

Contract No. and Disclaimer:

This manuscript has been authored by Savannah River Nuclear Solutions, LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.

SRNL-STI-2010-00601

ADVANCED CERAMIC MATERIALS FOR NEXT-GENERATION NUCLEAR APPLICATIONS

John Marra

Savannah River National Laboratory

Aiken, SC 29802 USA

**A PAPER FOR PUBLICATION IN THE PROCEEDINGS OF
THE THIRD INTERNATIONAL CONGRESS ON CERAMICS**

Osaka, Japan

14-18 November 2010

Organized by the Ceramic Society of Japan

Co-Organized by the Iketani Science and Technology Federation

Endorsed by:

- The International Ceramic Federation
- The Asia-Oceania Ceramic Federation
- The European Ceramic Society
- The American Ceramic Society

Published as part of the IOP Conference Series

(<http://www.editorialmanager.com/icc3/>)

This manuscript has been authored by Savannah River Nuclear Solutions, LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.

ADVANCED CERAMIC MATERIALS FOR NEXT-GENERATION NUCLEAR APPLICATIONS

John Marra

Savannah River National Laboratory

Aiken, SC 29802 USA

EXECUTIVE SUMMARY:

The nuclear industry is at the eye of a ‘perfect storm’ with fuel oil and natural gas prices near record highs, worldwide energy demands increasing at an alarming rate, and increased concerns about greenhouse gas (GHG) emissions that have caused many to look negatively at long-term use of fossil fuels. This convergence of factors has led to a growing interest in revitalization of the nuclear power industry within the United States and across the globe. Many are surprised to learn that nuclear power provides approximately 20% of the electrical power in the US and approximately 16% of the world-wide electric power. With the above factors in mind, world-wide over 130 new reactor projects are being considered with approximately 25 new permit applications in the US. Materials have long played a very important role in the nuclear industry with applications throughout the entire fuel cycle; from fuel fabrication to waste stabilization. As the international community begins to look at advanced reactor systems and fuel cycles that minimize waste and increase proliferation resistance, materials will play an even larger role. Many of the advanced reactor concepts being evaluated operate at high-temperature requiring the use of durable, heat-resistant materials. Advanced metallic and ceramic fuels are being investigated for a variety of Generation IV reactor concepts. These include the traditional TRISO-coated particles, advanced alloy fuels for ‘deep-burn’ applications, as well as advanced inert-matrix fuels. In order to minimize wastes and legacy materials, a number of fuel reprocessing operations are being investigated. Advanced materials, continue to provide a vital contribution in ‘closing the fuel cycle’ by stabilization of associated low-level and high-level wastes in highly durable cements, ceramics, and glasses.

Beyond this fission energy application, fusion energy will demand advanced materials capable of withstanding the extreme environments of high-temperature plasma systems. Fusion reactors will likely depend on lithium-based ceramics to produce tritium that fuels the fusion plasma, while high-temperature alloys or ceramics will contain and control the hot plasma. All the while, alloys, ceramics, and ceramic-related processes continue to find applications in the management of wastes and byproducts produced by these processes.

INTRODUCTION:

Rising global energy demands coupled with increased environmental concerns point to one solution; we must reduce our dependence on fossil fuels that emit greenhouse gases. As the global community faces the challenge of maintaining sovereign nation security, reducing greenhouse gases, and addressing climate change nuclear power will play a significant and likely growing role. In the United States (US), nuclear energy already provides approximately one-fifth of the electricity used to power factories, offices, homes, and schools with 104 operating nuclear power plants, located at 65 sites in 31 states. Additionally, 19 utilities have applied to the US Nuclear Regulatory Commission (NRC) for construction and operating licenses for 26 new reactors at 17 sites. This planned growth of nuclear power is occurring worldwide (see Figure1) and has been termed the ‘nuclear renaissance.’

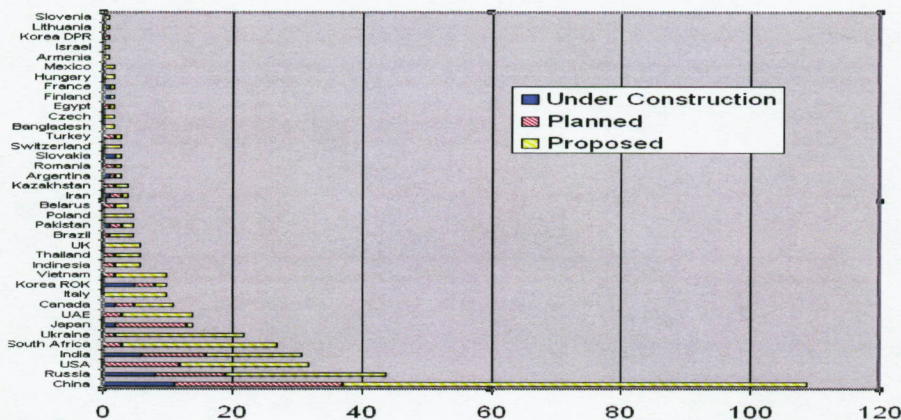


Figure 1 – Worldwide growth of nuclear power (Source: World Nuclear Association – Reactor Data – January 2009, see <http://www.world-nuclear.org/info/reactors.html>)

As major industrial nations craft their energy future, there are several important factors that must be considered about nuclear energy:

- It has been **proven** over the last 40 years to be **safe, reliable and affordable** (good for Economic Security)
- Its technology and fuel can be **domestically produced** or obtained from allied nations (good for Energy Security)
- It is nearly free of **greenhouse gas** emissions (good for Environmental Security)

Already an important part of worldwide energy security via electricity generation, nuclear energy can also potentially play an important role in industrial processes and supporting the nation's transportation sector. Coal-to-liquid processes, the generation of hydrogen and supporting the growing potential for a greatly increased electric transportation system (i.e. cars and trains) mean that nuclear energy could see dramatic growth in the near future as we seek to meet our growing demand for energy in cleaner, more secure ways.

In order to address some of the prominent issues associated with nuclear power generation (i.e., high capital costs, waste management, and proliferation), the worldwide community is working to develop and deploy new nuclear energy systems and advanced fuel cycles. These new nuclear systems will address the key challenges and include:

- Extracting the full energy value of the nuclear fuel
- Creating waste solutions with improved long term safety
- Minimizing the potential for the misuse of the technology and materials for weapons
- Continually improving the safety of nuclear energy systems
- Keeping the cost of energy affordable

THE ROLE OF ADVANCED CERAMICS IN FUTURE NUCLEAR FUEL CYCLES

Already critical to current nuclear technology, advanced ceramic, glass, and composite materials will have to be developed to enable improved nuclear fuel cycles that will address the above mentioned issues. These advances will encompass the entire nuclear fuel cycle – from fuel fabrication to waste disposal – and are discussed below.

Nuclear Fuels & Cladding

Advanced materials play a major role in the generation of electrical power from heat produced by nuclear fission and in special applications by radioactive decay. Ceramic fuels (nominally UO_2 or Pu-U mixed oxide (MOX) fuels) offer higher melting temperatures, chemical compatibility with cladding materials, improved resistance to corrosion, and dimensional stability combined with fission product retention during irradiation. These properties of ceramics provide for an increased margin of safety over metallic fuels, even with metal's higher thermal conductivity and ease of fabrication.

Various processing techniques have successfully produced UO_2 fuels as well as PuO_2 , ThO_2 , and the various combinations of mixed oxides. All of these dioxides have a face centered cubic crystal structure with no phase changes from room temperature to their melting point ($>2450\text{ }^\circ\text{C}$). Phase changes and their associated volume changes in brittle materials such as these ceramics generally cause localized stresses that can lead to cracking. The absence of any phase change not only facilitates fuel fabrication, but also enhances the integrity of the fuel by minimizing the impact of temperature changes during processing, encapsulation, final assembly, transport and end use.

For power reactors, UO_2 fuel pellets are commonly fabricated by conventional cold pressing and sintering techniques. The sintered pellets are machined to size, inspected and then encapsulated in Zircalloy or stainless steel cladding to form fuel rods. The rods are then assembled or bundled for loading into the nuclear reactor. Various reactor operational problems have been overcome by controlling the microstructure and chemistry of the fuel. For example, the dimensional stability of the fuel during irradiation can be controlled by coarsening the residual (~6%) porosity of the fuel during fabrication by compacting milled powder, followed by granulation and repressing prior to sintering.

Tri-isotropic (TRISO) fuels were originally developed in Germany for high-temperature gas-cooled reactors. In TRISO fuels, uranium carbide or oxide is usually coated in several layers of pyrolytic carbon and silicon carbide, and a porous carbon buffer (see Figure 2) to retain fission products at elevated temperatures. The resulting product

resembles black beads the size of salt grains. These particles are molded into graphite pebbles or into graphite fuel rods (for prismatic core gas cooled reactors). TRISO-type fuel would also be used in some of the Generation IV reactors being developed for use in ~30 years by a multinational consortium (GIF, the Generation IV International Forum) including the USA, UK, Brazil, France and Japan (see <http://www.nuclear.gov>). A very high temperature reactor (VHTR) is a long-term concept being developed by the US Department of Energy (DOE) uses high temperature helium as a coolant. This highly efficient, power-producing reactor would deliver heat at a high enough temperature to produce hydrogen from water more cheaply than electrolysis for automotive applications and household fuel cells.

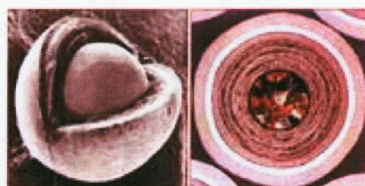


Figure 2 – Photomicrographs showing the coating structure of a typical TRISO particle.¹

As the use of nuclear power becomes more widespread, security risks increase as a direct result of an increasing plutonium stockpile.² Several options are available for dealing with waste Pu.³ The Pu (which is mostly stored as oxide) can be mixed with UO₂ to form a mixed U/Pu oxide (MOX) reactor fuel which can be used to generate power in Pressurized Water Reactors (PWRs) while burning up much of the radioactivity.

To address security concerns over Pu, several nations including the US, France, Japan, and Russia are developing an advanced technology base to demonstrate advanced fuel cycles that offer inherent proliferation resistance. Inert Matrix Fuels (IMFs) are being considered for use in three distinct fuel cycle concepts,⁴ namely burning of Pu in existing Light Water Reactors (LWRs), Pu burning in fast reactors, and the transmutation of minor actinides. An IMF is a material that burns Pu and other actinides without breeding Pu (or other actinide materials). Therefore, IMFs can be used to produce energy while beneficially eliminating actinide excesses. There are two major categories of IMFs: ‘non-fertile’ fuels which do not contain uranium and produce no fissionable isotopes and ‘low-fertile’ fuels that contain uranium and, therefore, breed Pu and other minor actinides. A variety of ceramic materials have properties making them attractive for IMFs (see Table 1). Each of these properties must be accounted for when designing an IMF for any given application. For example, ZrO₂ is very difficult to reprocess and is considered proliferation resistant, making it a desirable candidate for a ‘once-through’ IMF (i.e., the fuel is not recycled after use). However, this property would clearly hinder use of ZrO₂ in an advanced fuel cycle relying on reprocessing and continuous ‘burn-down’ of fuel materials.

Table 1 – Material properties of several ceramic materials for inert matrix fuels.

	ZrO ₂	MgO	MgAl ₂ O ₄	A ₂ B ₂ O ₇	TiN	ZrN
Melting Point (°C)	2675	2832	2135	~2200	2930	2980
Thermal Conductivity (W/mK)	~4	~10	5.9	1.5 – 2.5	~19	~11 – 24
Thermal Expansion (x 10 ⁻⁶ /°C)	7.5 – 13	~13.5	~7.5	~8 – 11	9.4	6.5 – 11
Heat Capacity (@1000°C, J/mol·K)	78	317	190	~280	55	55
Fabricability	Standard Cold Press & Sinter Technique				Sintering Aids, Hot Press	
Reprocessibility (Proliferation Resistance ⁻¹)	Poor	Good	Poor	Poor	Reasonable	
Radiation Tolerance	Good				Good	

An additional option for immobilizing Pu if it is not to be recycled in fuel or if it is contaminated and not usable in fuel is within a ceramic matrix.⁵ Active research is currently looking at suitable ceramic wastefoms both multiphase

(such as 'Synroc') and single phase based (on pyrochlores) such as $Gd_2Zr_2O_7$ and zirconolite. A potential problem with such crystalline ceramics is radiation damage leading to swelling. Additional work is needed on the ceramic processing and design of suitable containers for the ceramic wasteforms.

In addition to these fuel materials, advancements in alloys for cladding nuclear fuel rods will enable increases in performance and energy derivation in existing reactor systems. The fuel life (or burn-up) in conventional LWR systems is often limited by the ability of the cladding material to contain fission products. Most fuel designs use Zircaloy as the reference cladding material and this induces limits on burn-up to less than 20% and operating temperatures to less than 400 °C. In order to achieve increased burn-up. Higher temperature environments will be encountered and increased fission gas build-up will need to be accommodated. Advanced oxide-dispersion strengthened (ODS) alloys will likely enable these higher burn-up conditions.

Advanced Reactor Systems

Current reactor designs whether LWR, Sodium Fast Reactors (SFR), or Gas Fast Reactors (GFR), use a variety of materials of construction as shown in Table 2. In the US, most of these materials have served as the baseline technology since the 1980's when the last reactor systems were constructed.

Table 2 – Materials of construction for several reactor types.

	LWR	SFR	GFR/VHTR
Coolant	Water	Sodium	Helium
Temperature	288-360°C	500-550°C	550-1100°C
Cladding	Zirconium-based	9 or 12Cr steels	SiC/SiC
Core Internals	304/316 SS	316 SS	SiC/Alloy 800H
Vessel	Steel/316 SS	316 SS	Steel/316 SS
Heat Exchanger	Alloy 600/690	9-12Cr/316 SS	Alloy 617
Piping	316 SS/LA Steel	9-12Cr/316 SS	Alloy 617

Alloy and material developments over the last 20 years will enable improvements in new reactor construction. Several key requirements will drive development:

- Economy: Reactor technology must be economically competitive.
- Flexibility: A number of different missions may be required (power generation, process heat, isotope burning).
- Safety: Both inherent safety features and defense in depth will be required.

Choosing the right materials can impact all three factors:

- Economy: Reduce capital costs through reduced commodities and design simplifications
- Flexibility: Increased material performance allows greater options to designers.
- Safety: Improved material performance promotes larger safety margins and more stable performance over longer lives

Advanced Nuclear Fuel Cycles

An increase in the use of nuclear power world-wide will result in an increased quantity of used nuclear fuel (UNF) that must be treated for reuse or long-term disposal. There is research being performed worldwide to evaluate advanced reprocessing techniques. The baseline separations technology for LWR fuel is the PUREX process developed in the 1940's and 1950's. The PUREX process is well know and is reliably operated at industrial scales worldwide. The PUREX process, as the acronym implies, doe, however, result in the separation of Pu which is a proliferation concern. The goal of advanced reprocessing technology is to develop new separation methods that enable the recycle and/or transmutation of key fuel constituents (e.g. actinides) without the separation of pure Pu. These methods must be economical (i.e. minimal processing), minimize waste streams and volumes and enable effective safeguarding of fissile material. Advanced processes are being evaluated for a number of different fuel cycles where recycle of used

fuel components or transmutation of used fuel components is involved. By separating used fuel components, it is possible to tailor waste forms to the specific component and disposal requirements, but this must be balanced with the additional cost of processing and storage.

Advanced aqueous technology research activities in the past have focused on development and demonstration of processes that are a variation of the PUREX process (namely 'UREX' processes which don't produce pure Pu). Several alternatives have been successfully demonstrated, but the complexity of the process flowsheets would likely be too costly and difficult to operate in an industrial-scale application. Improvements in separations media and materials could enable a simplification of the alternative processes that would improve their economy and ability to be deployed at the large scales needed to accommodate the UNF resulting from reactor operations.

Electrochemical processing is of particular interest for processing metal fast reactor fuels, or small-scale processing of oxide-fuels for recycle of transuranics in fast reactors. Electrochemical processing uses molten salt (often halide-based) and has been demonstrated on an engineering-scale. However a few very important technical issues for a sustainable closed fuel cycle have not been demonstrated, such as recovery of the transuranic elements, salt cleanup and recycle, determination of process losses, etc. Research into all of these areas is critical for the potential use and deployment of electrochemical processing in a fully-closed sustainable fuel cycle that employs fast reactors. Additionally, improved materials are need for both the separations media and process equipment that will enable economical deployment.

The impact of nanotechnology will be felt in several areas of the nuclear industry in the next few decades; no more so than in separations technology in waste clean up and decommissioning. Materials such as the SAMMs (Self-Assembled Monolayers on Mesoporous Supports) filters first invented by the petrochemical industry are being developed (at the Pacific Northwest National Lab, PNNL) to filter out from dilute aqueous waste streams difficult species such as pertechnetate, I, Cs, and Sr. These use zeolite monolayers on silica supports and are available as powders, beads and membranes and current research is aimed at tailoring both monolayer and support to target particular species.⁶

Nuclear Waste Stabilization

Glass is now the material of choice for incorporating and immobilizing the potentially hazardous radionuclides in high-level nuclear wastes (HLW). Factors that contribute to the suitability of glass waste forms fall into two main categories. First, glass waste forms possess good product durability. Various glass systems are able to incorporate a variety of waste compositions into durable waste forms. These forms have demonstrated good chemical and mechanical performance as well as good radiation and thermal stability. Second, waste-glass forms possess good processing characteristics. The technology for making waste-glass forms is both well developed and well demonstrated. Waste-glass forms ranging in size from bench- and laboratory-scale products to multi-ton canisters have been successfully produced by using ceramic melters as well as in-can melting techniques. Waste-glass forms have also been produced for a variety of simulated as well as actual radioactive wastes. Vitrification has been used for nuclear waste immobilization for more than 40 years in France, Germany, Belgium, Russia, the UK, Japan, and the USA.

Cement and cement-based materials also provide a simple and cost effective means of waste stabilization and are widely used for low-level waste (LLW) and intermediate level waste (ILW) treatment. Common advantages of cement stabilization include; continuous or batch processing at ambient temperatures, low-cost raw materials, suitability for large or small volumes of many different waste types, and ability to use modular equipment. Waste stabilization/solidification is most commonly accomplished by mixing aqueous-based wastes with hydraulic or pozzolanic materials such as Portland cements, calcium aluminate cements, calcium sulfo-aluminate (CSA) cements, magnesium (aluminum) phosphate cements, kiln dusts, fly ashes and reactive slags. These materials react with water to form insoluble binders. Composite cement systems using several of these phases are commonly used by the nuclear industry. The hydrated binder phases encapsulate solid particles in the waste, co-precipitate selected contaminant species, and adsorb excess water and soluble contaminants. In addition, the aqueous chemistry of the cement-waste mixture can be adjusted so that the soluble contaminants are precipitated from solution simultaneously with the formation of the matrix phases. Mixtures of the cementitious ingredients plus other additives such as sodium silicate (hardening agent), set accelerators and retarders are commonly used. As a result, a monolithic waste form can be produced at ambient temperatures. The waste forms can also be designed to have a wide range of properties. Compressive strengths typically range from 50-3000 psi. Viscosity and set time can also be adjusted to meet mixing

and placement requirements dictated by the production process. Composite cements are typically associated with a highly alkali environment that is not suitable for all wastes; Al metal for example will corrode in such an environment. As a result, a toolbox of cement systems is being developed including geopolymers, CSA cements, and alkali activated systems with at least one suitable for all waste types.⁷

Hydrated waste forms are typically used for stabilizing aqueous wastes, such as, condensed off gas wastes, electroplating sludges, salt solutions, incinerator ash, electrostatic precipitator and bag house wastes, and process residues, such as, metal chloride and hydroxide bottoms from ore refining processes. Cementitious materials are also used in a variety of environmental remediation actions to stabilize seepage basin sludges, contaminated soils, and waste disposal sites. In addition, cement-based materials are also used for underground waste tank and pipeline closures. The standard requirement for this application is subsidence prevention. Portland cement based grouts or pumpable, self-leveling, self-compacting backfills containing Portland cement are typically used for tank stabilization. Special grout or backfill formulations are also being designed to stabilize residual contaminants which may not have been removed from these tanks.

CONCLUSIONS

As illustrated, advanced materials play an important role in the nuclear cycle, from fuel fabrication to irradiation and reprocessing to safe encapsulation of nuclear waste products. Beyond that, development of advanced materials and processes for nuclear applications has led to material and process enhancements that have improved conventional, commercially-available materials. For example, many of the processes and waste-forms developed to encapsulate and stabilize highly-radioactive nuclear wastes are now being employed to mitigate hazardous and toxic waste issues associated with numerous other industrial processes. Likewise, continued advancements made by the materials community have improved nuclear processes. Examples include; advanced alloy and ceramic components in valves and pumps for improved radiation and corrosion resistance, ceramic or composite crucibles for handling highly radioactive materials, and improved low-cost melters for encapsulation of nuclear waste products.

The increased use of nuclear power to meet growing worldwide energy demand creates even more opportunities for advanced materials. As discussed, peaceful deployment of nuclear power requires increased reliance on fuels that are inherently proliferation resistant. Additionally, advanced fuel cycles will be increasingly 'closed,' relying on reprocessing to minimize wastes and eliminate proliferation concerns. Advances and widespread deployment of these technologies will require continued development of the advanced materials that are central to the fuel form and byproduct stabilization portions of these fuel cycles. Finally, as further advances are made all leading to planned deployment of fusion energy systems in the 2050 timeframe, advanced materials will be key enabling materials in numerous areas.

REFERENCES:

- ¹Oak Ridge National Laboratory, "Nuclear Energy: Assuring Future Energy Supplies," ORNL Review, **35**, 2002.
- ²United States National Academy of Sciences, "Management and Disposition of Excess Plutonium," (1994).
- ³M.I. Ojovan and W.E. Lee, "An Introduction to Nuclear Waste Immobilisation," (Elsevier, Oxford UK 2005).
- ⁴R. Chawla and R.J.M. Konings, "Categorisation and Priorities for Future Research on Inert Matrix Fuels: An extended synthesis on the panel discussions," Progress in Nuclear Energy, **38**, 455-458 (2001).
- ⁵G.R. Lumpkin, K.L. Smith, and M.G. Blackford, "Heavy Ion Irradiation Studies of Columbite, Brannerite and Pyrochlore Structure Types," J. Nucl. Mats. **289** [1-2] 177-187 (2001).
- ⁶G.E. Fryxell, J. Liu, and S. Mattigood, "Environmental Applications of Self-Assembled Monolayers on Mesoporous Supports (SAMMS)," Materials Technology **14** 188 (1999).
- ⁷N.B. Milestone, "Reactions in Cement Encapsulated Nuclear Wastes: Need for a Toolbox of Different Cement Types," Adv. Appl. Ceramics **105** [1] 13-20 (2006).
- ⁸W.E. Lee, M.I. Ojovan, M.C. Stennett, and N.C. Hyatt, "Immobilisation of Radioactive Waste in Glasses, Glass Composite Materials and Ceramics," Adv. Appl. Ceramics **105** [1] 3-12 (2006).

ACKNOWLEDGEMENTS:

This manuscript has been authored by Savannah River Nuclear Solutions, LLC under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting this article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for United States Government purposes.

The author wishes to thank the many people – too numerous to cite individually – who contributed information during the generation of this manuscript.