	2Al ³⁺ + 4Ca ²⁺ + 2Cl ⁻ + 4H ₂ O + 12OH ⁻ = 2Ca ₂ Al(OH) ₆ Cl·2H ₂ O	93.07	0.27624
8	Thaumasite	3Ca ²⁺ + H ₄ SiO ₄ + SO ₄ ²⁻ + HCO ₃ ⁻ + 11H ₂ O + 3OH ⁻ = CaSiO ₃ ·CaSO ₄ ·CaCO ₃ ·15H ₂ O	31.70	0.32940
9	Monocarboaluminate	2Al ²⁺ + HCO ₃ ⁻ + 4Ca ²⁺ + 3.68H ₂ O + 13OH ⁻ = 3CaO·Al ₂ O ₃ ·CaCO ₃ ·10.68H ₂ O	101.4	0.26196

SIMULATION SCENARIO

From ACI-349 Appendix A[1], for most storage and disposal casks and conditions, the bulk-concrete shield temperature is limited to 150°F(65.5°C). But localized temperatures at the inner walls of the shielding casks could be up to 200°F(93°C). Therefore, two cases of simulations are as follows.

Case 1: bulk-concrete shield maximum temperature is 66°C

Case 2: bulk-concrete shield maximum temperature is 93°C

The study considered the thermo-hydro-geochemical transport of 9 components, as follows: Na⁺, K⁺, Ca²⁺, Al³⁺, H⁺, HCO₃⁻, Cl⁻, SO₄²⁻, H₄SiO₄, 22 aqueous species, and 9 precipitation/dissolution reactions. The model simulation time was 100 years with an initial time-step of 1.0 x 10⁻⁵ year, and a maximal allowable time-step of 0.01 year.

Table VII Aqueous complexation reactions considered in this study.

No.	Species	Aqueous complexation reactions	Log K(25°C)
1	OH ⁻	H ₂ O = OH ⁻ + H ⁺	-14
2	AlH ₃ SiO ₄ ⁺⁺	Al ⁺³ + H ₄ SiO ₄ = AlH ₃ SiO ₄ ⁺² + H ⁺	-2.38
3	H ₂ SiO ₄ ⁻⁻	H ₄ SiO ₄ = H ₂ SiO ₄ ⁻² + 2 H ⁺	-23.14
4	Ca(H ₃ SiO ₄) ⁺	Ca ⁺² + H ₄ SiO ₄ = CaH ₃ SiO ₄ ⁺ + H ⁺	-8.83
5	H ₃ (SiO ₄) ⁻	H ₄ SiO ₄ = H ₃ SiO ₄ ⁻ + H ⁺	-9.84
6	NaH ₃ SiO ₄ ,aq	Na ⁺ + H ₄ SiO ₄ = NaH ₃ SiO ₄ ,aq + H ⁺	-8.01
7	Al(OH) ₄ ⁻	Al ⁺³ + 4 H ₂ O = Al(OH) ₄ ⁻ + 4 H ⁺	-22.87
8	KAl(OH) ₄	K ⁺ + Al ⁺³ + 4 H ₂ O = KAl(OH) ₄ + 4 H ⁺	-24.22
9	NaAl(OH) ₄	Na ⁺ + Al ⁺³ + 4 H ₂ O = NaAl(OH) ₄ + 4 H ⁺	-23.63
10	CaCl ⁺	Ca ⁺⁺ + Cl ⁻ = CaCl ⁺	-0.29
11	CaCO ₃	Ca ⁺² + HCO ₃ ⁻ = CaCO ₃ + H ⁺	-7.11
12	CaOH ⁺	Ca ⁺² + H ₂ O = CaOH ⁺ + H ⁺	-12.78
13	CaSO ₄	Ca ⁺² + SO ₄ ⁻² = CaSO ₄	2.31
14	CO ₃ ⁻⁻	HCO ₃ ⁻ = CO ₃ ⁻² + H ⁺	-10.33
15	KCl	K ⁺ + Cl ⁻ = KCl	-0.5
16	KOH	K ⁺ + H ₂ O = KOH + H ⁺	-14.46
17	KSO ₄ ⁻	K ⁺ + SO ₄ ⁻² = KSO ₄ ⁻	0.88
18	NaCl	Na ⁺ + Cl ⁻ = NaCl	-0.5
19	NaCO ₃ ⁻	Na ⁺ + HCO ₃ ⁻ = NaCO ₃ ⁻ + H ⁺	-9.039
20	NaOH	Na ⁺ + H ₂ O = NaOH + H ⁺	-14.75
21	NaSO ₄ ⁻	Na ⁺ + SO ₄ ⁻² = NaSO ₄ ⁻	0.94

RESULT AND DISCUSSION

Lune et al. [11] based on the reviewed experimental work and modeling study, showed that the hydrogen ion results in the dissolution of portlandite and increases the concentration of calcium in the pore water. The sulfate anion reacts with cement to form ettringite. The chloride from the pore water enters the cementitious materials

to form Friedel's salt. Thaumasite and monocarboaluminate are also formed as carbonate aggregates by sulfate attack, and carbonate intrusion, respectively. The ettringite can cause volumetric expansion and eventually lead to fracture development in the concrete. An excess of chlorite may produce corrosion of the reinforcement element and also cause a volume expansion, which may lead to micro-fracturing in the concrete. The formation of ettringite, Friedel's salt thaumasite and monocarboaluminate are also associated with a volume increase, which could eventually leads to fracture formation and weakens the concrete. The concrete cask may form the degradation species in effects of humid, salt, acid rain, and sulfate attack on the degradation of cementitious materials of concrete-cask facility under thermo-hydro-geochemical evolution and could cause volumetric expansion.

Figure 3 and Figure 4 show the sulfate and chloride ion distribution after 100 years in case 1 (66°C) and case 2 (93°C) at the front view and bottom view, respectively, resulting from continuous sulfate, chloride ion and carbonate intrusion to the concrete cask from the rain water. Nevertheless, Figure 5 indicates that Ettringite, Friedel's salt, Thaumasite, and Monocarboaluminate do not form on the concrete surface and within the concrete cask. Actually, this study also show these degradation species are not presented for the period between 0 and 100 years. Figure 6 showed the Portlandite distribution for case 1 and case 2 after 100 years at the front view and cross-section view, respectively. The amount of portlandite precipitated in the case 1 and 2 was the same. The portlandite formed all over the concrete cask in less than 100 years. Portlandite remained stable at all times.

CONCLUSION AND SUGGESTION

Results from previously published literature showed that the main processes responsible for concrete degradation are species induced from hydrogen ion, sulfate and chloride. This study simulated 100 years of storage for two temperature scenarios. The results indicated that the hydrogen ion, sulfate anion, and chloride do not result in the dissolution of portlandite, or formation of ettringite and Friedel's salt. Therefore, the concrete cask may remain in a durable condition.

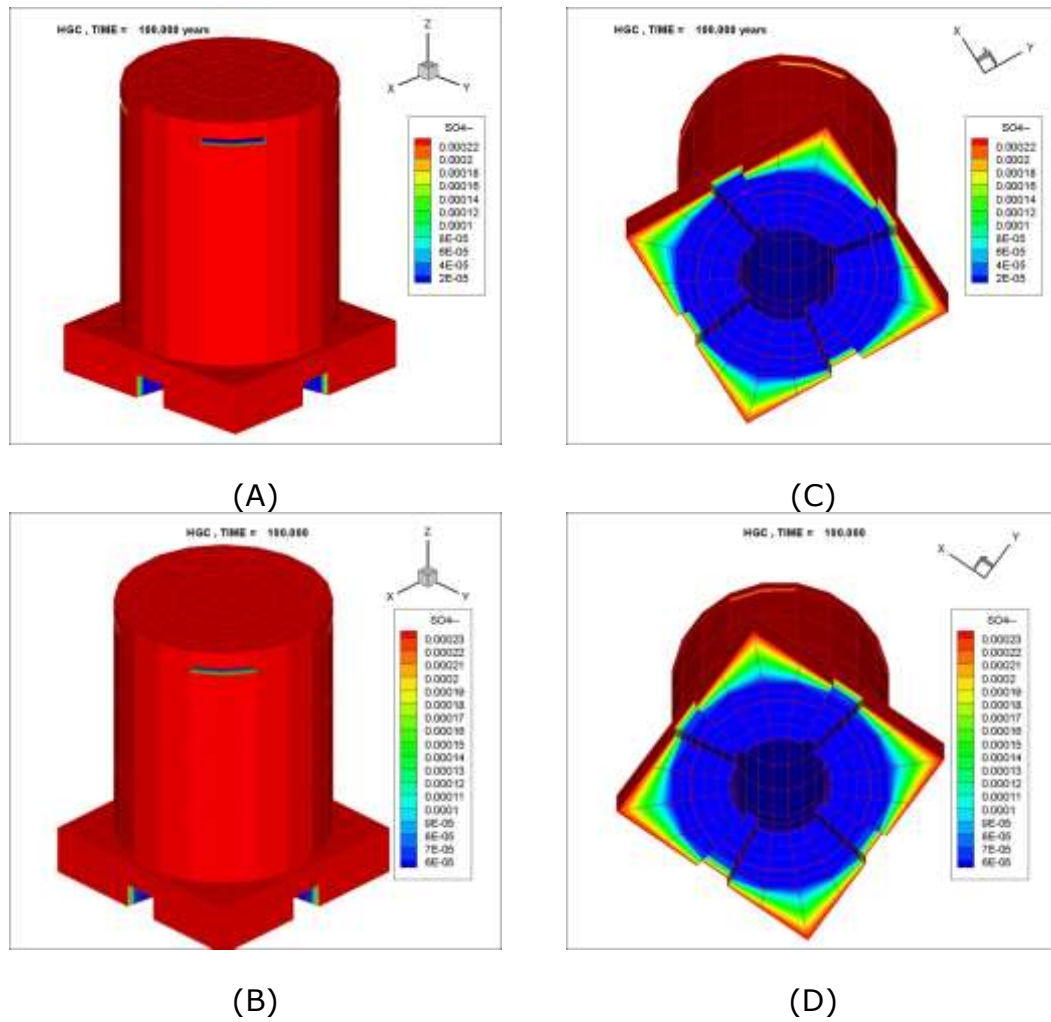


Fig. 3. Sulfate distribution (Unit: Mole/l) after 100 years: (A) Front view in case 1 (66°C) (B) Front view in case 2 (93°C), (C) Bottom view in case 1 (66°C), (D) Bottom view in case 2 (93°C)

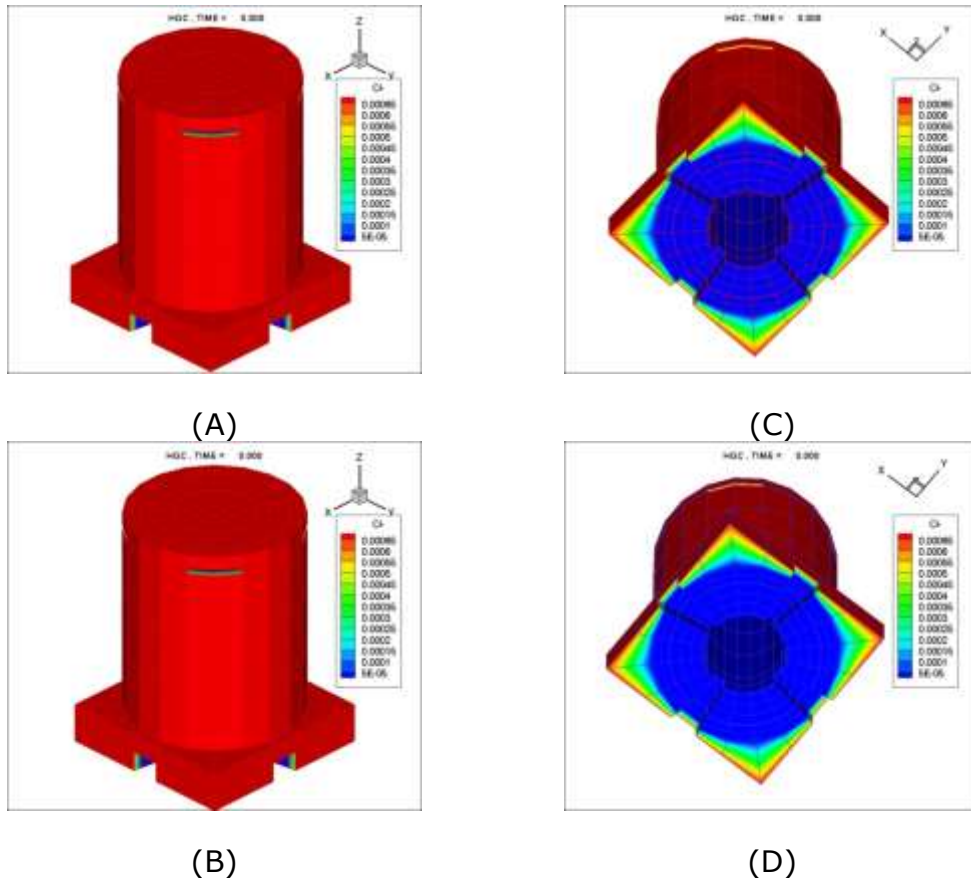


Fig. 4. Chloride ion distribution (Unit: Mole/l) after 100 years: (A) Front view in case 1 (66°C) (B) Front view

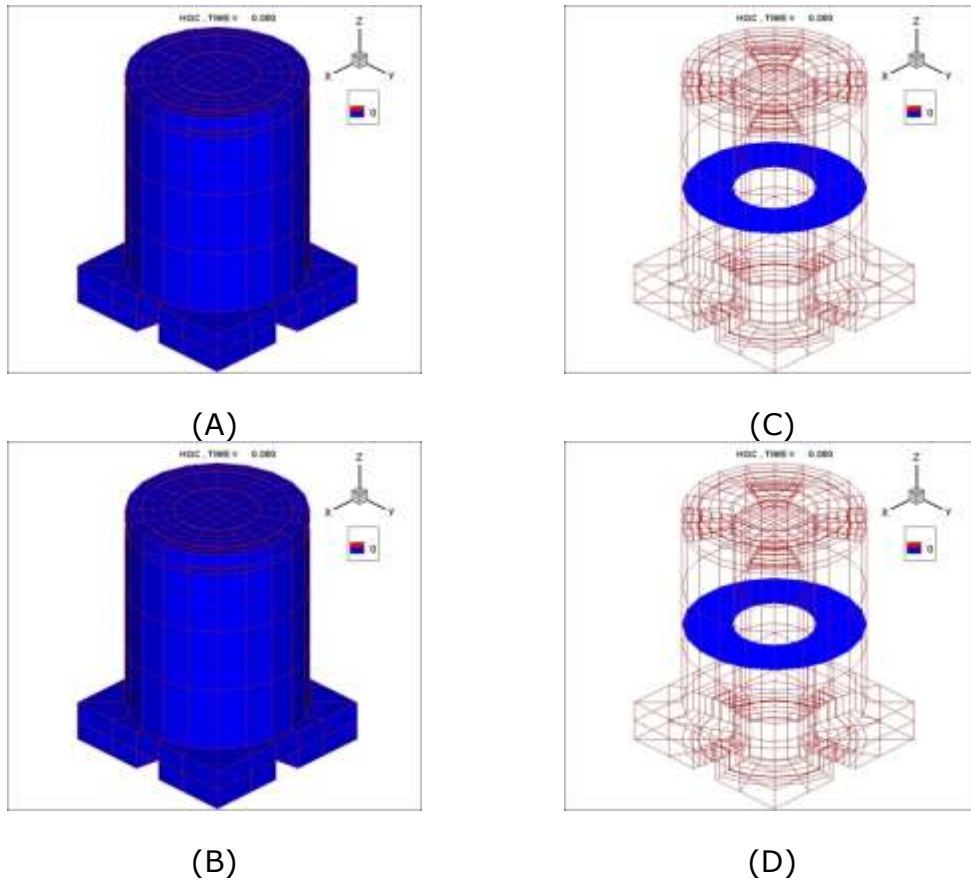


Fig. 5. Ettringite, Friedel's salt, Thaumassite, and Monocarboaluminate distribution (Unit: Mole/l) for case 1 and case 2 after 100 years: (A) Front view in case 1 (66°C) (B) Front view in case 2 (93°C), (C) Cross-section view in case 1 (66°C), (D) Cross-section view in case 2 (93°C)

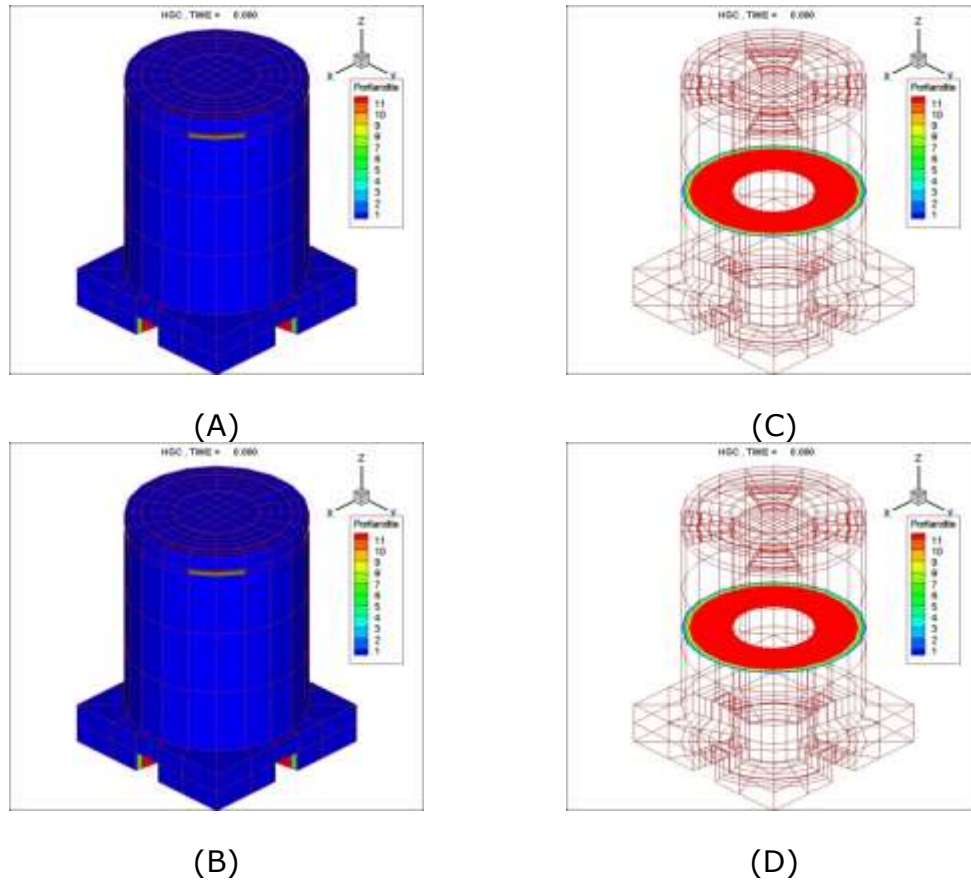


Fig. 6. Portlandite distribution (Unit: Mole/l) for case 1 and case 2 after 100 years: (A) Front view in case 1 (66°C) (B) Front view in case 2 (93°C), (C) Cross-section view in case 1 (66°C), (D) Cross-section view in case 2 (93°C)

ACKNOWLEDGEMENT

The authors are grateful to the National Science Council and Ministry of Science and Technology, Republic of China, for financial support of this research under contract No. NSC 101-NU -E-002 -002 -NU, MOST 104-NU -E-002-001 -NU.

REFERENCES

1. ACI Committee 349, *Code Requirements for Nuclear Safety Related Concrete Structures (ACI 349-90)*, American Concrete Institute, Detroit, Michigan (1990).
2. C. T. Liu and C. T. Huang, "Management Of Spent Nuclear Fuel Dry Storage in Taiwan", *Proceedings of the 15th International Symposium on the Packaging and Transportation of Radioactive Materials (PATRAM 2007)*, Miami, Florida, October 21-26 (2007).
3. K. Horak, T. Giles, H. N. Jow, R. Finch and H. L. Chiu, *An Information Management System for A Spent Nuclear Fuel Interim Storage Facility*, Sandia National Laboratories, SAND2011-7181C, (2011).
4. Atomic Energy Council, *National Report: under the Joint Convention on the Safety of Spent Fuel Management and on the Safety of Radioactive Waste Management*, p.129, Taiwan (R. O.C.) (2012)
5. G. T. YEH, J. SUN, P. M. JARDINE, W. D. BURGOS, Y. FANG, M. H. LI AND M. D. SIEGEL, *HYDROGEOCHEM 5.0: A three-Dimensional model of coupled fluid flow, thermal transport, and hydrogeochemical transport through variably saturated conditions – version 5.0*, p. 243, ORNL/TM-2004/107, Oak Ridge National Laboratory, Oak Ridge, TN (2004).
6. PH. BLANC, X. BOURBON, "A. Lassin, E. C. Gaucher, Chemical model for cement-based materials: Thermodynamic data assessment for phases other than C-S-H," *Cement and Concrete Research*, **40**, 1360 (2010a)
7. PH. BLANC, X. BOURBON, "A. Lassin, E. C. Gaucher, Chemical model for cement-based materials: Temperature dependence of thermodynamic functions for nanocrystalline and crystalline C-S-H phases," *Cement and Concrete Research*, **40**, 851 (2010b)
8. J. M. GALÍNDEZ, J. MOLINERO, "On the relevance of electrochemical diffusion for the modeling of degradation of cementitious materials," *Cement & Concrete Composites*, **32**, 351 (2010).
9. EPA-NCU, *Acid Rain in Taiwan*, <http://acidrain.epa.gov.tw/index.htm>, ENVIRONMENTAL PROTECTION AGENCY, TAIWAN (2010).
10. USGS. 2014. PhreeqcI--A Graphical User Interface for the Geochemical Computer Program PHREEQC, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqi/.
11. M. Luna, D. Arcos, L. Duro, *Effects of grouting, shotcreting and concrete leachates on backfill geochemistry*, p. 51, Svensk Kärnbränslehantering AB, SKB R-06-107 (2006).