INVESTIGATION INTO THE APPLICATION OF POLYETHERIMIDE TO NUCLEAR WASTE STORAGE CONTAINERS

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Abstract

The procedure of the analysis of the effects of irradiation on the mechanical and chemical properties of the polyetherimide (PEI) is outlined. Previous research in this field at the Royal Military College of Canada is presented. Samples of PEI will be exposed to a mixed radiation field, in the pool of a SLOWPOKE-2 nuclear reactor, then changes in mechanical properties, degradation product formation, and physical property changes will be assessed. Additionally, the heat transfer in the sample will be calculated in order to model the heat transfer rate and heat diffusion profile of PEI. The purpose of the proposed research is to determine the feasibility of using PEI for spent CANDU nuclear fuel and nuclear waste storage containers.

1. Introduction

In Ontario, over 52 % of the electrical energy used by the province is derived from nuclear energy, nationwide this percentage is 14.6 % **[1].** Since the first nuclear power reactor (the Nuclear Power Demonstration reactor (NPD)) began supplying electricity to the Ontario grid in 1962 [2], the percentage of energy derived from nuclear energy has increased from 20MW in 1962, to 12,612 MW as of August 14 2007 [3]. This increase is a result of the limited petroleum resources, as well as the need for a sustainable energy source.

Nuclear fission is an efficient low CO_2 (22 g $(\text{kW h})^{-1}$) [1] production pathway for electricity generation. In Canada, there are a total of 22 nuclear power reactors (18 of these 22 being operational at the present time), and 8 research reactors, all of which generate waste. Canada's unique reactor is the CANDU reactor (CANadian Deuterium natural Uranium reactor).

Nuclear waste, in Canada has been classified into three categories: low level radioactive waste (LLW), intermediate level radioactive waste (ILW) and high-level radioactive waste (HLW). It is common to forgo the classification of intermediate, and classify waste as either HLW or LLW. Spent nuclear fuel is considered as part of HLW. In Canada, there is presently an estimated 2 million used fuel bundles. Furthermore, if one assumes that a power plant has a service life of 40 years, then the expected production of used fuel bundles in Canada's existing power facilities will likely increase this number to 3.7 million [4]. Since there is no reprocessing of the used fuel in Canada, the spent fuel and other waste is being stored in temporary storage sites, in wet storage (pools), in dry storage (in concrete canisters). It is accepted that these methods are only temporary and a permanent solution is becoming imperative.

In this context, there is a need for a solution to the problem of nuclear waste. The Nuclear Waste Management Organization (NWMO) has considered several solutions to this problem. Namely: deep geological repository, which involves waste storage in the deep underground stable rock formations of the Canadian Shield. The Department of Energy Mines and Resources first proposed the concept of nuclear waste storage in the Canadian Shield in 1977. Moreover, it has also been investigated by AECL from 1978 to 2007 when it was officially adopted by the NWMO as the solution to nuclear waste disposal. AECL's solution involves the use of natural and engineered barriers for the storage of waste in vaults 500 to 1000 meters deep in the intrusive igneous rock (termed plutons) of the Canadian Shield. The fuel waste, sintered uranium dioxide pellets in zirconium alloy cladding, is to be stored in a container filled with glass or, as suggested by Miedema et al [11], thorium dioxide beads, and the container is to be placed in a vault which will be buffered with clay, sealed and back-filled. This idea represents a permanent solution to the problem of nuclear waste management. Canada has invested over 800 million dollars [4] in used fuel technology since 1978, and it is not the only country studying deep geological repository as a technique for waste storage, as Table 1 below shows.

Table 1. Deep underground repository worldwide [6]

Country	Storage Media
Sweden	Bedrock
Switzerland	Bedrock/ Opalinus Clay
Argentina	Granite
Germany	Salt Dome
Japan	Sedimentary Rock
Finland	Bedrock
Czech Republic	Granite
France	Mudstone
United Kingdom	Igneous/metamorphic rocks/strong sedimentary rocks
United States	Ignimbrite and salt dome

The Ontario Power Generation is presently researching the feasibility of a deep geologic repository at 680 meters in the limestone/shale rock near the western waste management facility in Kincardine, Ontario. AECL has published research that was undertaken at the AECL's underground research laboratory in Lac-du-Bonnet, Manitoba. The research has been primarily concerned with stress, seismology and other issues related to deep geological storing [21]. The safety of geological barriers in underground storage in the biosphere can be illustrated by the example of the 16 natural reactors sites found in Oklo, Gabon. These reactors achieved criticality approximately 1.5 billion years ago and ran for thousands of years, and most of the fission products remained contained underground with no contamination to the biosphere until they were found in 1972 by French physicist Francis Perrin [7]. Nevertheless, containment is still a primary issue in safe waste storage. At the Nuclear Fuel Waste Disposal Concept and Environmental Assessment Panel (Seaborn Panel) in 1998, one of the issues that arose was the need for a robust long-lived container for the storage of the nuclear waste [4].

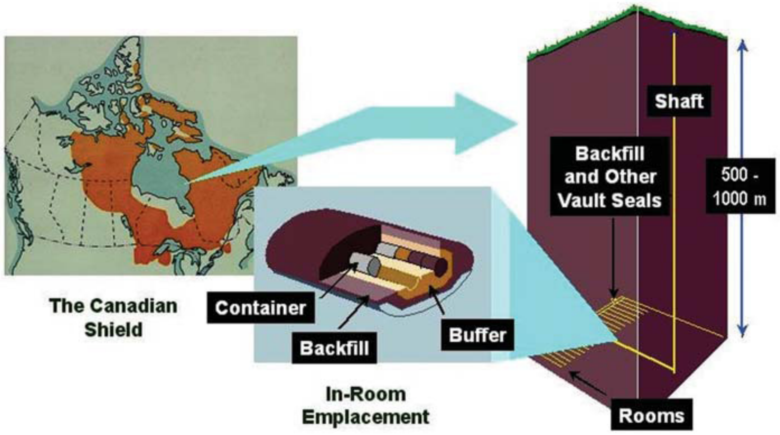

Figure 1. Proposed Deep Geological disposal [8]

2. State of the art

Several engineered barriers will be used to separate the waste from the biosphere; one of these barriers is the storage container. These containers must be corrosion resistant, mechanically strong, and radioactively stable, as well as be able to resist alkaline water and salinity, fluctuations in temperature, and be cost efficient. The storage container proposed by AECL (Figure 2) is constructed of copper with a titanium shell, and can hold 72 fuel bundles. This allows for a total of 10 million used fuel bundles in storage within the vault.

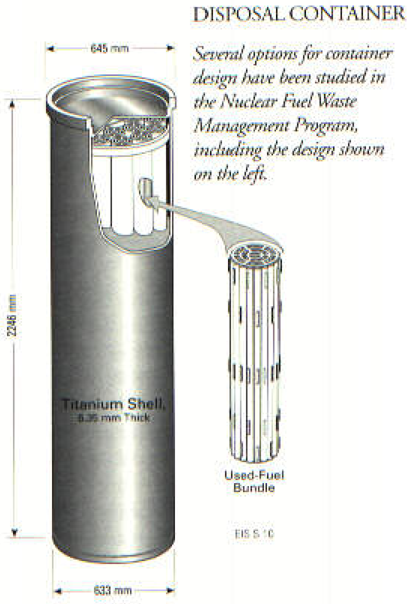

Figure 2. Proposed AECL storage container [9]

The choice of copper is based on the availability of copper artefacts that can be used to approximate the container lifetime, and as for titanium and its alloys; they have excellent mechanical properties and high resistance to salinity. The AECL container has a projected safe lifetime of over 500 years which is the time necessary for the activity of the waste to decay by a factor of over 200 000 [10]. Radiation emitted by used fuel is 1.150mSv/h (at 1.3m) for a 50 year old bundle and subsequently drops to 0.82 mSv/h after 500 years of decay, and finally to 0.09 mSv/h after 1000 000 years [4]. Therefore one of the main motivations for investigating alternative construction materials is to increase the fail-safe container life and permit the storage of radioactive waste until the activity has decreased to a safe level.

The main problem with the use of a metal container in the presence of ground water (saline and alkaline) is corrosion. It is hard to predict the actual corrosion of the container in the storage conditions, and it is hard to accurately predict factors such as chlorine in groundwater, microbial effects, and oxidizing conditions, which can also accelerate corrosion.

3. Polymer Composites

Failure of metal containers results from containment breach caused by electrochemical corrosion. Polymer composites have comparable and even superior mechanical properties to metals and their oxides In addition, they do not corrode. Containment breach in polymers occurs from diffusion resulting from physiochemical degradation. The aim of this study is to investigate the feasibility of using polyetherimide (PEI) as a construction material for the storage container. The design of the container must be specified in a way to resist to pressures exceeding 12.5MPa, mixed radiation fields, and temperatures up to 100 °C without alteration of the mechanical and chemical properties in a way that would lead to failure.

3.1 Previous research

Poly ether ether ketone (PEEK), a thermopolymer, was studied by Miedema et al. [11] at the Royal Military College in Kingston; the material was exposed to temperatures ranging from 20 to 75 °C, and radiation doses up to 1MGy, with very little effect on the mechanical and material properties. Changes to the polymer did not exceed one standard deviation of the values of un-irradiated sample properties. PEEK displayed high radiation resistance and it was found to be resistant to mixed fields of radiation of up to $\sim 10^{6}$ Gy. From this research it was found that, at low radiation doses, cross-linking of the polymer occurred, resulting in a reinforcement of the structure, whereas high doses lead to chain scission and a decrease in mechanical properties. Although PEEK displays excellent material and mechanical properties, it is not an ideal candidate for an application in the AECL project due to its high manufacturing cost.

Irradiation and mechanical testing of several polymeric samples was done recently by J.R Van Tine et al. [12] at the Royal Military College, where it was found that PEEK and PEI offered the best combination of radiation resistance, desirable mechanical properties, and cost efficiency. PEI was retained as the selected candidate for the design of the storage container due to its economic advantage over PEEK. Preliminary radiation testing was done on PEI by J.R Van Tine et al. [12], with exposure of 30% GF (Glass Fibre) PEI samples to a mixed field of radiation in the SLOWPOKE-2 reactor at the Royal Military College of Canada. The total dose received by the PEI container was 2.89×10^{4} Gy, mechanical properties of the PEI were then investigated. It was found that under the given irradiation conditions, the modulus of elasticity increased of 5.63 % ± 0.23%.

3.2 Polyetherimide

Polyetherimide is an amorphous thermoplastic polymer with high thermostability, resistance to biological degradation, and resistance to long-term effects of chemicals. The polymer consists of a backbone of aromatic imides, propylidene and ether groups, it can have two structures: linear (L-PEI) or branched (B-PEI), the linear form is known as crystalline PEI [22].

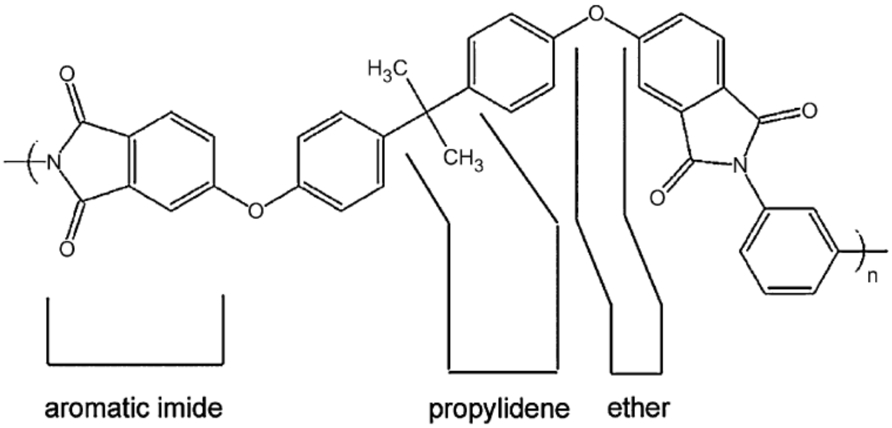

Figure 3. Structure of PEI [13]

Aromatic structures in polymers result in high radiation resistance because the imparted energy is retained in a way that does not modify the structure of the compound; aromatic groups absorb excitation energy and decay to ground state with very little bond breaking. Benzene rings have resonant energy dissipation as a result of the resonant structure, which prevents bond breaking. [14] It can therefore be assumed that, due to its high aromatic ring content, PEI will display excellent radiation resistance, as it will be capable of dissipating the absorbed energy into heat.

PEI is manufactured by under the name Ultem. From the material data sheet of Curbell plastics PEI and 30% GF (Glass-Fibre), PEI is listed to have the following physical and mechanical properties:

Table 2 Properties of PEI and 30 % Glass-Fibre PEI [15]

Property	Ultem (Unfilled)	Ultem (30 % GF)
Specific gravity	1.27	1.51
Water absorption (24hr. 23°C)	0.25%	0.16%
Tensile strength at break (PSI)	15,200	24,500
Tensile elongation at break (%)	7	3
Flexural Strength (PSI)	22,000	33,000
Flexural Modulus (PSI)	480,000	1,300,000
Compressive strength (PSI)	21,900	30,700
Compressive modulus (PSI)	480,000	938,000

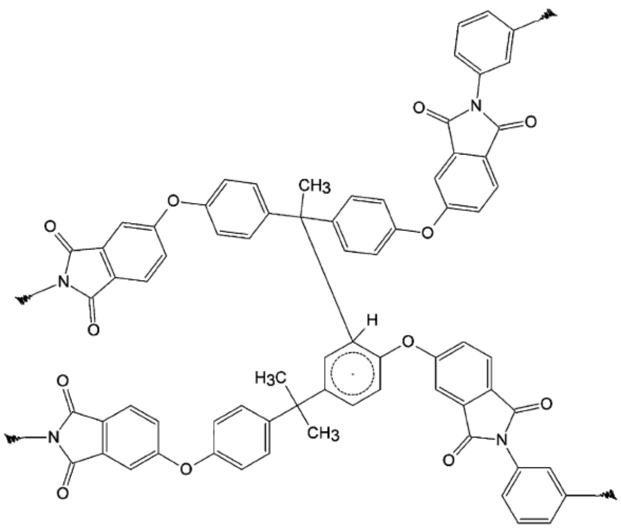

Figure 4. Thermal cross-linking of PEI caused by free-radicals [13]

Cross-linking of the polymer is believed to occur from the linking of two radicals produced in the chain-scission of isopropylidene and substitution of a phenyl radical into the benzene ring [13]. During thermal degradation of PEI, cross-linking dominates over chain scission, due to the presence of ester and imide bonds, resulting in an overall increase in molecular weight [16]. PEI is hydrolytically stable, it was shown that after 10 000 hours of immersion in water at 100°C, the tensile strength decreased by less than 10% [17] and by less than 5% at 23 °C [18]. The irradiation by Co60 for 1000 hours at a dose of 1 Mrad h^{-1} (for a total dose of 500 Mrad) resulted in negligible changes in tensile strength (less than 5 %) [18].

3.2.1 Effects of irradiation and temperature on polymers

Free radicals created from irradiation by ionizing radiation lead to chain-scission and cross-linking; the number of cross-links is proportional to the dose. At very high doses, when the cross-linking density exceeds the critical value [14], the gel point is reached, and a three dimensional network is formed between molecules. When cross-linking occurs, the elongation of the polymer is decreased, but its tensile strength and modulus are increased. Chain-scission leads to increased brittleness and fracturing [19]. Irradiation causes ionization and excitation, as energetic particles interact with the molecules of the polymer: gamma and electron particles form anions, cations, excited states, and radicals. In PEI, the radicals undergo further reaction in the polymer para-substituted dipheneylether as principal radiation damage sites, and damage to the imide groups [20].

High temperatures lead to the oxidation of polymers. Temperature resistant groups are similar to radiation resistant groups in the manner that they are able to absorb energy with limited bond breaking; aromatic groups are very stable at high temperatures.

4. Proposed research

To determine the feasibility of using PEI as a material of construction for the HLW storage container, it's resistance to radiation and stress and temperature, must be assessed. To do so, the polymer will be exposed to doses of radiation comparable to the lifetime dose exposure of the storage container calculated by Miedema et al [11], to be 12 MGy for glass bead filling and 56 kGy for thorium dioxide filling. The method followed by Miedema et al. [11] with PEEK will be used with PEI.

The irradiation of the samples will be done in the SLOWPOKE-2 reactor at the Royal Military College of Canada. This reactor is a 20 kWth reactor which is usually operated at half power, at steady state. The samples will be placed in the reactor pool against the reactor vessel, 31.4 cm from the centre of the core and in line with the reactor core at mid-plane. At the chosen irradiation site the flux has been calculated to be 37 kGy h^{-1} ± 28 % [23]. The irradiation field is a mixed field consisting of 1% neutron, 3 % proton, 9% gamma and 87 % electrons. [23].

In addition to the exposure to radiation, the samples will be placed in a heated chamber during irradiation to achieve simultaneous irradiation at high temperatures. The range of temperatures will range from the reactor pool temperature (about 20 °C) to 100°C. It will be attempted to reach an irradiation temperature of 100°C, since this is the temperature listed by AECL as the possible temperature from the decay of waste. A system will have to be designed to achieve stable temperature in the irradiation chamber.

Irradiation will be done for varied periods of time dependent on the desired dose. Following exposure, samples will be left to safely decay below a dose rate of 2.5 μSv h^{-1}, in a lead container, prior to analysis. The mechanical and material properties of the samples will be measured and compared to the un-irradiated samples to determine the damage incurred.

4.1 Measuring material properties

Changes in material properties are an indirect way to measure changes occurring to the polymer structure from irradiation. It is also a way to determine whether the effects of irradiation will affect the material properties in a way that will render the material unsuitable to an application to waste storage containers. Differential scanning calorimetry is a thermoanalytical method that will be used to obtain:

- The glass transition temperature (T_g),
- The crystallisation temperature (T_c),
- The melting temperature (T_m),
- The re-crystallization temperature (T_{rc}).

Wide angle x-ray scattering is a material analysis method that will be used to determine the degree of crystallinity of the polymer. This will allow the measuring of the increase or decrease in the degree of crystallinity, and therefore the changes in the strength of the material.

4.2 Determining changes in chemical properties

In order to understand the combined effects of temperature and irradiation, the chemical changes to the polymer will be investigated using Fourier-Transform Infrared spectroscopy. This technique aims at obtaining information on the changes in chemical structure, the rate of appearance of degradation products, and the changes in degree of crystallinity.

4.3 Imaging the surface

Fibre damage from irradiation and break pattern following flexural testing will allow one to determine the method of failure and the damage imparted to the material. Scanning electron microscopy provides magnification of up to 250 000 times, and permits imaging of details from 1-5nm in size. Surface imaging will allow the observation of physical damage at the surface of the polymer.

4.4 Mechanical changes

Flexural testing will be done on the samples to obtain the flexural strength, flexural stress at different strain levels, and the flexural modulus. Flexural testing measures the strength needed to bend a sample using three contact points on the sample. These properties indicate the mechanical strength of the polymer. The strength of the polymer must remain at a level where safe containment can be ensured, and the overall material performance must be unaffected or negligibly affected by irradiation.

4.5 Modelling heat transfer

The heat transfer across the PEI sample will be measured using thermocouples and the temperature profile will be calculated from the heat transfer equations applied to the heat diffusion in the sample at the given conditions. It is planned to use the COMSOL™ [24] software to do the computer modelling of the heat transfer through the container. This will be done to model the heat transfer in the polymer and therefore determine the effect of the decay heat of the nuclear waste on the container.

5. Conclusion

The experimental procedure that will be followed in the investigation of the feasibility of the use of PEI in the proposed AECL container for the storage of nuclear waste has been outlined. PEI was shown by previous research to be very effective at resisting radiation. Combined with the mechanical properties, and the economical cost of this polymer, PEI to be a promising candidate for the fabrication of the HLW container. Samples of PEI will be irradiated to doses up to 1MGy in the SLOWPOKE-2 reactor, at the Royal Military College of Canada, in Kingston, and select properties of the polymer that translate to strength and enable the assurance of safe containment will be measured. Additionally, heat transfer through the samples will be investigated via experimental measurements and computer modelling.

References

[1] Canadian Nuclear Association, "Nuclear Facts, the Number of Operating Reactors in Canada", http://www.cna.ca/, 2007

[2] Canadian Nuclear Association, "Canada's First Nuclear Power Generator- NPD", http://www.cna.ca/ , 2008

[3] Canadian Centre for Energy Information, “Canada- Statistics”, http://www.centreforenergy.com/, 2002-2008

[4] Nuclear Waste Management Organization, “Choosing a Way Forward the Future Management of Canada’s Used Nuclear Fuel. Final Study”, 2005

[5] Galson Sciences Ltd, “The Virtual Repository of Radwaste Information”, http://www.thevirtualrepository.info, 2007

[6] United Kingdom Nirex Limited, “CONTEXT NOTE 2.6: Repository Design and Construction”, Number : 485160, Oxfordshire, United Kingdom, December 2005

[7] Meshik, A.P. "The Workings of an Ancient Nuclear Reactor", Scientific American, November, 2005

[8] Petrunik, Ken, “Nuclear Sells Clean Air, Enhances Safety for New Generation Reactors”, Electricity Today, Vol 20 No 1, January/February 2008

[9] Whitlock, Jeremy, “Answers to “Frequently Asked Questions” (FAQs) About Canadian Nuclear Science & Technology”, www.nuclearfaq.ca/wste_con.jpg, 2009

[10] Atomic Energy of Canada Limited, “Response to Request for Information”, AECL-11602-V1, COG-96-237-V1, May 1996

[11] I.Miedema, H.W.Bonin, & V.T. Bui, “Application of Advanced Polymer Composites to Spent Nuclear Fuel Disposal Containers”, Master’s degree thesis, Royal Military College of Canada, Kingston, Ontario, April 2002

[12] J.R Van Tine, H.W.Bonin, & V.T. Bui, “Polymer-Based Composite Materials for the Design of a Container for the Ultimate Disposal of Spent Nuclear Fuel and Radioactive Waste”, Final Report, CCE417 Chemical Engineering Design Project, Royal Military College Canada, Kingston, Ontario, March 2008

[13] S.T. Amancio-Filho, J. Roeder, S.P.Nunes, J.F dos Santos, F. Beckham, “Thermal Degradation of Polyetherimide Joined by Friction Riveting (FricRiveting). Part I: Influence of Rotation Speed”, Polymer Degradation and Stability, Vol 93, No 8, pp 1529-1538, Elsevier Science, Oxford, United Kingdom, 2008

[14] D. W. Clegg, A. A. Collyer, “Irradiation Effects on Polymers”, Springer, pp.83, 1991

[15] Curbell plastics, Ultem (polyetherimide) Plastic Sheet, Rod- Ultem Properties, Data Sheets

[16] Shin-ichi Kuroda, Koichiro Terauchi, Kyohei Nogami & Itaru Mita, “Degradation of Aromatic Polymers - I. Rates of Crosslinking and Chain Scission During Thermal Degradation of Several Soluble Aromatic Polymers”, Eur. Polym. J. Vol 25, No 1, pp 1-7, 1989

[17] D. Kemmish, “High Performance Engineering Plastics”, iSmithers Rapra, Rapra Technology Limited, pp 17-19, 1995

[18] Margolis M. James, “Engineering Thermoplastics: Properties and Applications”, CRC Press, pp 292-293, 1985

[19] Roger. L. Clough & Shalaby W. Shalaby, “Radiation Effects on Polymers”, American Chemical Society, Washington DC, 1991

[20] David J.T.Hill, “Aspects of the Radiation Chemistry of Some Transparent Polyimides”, A.C.S. symposium series, American chemical society, Vol. 978, pp 116-130, 2008

[21] M.M. Ohta, N.A. Chandler, “AECL’ Underground Research Laboratory: Technical Achievements and Lessons Learned”, AECL-11760, March 1997

[22] Herlem. Guillaume, Lakard. Boris, “Ab initio Study of the Electronic and Structural Properties of the Crystalline Polyethyleneimine Polymer”, Journal of Chemical Physics, Vol. 120. No. 19, 15 May 2004

[23] Lamarre, G.B., “Experimental and Computational Determination of Radiation Dose Rates in the SLOWPOKE-2 Research Reactor at the Royal Military College of Canada”, Master’s degree thesis, Kingston, Ontario, 1999

[24] COMSOL Multiphysics, www.consol.com