Nuclear Waste Management Strategy for Molten Salt Reactor Systems

Dr. John Vienna and Dr. Brian Riley, PNNL, USA

Berta Oates
Welcome, everyone, to the next Gen IV International Forum Webinar Series Presentation. Today's presentation on Nuclear Waste Management Strategy for Molten Salt Reactor Systems will be presented by Dr. Brian Riley and Dr. John Vienna.

Doing the introduction today is Dr. Patricia Paviet. Patricia is the Group Leader of the Radiological Materials Group at Pacific Northwest National Laboratory. She is also the Chair of the Gen IV International Forum, Education and Training Working Group. Patricia?

Patricia Paviet
Thank you so much, Berta. Good morning, everyone, or good evening. It's a pleasure to have Dr. Brian Riley and Dr. John Vienna with us today, and it's a double joy for me because they are, of course, internationally recognized experts in the waste form development arena, but also a part and staff member of my group at the PNNL. It's very important for me to introduce them. I am very happy to have them giving this talk.

Dr. Brian Riley has a Ph.D. in Material Science and Engineering from Washington State University. He is a Senior Materials Scientist at the Radiological Materials Group at PNNL, and he is a Technical Team Leader for the Waste Form Development team. His research primarily focuses on salt waste form development and salt waste partitioning methods with funding from DOE Office of Nuclear Energy. Recently, Dr. Riley has been performing and leading research on various projects in these areas as well as looking at methods for treating salt wastes from molten salt reactor and developing and testing sorbents for capturing volatile radionuclides such as iodine gas.

Dr. John Vienna is a Laboratory Fellow in Materials Science at PNNL. He earned his Bachelor of Science and Master of Science degrees in Ceramics Engineering from Alfred University, and a Ph.D. degree in Materials Science from Washington State University. Dr. John Vienna joined PNNL in 1993. Throughout his career, he has served in numerous technical leadership roles in nuclear waste management, including serving the US Department of Energy's Office of Nuclear Energy as a technical lead for nuclear waste treatment.

Without any delay, I am going to give the floor to Brian and John, and I thank them for volunteering to give this talk. Again, thank you.

Brian Riley
Thank you very much for that introduction, Patricia and Berta. This is Brian Riley. The first thing I want to talk about here is the funding that we have received to do this work. It's coming from the United States Department of Energy, the Office of Nuclear Energy. Our federal managers are Kim Gray, Stephen Kung, Brian Robinson. National Technical Directors from the National Labs are Patricia Paviet for the Molten Salt Reactor Campaign; Ken Marsden at INL for the Material Recovery and Waste Form Development Campaign, and the Joint Fuel Cycle Studies.

Throughout all this work, we have got lots of people that we have done different research projects with from universities to national labs. We have collaborated with several people from our lab as well as Oak Ridge National Lab; Idaho National Lab; Argonne National Lab; and then several universities from RPI to the University of Utah, to the University of Reno in Nevada; Washington State University, Go Cougs; Clemson University; the Korea Atomic Energy Research Institute in South Korea; the Australian Nuclear Science and Technology Organization, or ANSTO, in Australia; National Nuclear Laboratory; and the University of Sheffield in the UK.

This is just some of the people we have collaborated with. If you are on the presentation and I missed you, I apologize, but this covers a large range of the people that we have worked with, and we couldn't have done it without them.

An overview of this presentation.

First, I'll provide a molten salt reactor overview at a high level, talk about different types of wastes that could be emitted from a molten salt reactor. This is a general overview, so there's lots of different types of molten salt reactors, different salt streams, different compositions, but we are going to talk at a very high level. There is off-gas treatment and monitoring examples, waste form examples, other considerations, and then, I will provide the summary and conclusions.

For the MSR overview, there's different types of MSRs. We have got burner reactors, breeder reactors. There's thermal spectrum and fast spectrum reactors. There are different salt compositions from the typical compositions that people are looking at different vendors are fluorides and chloride salts. Different abbreviations that you might see in the literature include FLiBe, which is a lithium-beryllium fluoride salt; and then FLiNaK, which is a lithium- sodium- potassium-fluoride salt.

If we look at this graphic here at the top, we have got the chloride versus fluoride salts. There are different types of fuels that can be used, different actinides, including natural uranium; thorium/uranium, low-enriched uranium; HALEU, which is high-assay low-enriched uranium; and then plutonium.

Then, in this table down here, this is from Ted Besmann, there's a couple of different examples of actual salt compositions that could be used in different types of reactors. These are just four of the different types of reactors, the different terms that are thrown around, like the molten salt breeder reactor, the advanced high temperature reactor, the very high temperature reactor, and the liquid salt cooled fast reactor.

One of the really neat things about MSR is just that there is a lot of processes that can be done with the salt, either while the reactor is being operated or post-processing of the salts. These are some different processes that we have listed. Fluorination/chlorination, UF6 purification/reduction, vacuum distillation, reductive extraction, hydrofluorination, the metal transfer process, electrolytic oxidation and reduction, oxide precipitation, selective crystallization, and electrochemical separations.

A lot of these processes are used to either pull fission products out of the salt. They are used to recover actinides and/or purify them, as well as several other things that can be done in situ with the salt.

A lot of benefits here. We have got ways of preparing different fuel salts from spent salts. You can remove things like protactinium-233, other fission products. You can also remove corrosion products, things that are in the salt from maybe corrosion of the reactor itself, so metal corrosion products. You can also recycle things like lithium-7 and chlorine-37. These are isotopically enriched materials that have benefits that I'll talk about in later slides.

You can reduce the waste volume through this recycle process, and a lot of these techniques can be used to promote waste form production. Partitioning of the salt will yield you with products that can be easier to immobilize in the specific waste form.

If you want more information on some of these slides, I have provided citations for the locations where we got some of this information, if you want more information there.

Talking about different types of wastes from molten salt reactors. In the 2017-'18 timeframe, we had a collaborative project with Oak Ridge National Lab here at PNNL, where we were looking at trying to figure out what these different waste streams would look like, and in doing so, we came up with some questions.

The first question was: What streams should be considered? What do we know about these different waste streams? Do we know enough to determine a treatment route? Are there any specific challenges associated with one stream or another? Are there disposition pathways available for some of these streams, or all of them? Are there restrictions on stream management, such as the storage, treatment, packaging, or disposal environment for them? How would effluence be treated and disposed? Which streams require additional research?

Things like determining or estimating the characteristics, developing the method or treatment of the waste form production from these different streams, identifying potential restrictions of tradeoffs with salt chemistry and processes, and we needed to generate data for MSR process models, so for source term calculations.

This report that came out of this joint ORNL-PNNL study is listed here. If you want more information, there's a link on the ORNL website for that. Subsequent literature review papers have been put out, where we have sort of delved into this process trying to figure out at a high level what waste streams would be there, how we could treat them. It sort of provides an à la carte, I guess, approach to treating each of them and preparing them for disposal environments.

These are the primary types of waste that we identified. You have got decommissioning and decontamination or D&D waste streams. You have got your metal from the reactor itself, the outside and containment. You have got the transfer lines, pumps, heat exchangers. You have got your off-gas, which is very complicated. Operating waste, carbon waste, this would be things like the graphite-moderator, silicon carbide, things like that. Spent salt and any separated salt, so this would be salt after several of the processes that I discussed earlier where the salt can be partitioned. If you want more information, there is a link down there.

I'll kind of cover the bolted list and then go through these different flow charts for each of these next few slides.

The first issue is that halide immobilization is complicated. The traditional nuclear waste form approach in the United States has been borosilicate glass. While halide solubility and immobilization options for borosilicate glass are extremely limited, the solubilities and loadings are very low. The temperatures required to vitrify; you typically would volatilize off the halides anyway.

One of the main issues and drivers here is that chlorine-36 and iodine-129 are long-lived radioisotopes and are dose drivers for repository environments. The halogen impact on disposal site can be high. There are also high doses from insanely short cooling from the salts. There are issues with salt storage and transportation. Radiolysis of these different salts can be a problem. At the MSRE at Oak Ridge National Lab, radiolysis of the salt in the dump tanks was causing fluorine gas generation, and so the tanks had to be vented. This is an example of how storage might be a complicated issue that needs to be addressed.

Certain stream compositions and characteristics can be uncertain. Then, we have got issues of these isotopes that we might want to recover. There are challenges for enriching them. There are challenges for recovering them. Are there additional wastes that are produced in, in recovering them? These are things that need to be considered.

For the different salts, there are some options that have been demonstrated for chloride salts, where the full salt could be immobilized or processed into some sort of a stable waste form. Things like appetite, things like sodalite, these are minerals that I'll talk about a little bit later, where the halides are actually immobilized inside the crystalline lattice. Then, those can be sort of encapsulated with a glass phase that helps prevent leaching during the chemical durability testing. There are things like halide metal composites, or halmets. There are ceramic metal composites called cermets. A lot of this work has been done with chlorides, but very little has been done with fluoride salt. More work is needed in that area.

Then, when you start thinking about partitioning, this plot is, it's a very high-level summary, and it's missing lots and lots of things that could be done. But it gives you somewhat of a flavor of options where you could take these salts and you could react them with things.

One of the processes I'll talk about later is where you react it with an ultra-stable H-Y zeolite. The hydrogen in the zeolite reacts with the salt to generate hydrogen chloride, which can be removed and recovered, and then your remaining product can be consolidated.

You have got options of salt-occluded zeolite, where you add a binder and you can yield a glass-bonded ceramic waste form or a sodalite, glass-bonded sodalite.

Then, there's lots of options where you can selectively remove components like rare earths, such as you have got metals that you can remove them as metals through reduction. You have got ways to convert them into oxides, oxychlorides. You can recover them as chlorides. You can precipitate them out as phosphate. There's lots of different options here that have been demonstrated for chlorides.

Then, there's some of these that could be applied for fluorides. Some of them have been demonstrated, but, again, a lot less work has been done in the fluoride salt systems.

When we think about off-gas, there's lots of challenges here. The US regulations require krypton-85 to be captured and stored. There are issues with corrosive daughter products that can come from decay of this isotope. Immobilization is expensive, and there's low loading options for mobilizing krypton-85. There's acid gas capture. That's an issue. You have got salt mist and entrainment that could cause clogging of solid sorbents beds.

There are high dose streams that require holdup for decay, such as xenon isotopes. You have got helium that needs to be recycled back into the reactor, and I'll show you a concept where a lot of this can be addressed in a single system, which is a molten hydroxide scrubber. Then, you need to deal with tritium partitioning and transportation so hydrogen can permeate through metallic reactor components, and this needs to be considered.

This is a very unique thing. When you think about dealing with off-gas from, say, used nuclear fuel reprocessing, this is quite different where we have got lots and lots of things such as aerosols, particulates, reactive gases, dusts, and things that need to be addressed before you start trying to capture things downstream. You have got an option for a molten hydroxide scrubber. Again, I'll talk about that later.

In these different graphics, the yellow boxes are sort of an intermediate product, and then the green is a final product. These are sort of steps to get to a final product.

Then, you have got things like tritium and water that need to be captured and immobilized zeolite might be an option. Your residual halides that come through this initial scrubber could be captured using some sort of solid sorbent like a silver mordenite, silver faujasite, or some sort of a metal functionalized aerogel or xerogel, and then put in some sort of hot-pressed matrix.

Nitrogen and oxygen can be trapped and released. Then, your noble gases need to be captured. They can be separated. There's lots of options for this that are being evaluated. Even currently, things like granulated, or granular-activated carbon. You have got zeolites. You have got metal organic frameworks. Or you could use cryogenic distillation, where the noble gases could then be stored and then subsequently released after decay.

For metal and carbon streams, salt impregnation will be a problem, where the salt will penetrate deep inside the different components. Making them could be very highly radioactive, greater than class C or high-level waste, depending on the amount of products that are present, the decay products. They are going to be high dose from the salt and the different gases penetrated inside. You have got different treatment options, but they might be challenging for metals or impractical for graphite. The untreated durabilities are questionable to poor, and there is an option for recycle. This is something I'll talk about, I think, in the next slide.

For metal, you have got different things like stainless steels. You have got Hastelloy alloys. Hastelloy-N was used with the MSRE. You have got Inconel alloys. Then, the thought was you could basically just size-reduce or decontaminate these. You could melt them or compact them into some sort of a metal waste form.

With carbon, you could hot press and then convert them into a carbon waste form. Then, there's other options that probably exist. We have left this as an unknown. Then, of course, there's the recycle option.

Then, in used nuclear fuel, we get this five-metal epsilon phase that can form. It's unclear whether or not this would form inside of an MSR, but if it did, it would likely settle to the bottom of the reactor, or it could potentially be collected in some sort of a filter. It doesn't build up somewhere else, such as in pumps or heat exchangers or whatever.

One of the options for immobilizing this five-metal phase is doing some sort of a collection in a hot press technique. This is an example from Jarrod Crum here at PNNL. More information there. This five-metal phase is a moly, palladium, rhodium, ruthenium, and technetium phase that forms.

This is an example of a way to recycle used graphite. This is a report out of Oak Ridge National Lab, where the material could be ground nuclear grade graphite, could be ground, and then mixed with different additives to create a final product that could be reused. One of the main issues with graphite moderated MSRs is that the graphite moderator is quite large, and the thought of trying to remove the moderator and replace it and continually doing that would be very expensive and would create a very large quantity of graphite waste. This might be one way to minimize that. I don't know how practical this would be at a large scale, but it's certainly an option.

We think of D&D and operating wastes as potentially high doses, significant fractions of greater than class C waste, potential for mixed LLW and mixed GTCC wastes. These could be very high volumes and masses. The characteristics are uncertain, and the amounts are uncertain, and they could be mixed wastes. Salt contaminated wastes are a challenge to dispose.

The D&D streams include things like metal, cement, or other carbon-based streams. The operating wastes include things like filters, cans, different types of job control wastes, glove boxes, manipulator boots, and things like that, different samples. It's unknown sort of what these quantities would be.

From this report, we identified several gaps that we feel needed to be addressed in subsequent years. We need more information on mass balances and compositions of expected wastes. We need to develop initial functional and operational requirements called FORs. From MSR wastes, we need to initiate off-gas treatment technology testing. This is sorbent development and evaluation under relevant streams. We need to investigate waste form options for salt-based waste streams. We need to evaluate treatment options of contaminated carbon-based materials, including things like graphite, silicon carbide.

Some of this work is already being done through the United States Department of Energy, Office of Nuclear Energy. This is through our Material Recovery and Waste Form Development campaign, NE-4, and the Molten Salt Reactor campaign, NE-5, that Patricia is the NTD for.

Now, I'll talk about off-gas treatment and monitoring examples. I alluded to the molten hydroxide scrubber earlier. This is a really interesting concept proposed by Bill Del Cul at ORNL, where the initial system is a packed-bed molten hydroxide scrubber using some sort of alkali hydroxide eutectic salt. This is non-aqueous, so it's rotting at, I'll say, 300, 400 degrees Celsius. This initial scrub can be used to remove things like particles, mists, aerosols. It can actually be used to neutralize reactive volatile species, including things like some of the halide gases.

Any halides that get through could be captured in a residual halide trap. Then, you have got your water trap for any residual water that does come through. You have got your oxygen trap. Then, you have got these noble gas delay beds. This could be used to capture the noble gases. It gives them an opportunity to decay so that they are not as hot.

Then, following the delay beds, they can be run through pressure swing or cryogenic distillation in order to separate out the noble gases from one another. I don't know how practical it is, but there is discussion of recovery of things like xenon and krypton for resell, and argon, because they are noble gases. They are difficult to capture, but they are actually quite valuable, and they have a lot of commercial value to scientific community. To just vent them and dispose of them might be not ideal, so this is an option.

Then, you have got your helium storage. Once this has been cleaned, it can run back to the reactor.

For iodine capture and immobilization, this is something that we have done quite a bit at PNNL looking at different ways to capture the iodine gas. A lot of work has been also done at Oak Ridge National Lab, Bob Jubin and his team since, I guess, 40 years ago plus. One of the options for capturing volatile iodine is using metal-impregnated zeolites, things like faujasite and mordenite. Silver is the common material, but other materials have been tested. Even recently in the literature, bismuth has been a hot topic.

There are also metal-impregnated things like silica aerogels, silica, alumina-silicate based xerogels that have been metal-impregnated with things like silver, bismuth, copper, as well as a wealth of other different metals.

Then, after these have been loaded with iodine, they can be hot pressed into waste forms. This is an example of a spark plasma-sintered iodine-loaded silver-functionalized silica aerogel by Joseph Matyas here at PNNL. This is the largest puck that he was able to make. These materials have very good chemical durability and very, very high iodine loadings. I should mention that these are all by chemisorption, so we are going from an iodine gas or some sort of iodine gas complex to a metal iodide complex. It's tightly bound into these materials in the form of some sort of metal iodide particle in the matrix.

Then, this is a hot isostatically-pressed iodine-loaded sodalite material that was made at PNNL. The HIP-ing was done at ORNL by Stephanie Bruffey. Then, this is some work by Stephanie Bruffey where she has taken iodine-loaded silver mordenite, and she has added different amounts of binders and she has hot-pressed that with HIP.

We talk about noble gas capture. I mentioned we have got some options such as cryogenic distillation. We have also got options like metal organic frameworks, which is some of these graphics here. The metal organic frameworks, there's a wealth of options in the literature, hundreds of thousands of options.

Researchers at PNNL, including being led by Praveen Thallapally, are looking at ways to computationally sort of predict what types of MOFs might work for these applications because you can't test 400,000 MOFs practically. A lot of these also have to be produced in the lab. They are not commercially available.

This is a summary here showing the xenon to krypton selectivity. It's a function of the Xenon Henry coefficient. Most of these MOFs have a xenon to krypton selectivity. Some of them are upwards of 16 or higher. There are very few, but he has found one krypton selective MOF. One of the thoughts here is that a two-bed approach could be used where MOF 1 is used to pull xenon out of the gas stream, and then MOF 2 is used to pull krypton out.

One of the issues with MOFs is that they are made in a very fine crystalline sort of, I would say, fine particle size. Putting those in some sort of a flowing stream is difficult because they'll transport downstream. One option is to create some sort of a mechanically high integrity engineered form of these materials. This is one option where we took polyacrylonitrile and it creates this very fine net porous structure. It's a polymer, and so you can embed your MOF crystals inside this polymer. This is a cross section of one bead, so you can see the distribution of the MOF particles is very uniform.

This is a scanning electron micrograph showing the MOF crystals embedded in the polymer. This is a cross-sectional view. Stuff like this, these are some of the engineering challenges that are needed to overcome in order to implement things like porous particles that can be used to do this type of screening, but we need to be able to isolate them inside of a flowing system. This is an example of how that could be done.

Some more work that's being done at PNNL as well as at Oak Ridge National Lab are things like in-situ off-gas monitoring. This is one of the really neat advantages of an MSR is that you can monitor the species concentrations, but you can also identify the species in the liquid gas molten salt phases. This can be used to track things like iodine gas, different other sorts of complexes like iodine chloride. You have got options for tracking xenon and things like hydrogen isotopes. They are working on deuterium currently, but the plan is to be able to detect tritium.

They use techniques like Raman spectroscopy, ultraviolet-visible-near infrared spectroscopy, laser-induced breakdown spectroscopy to achieve the ability to quantify and the ability to identify these different species. These are just some examples of some different probe lasers that they can use to do this. More information down here if you would like to read more about that.

Now, I'll talk about some examples of different waste forms. Before I do that, I want to define some terms that I often throw around, like everyone knows what I am talking about, and I sort of feel like I have made some of these up.

The dehalogenation process is a technique to remove halides from the salt. There's lots of reasons why you would do this. The main one I alluded to earlier is that immobilization of halides is quite challenging. If you can remove them and deal with them separately, then the products that are remaining are then converted to things like oxides or phosphates, and the waste form immobilization options are increased and are a little more straightforward.

There are things like waste loading, which we define as the mass fraction of waste in the waste form. The term waste can be defined differently. There's full salt where if I have got a full salt that I have not partitioned, I can directly immobilize that. That's full salt waste loading.

There are things like the salt cation loading. This is a way of normalizing the discussion of waste loading across the different waste forms, including things that have been dehalogenated and things that have not, or things that have been partitioned and things that have not been partitioned.

Then, there's salt cation oxide loading, which is a way of sort of discussing different waste forms that are containing the salt cations that have been converted from some sort of halide to an oxide.

Storage volume is a term that is defined as the volume of final waste form required to immobilize starting salt mass. This is a way of thinking about the number of additives required to create the waste form.

Density, of course, is mass over volume, and this is a part of the storage volume calculation. The higher the density waste form, the smaller the volume of waste form in a repository. This can affect cost. It can affect a lot of storage issues that could arise.

Porosity is a way of comparing waste forms that have porosity such as the glass-bonded sodalite with things that don't, such as an iron phosphate waste form that I'll talk about later. These are important when we are comparing one to another.

Then, there's chemical durability, which is the leach rate in standardized accelerated leaching tests that we conduct here at PNNL, and Bill Ebert at Argonne National Lab, things like the product consistency test and the C1308 coupon tests that Bill runs.

Some different types of waste forms. We have got the single-phase waste form. This is a lead telluride glass that's been loaded with a rare earth chloride mixture. There are things like, maybe you could have a hot-pressed monocyte waste form. This is all single phase. There are no added binders.

Then, there's a whole series of different multi-phase waste forms, things like ceramic metal composites, or cermets. There are halide metal composites called halmets. Glass-bonded ceramics, things like the sodalite, and then there's glass ceramic waste forms.

This table is designed to provide an overview. I am not going to go through this tedious table here that you are looking at, but it basically provides a summary of different families of minerals and different specific types of those minerals. It gives you examples of different species within the salt waste that could be immobilized in these different minerals. The halides, of course, you have got limited solubility for most of the minerals. But then, some of these can actually also incorporate alkalis. You have got alkaline earth options. Some of them have been demonstrated for rare earth and actinide mobilization.

Then, I have listed 'L' as things that could likely be used for these different species. This is sort of to give you hope that there are options for minerals for almost everything in the different salt waste streams that we could expect.

Some graphical representations of some of these definitions I provided. As you start to increase your waste loading and your waste form, the amount of volume required to immobilize that specific amount of waste, it actually starts to drop. The more specific waste forms we start to target, things like rare earth specific waste forms, you have got options like the lanthanide borosilicate or lanthanide alumina borosilicate glass that has waste loadings of up to 60 weight percent of rare earth oxides.

Things like the zinc-in-titania glass composite waste form that has waist loadings of around 40 weight percent rare oxides. Then, as I start to go to less specific waste forms, things that are more designed for processing the full salt that hasn't been partitioned, the cations haven't been partitioned. The storage volume starts to go up quite a bit, whereas the waste loading starts to drop.

Another way of thinking about storage volume is if I have a specific amount of waste starting with the same amount, and I start adding more binders, then my storage volume is going to go up. The goal is to start finding ways to add as little amount of binder and additives as possible.

I mentioned the other waste loading definitions instead of just full salt, because when I start trying to compare the glass-bonded sodalite ceramic waste form to the iron phosphate waste form, this waste form has the halide still in the salt, whereas these halides have been removed and the salt cations have been converted into oxide. We can't just say salt loading or full waste loading, we have to be specific, and so we use this term salt cation loading.

You can see here this is the benefit of doing work to improve your waste form options, and it's that we can go from a 3.8 salt cation percent loading, this is by mass, to almost 18, if we start using some of the more advanced waste form options, such as the iron phosphate waste form.

These graphics are designed to provide you with hope, I would say, where you have got the un-partitioned salt to partially dehalogenated salt, to fully dehalogenated salt. Depending on how much you want to work with your salt, you have got different options available for actually immobilizing that product that you get. That's what this is for. This specific chart here is to allow you to see that you have got options to remove specific partitions of the salt using different techniques, things like oxidative precipitation, reactive precipitation, reactive distillation to remove rare earths. This gives you some options for different partitions that you can do.

When we think about sodalite, the specific sodalite we are working with here is alumina silicate sodalite. This is a beta cage that's formed by the alumina silicate network. Inside the beta cage, you have got the halide alkalide tetrahedron that is represented here, that's immobilized inside the beta cage. What that means is that for every four alkalis, you can have one halide. You have got stoichiometric limitations on what you can actually immobilize in the sodalite, where almost the entire sodalite is actually non-waste. It's all alumina silicate. The amount of waste you can immobilize in a specific amount of sodalite is not very high.

These are some examples of different glass-bonded sodalities that Steve Frank made at Idaho National Lab. The different colors represent different binders, different binder loadings. Binder means glass here. And different salt loadings that I talked about. Porosity is a problem. This is a 26-weight percent glass bonded sodalite with 8 weight percent salt.

In this, you can see the block represents the porosity. The porosity is rather high in this material, whereas if I go to a 40-weight percent glass and a 10-weight percent salt, I can reduce a lot of that porosity. But now that I am adding more glass, I am actually making the waste form larger. I am negatively affecting my storage volume, but I am positively affecting my porosity and my durability should go up here.

I should go back and say this that the way that this sodalite is made is the salt is occluded into zeolite 4A particles at 500 degrees C, and then a glass binder is added, and it's subsequently fired using pressureless sintering at 925 degrees C. That's how that waste form is made.

The iron phosphate process is summarized in this graphic, where we take salt wastes, react them with phosphates. In this case, we are talking about ammonium dihydrogen phosphate. The product from this yields an ammonium chloride that can be reacted with uranium metal to create uranium chloride, if so desired, to return to the electro-refinery or to your molten salt reactor.

The other products that conform are things like acids, like hydrogen chloride, hydrogen iodide. Iodine gas is a possible product. Depending on how this is run, you can get ammonium iodide, and of course, water is a byproduct. Byproducts from this reaction include ammonia and hydrogen.

The intermediate that comes from this initial reaction at 600 degrees C is an intermediate phosphate glass. That's not chemically durable, so it's reacted with glass forming chemicals like ferric oxide, vitrified at high temperatures up to, say, a 1,000 to 1,200 degrees C to create a chemically durable iron phosphate glass waste form that can have different iron phosphate crystals in it as well.

This picture represents some examples of different materials we have made with different ammonium-to-chloride ratios and different salt-loadings. You can see that some of these produce very crystalline products, where some of these are very amorphous. We have tried to optimize the salt-loading and the phosphorous-to-iron ratio to create the highest waste-loading material we can that has the best chemical durability. This is something we have been working on for a few years, where we make these at PNNL and then Bill Ebert at Argonne National Lab does the durability testing.

One of the issues with phosphates is that they tend to create lots of different phases upon slow cooling. If these were to be made in a large scale, we would melt them in a melter and we would pour them into canisters. You can see here this is a canister centerline cooled sample. This is an EDS dot-map. But what I want to draw your attention to is the seven different phases that are present here in the sample that are all very, very similar compositionally. There's a lot of work that we are trying to do to understand the phase distribution as a function of cooling rate and initial sample composition. This is a complicated process that we are trying to understand better for this waste form.

To make these iron phosphate waste forms, we use our dechlorination furnace. This is our five-zone dechlorination furnace, the Generation II furnace. More information down here if you are interested.

This furnace is really neat because it actually opens up, the front opens and then the whole thing opens up as a clamshell, where I can load my off-gas line, which is represented here in this schematic, into the furnace with the crucible at the same time. The off-gas line is connected to a set of condensers to condense any liquid products that come through into the collection flask.

The ammonium chloride that comes through from the reaction in the crucible gets condensed in the glassware that I can recover the ammonium chloride. We have had recoveries up to 97 mass percent – mass balance. This is a pretty neat little system. It's got, as I said, five zones, but we also have over-temperature controllers to make sure that everything is running as it's supposed to, and we don't have anything heated to too high of temperatures.

The ultra-stable H-Y zeolite process I mentioned earlier, it's a way of dechlorinating salt using a hydrogen zeolite, where the hydrogen reacts with the chlorine and the salts and creates HCL. Then, your dechlorinated product can be hot-pressed into a monolithic waste form.

The process, this was developed at the University of Utah by Mike Simpson. This is Manish Wasnik and then Krista Carlson. They estimated that 120 hours would be required at 625 degrees in order to yield a 99% dechlorination efficiency. This is a long time to run this, but when Levi Gardner was doing this testing on these different pellets, he was trying to figure out does it have to be fully dechlorinated, so that's what these different numbers represent is the dechlorination percentage.

The materials worked pretty well. The durabilities were pretty comparable to the glass-bonded sodalite.

Tellurite glass is a very unique glass system that we have worked with here at PNNL that you can use to dissolve various different salts. What we found is that even though the strontium chloride, the lithium chloride-lithium oxide, and then the potassium lithium chloride with fission products, these particular glasses, while they look single phase, there's very incongruent dissolution that occurs. With the high alkali tellurite glass, the durabilities aren't very good.

But when we start looking at things like rare earth chloride immobilization, these particular glasses were single phase, and they had very good chemical durability. These are an option, I say a potential option, because they are very expensive to make. TeO2 is very expensive because it's a very rare compound. I don't know how plausible this would be to implement, but it is certainly something that could be considered.

Looking at the lead tellurite system, this is the binary phase diagram. We have got the glass forming region in gray. All of our work pretty much is focused on this red line, or the 78-mass percent TeO2, 22 mass percent PbO. We did look at these other lines to see if we moved closer to the metal of the GFR if these glasses would behave better and they tend to crystallize a lot more, and the durabilities just weren't as good. I feel like a lot more work could be done to optimize these particular glasses if waste forms were to be made.

One of the interesting things we saw with these glasses is you have got your single-phase glass at the bottom. These are very pretty transparent red glasses. At the top, you have got this phase separation that occurs that creates this opaque layer, where you have got salt droplets that start to precipitate out or freeze into the material as the top layer cools slower during quenching. This is the 15-mass percent ER salt at the lower loadings, the 10. It looks like it's a pretty homogeneous glass. Then, these are TEM micrographs showing that the phase separation starts to occur even at the 14 at very small scales. This is the nanoscale.

These are C1308 tests that were run on coupons of tellurite glass. You can see that this is the penetration layer where the chlorine is actually being depleted from these different glass coupons. This is some graphics that can be used to sort of track corrosion, and then we use EDS dot-maps to track compositional changes within the coupon at that interface boundary layer.

As I mentioned, very few studies have been done looking at fluoride waste forms. This is a study done at ANSTO by Dan Gregg and Lou Vance before he passed away. This was one of his last projects that he worked on. It's a really neat process that they developed where they took a FLiNaK salt, mixed with different fission products. The stimulant was alkali and alkaline earth nitrates, as well as antimony and moly oxide.

These salts were added to boric acid, aluminum nitrate, calcium hydroxide, and colloidal silica. They were mixed, heated, and dried. They were calcined. This calcined powder was milled, and then they were either cold press and sintered or HIP-ed. This is a really neat system because they found that the fluorine was partitioning to calcium fluoride. It's reacting with this calcium hydroxide phase to form environmentally stable calcium fluoride inclusions encapsulated by the glass phase.

They also found some residual fluorine present in the glass, and these materials had fluoride loadings up to 7.2 mass percent and full waste loadings of 17 to 21 mass percent. This is a really neat idea to basically force the fluorine, which is known to be very difficult to immobilize, into a very nice, stable, chemically durable phase of calcium fluoride.

This is an example of their HIP can before and after. I just thought that was kind of cool, so I wanted to show that. More information down here at the link.

Some other things that need to be considered. We talked about chlorine-37 earlier. Chlorine-35, natural chlorine-35 can be neutron activated to 36, which is a long-lived half-life of 300,000 years. Chlorine-37 could be an option to enrich these salts to prevent the chlorine-36 production. The options I mentioned for dehalogenation could include things like phosphate, ammonium phosphates like ammonium hydrogen phosphate, dihydrogen phosphate or diammonium hydrogen phosphate to yield ammonium chloride. You can also react with phosphoric acid or the hydrogen zeolite to create hydrochloric acid, where the chlorine-37 could then be recycled into subsequent batches of salt.

The other thing is minimizing tritium production. This can be produced through activation of lithium-6 or fluorine-19. This is an option for another example of why you might want to recover things, things like the chlorine-37 I mentioned, but lithium-7 as well. The processes to create these enriched salts can be very expensive, and you don't want to just throw them out. Options for recovering these and enriching them need to be explored and need to be evaluated.

Another thing that needs to be considered is technology readiness levels. I want to make it very clear that a lot of the things I have talked about are sort of one-off studies or very initial low-TRL-level technologies. Our work is needed to bring these technologies. If we want to use them, they need to be brought up the TRL level chart here. The problem with the TRL level chart is that bringing things higher up on the chart can be very expensive, and they can take years to do. These are just things that need to be considered.

To summarize, high-level takeaway. I want to make very clear is that we believe that the waste problem for MSRs is solvable. Starting points exist for technology development in every topic area that I have mentioned. I have provided data that shows that some of these might be promising technologies. But a lot of the TRL levels of these are very low, so they need to be demonstrated at larger scale. They need to be demonstrated with radioactive salts. Chlorine technologies need to be demonstrated with fluoride-based salts.

Some of the waste form and salt treatment options are better than others. This is something I alluded to multiple times. Things like the waste loadings can be very different. Things like the volume, so if a waste form is cheap to make but it occupies four times the volume in a repository, is it ideal?

Things like simple and multiple process steps required to make different waste forms. Some of these require four or five steps to make, whereas some of them are a simple added to a glass, a frit and melt. Cost, of course, is a big driver for all of these processes.

Several opportunities exist for R&D in each of these areas, which I think is pretty exciting. It gives us a lot of opportunity to develop new processes and techniques.

There's a lot of potential for component recycle. I have alluded to it multiple times, things like chlorine-37 and lithium-7 recovery, as well as graphite recycled for waste minimization of things like the graphite moderator.

With that, I'll turn it back.

Berta Oates
Thank you. We'll take a quick look at the upcoming webinar presentations.

In July, a presentation on Gas Cherenkov Muon Spectrometer for Nuclear Security Applications.

In August, China's Multi-purpose SMR-ACP100 Design and Project Progress.

In September, Development of In-Service Inspection Rules for Sodium-Cooled Fast Reactors Using the System Based Code Concept.

With that, I apologize again for the technical difficulties. In practice and rehearsal, that worked perfectly. Brian was not able to attend with us and we thought we could slip in a video, but Dr. Vienna is here to answer questions live. If you have questions, please go ahead and type those into the question pane, and we will take your questions as long as we have time.

John, are you able to see the question pane? The first question that I see is, is there a potential for a radioactive cesium release?

John Vienna
Hello?

Berta Oates
Hello?

John Vienna
The reactors and waste – can you hear me?

Berta Oates
I can hear you, yes.

John Vienna
Okay. The reactors and the waste form fabrication processes will be designed and implemented in a way that greatly restricts the possibility of cesium or any radionuclide release as is done now with other waste plants.

Berta Oates

Thank you. The next question is a little longer. Last month, one paper from Stanford insisted that the amount of radioactive waste from SMR will be way higher than large power water reactors. The paper said that in the case of a SFR, sodium coolant is high-level waste, therefore, the amount of waste from SFR is 30 times bigger than a large power water reactor. I hope to know whether sodium coolant is equal to spent fuel in terms of radioactive waste. Unlike SFR, the paper does not consider salt coolant of MSR as high-level waste. I know that's kind of long and I am going to post it now so people can see it. Sometimes reading it helps. Do you have thoughts on that, Dr. Vienna?

John Vienna
I don't have thoughts on that. There is a very significant debate on that paper right now, and I don't care to weigh in on it at this point.

Berta Oates
Thank you. Waste from solid fuel reactors can be readily isolated and stored until the problem of waste disposal is solved later. Since MSR waste processing is done online, does this mean that the process has to be demonstrated before the first MSR prototype is ever built?

John Vienna
There are more than one approaches to MSR salt waste processes. Some MSR vendors have the approach that the salt will remain in the reactor and will only be managed at end of reactor life. Others believe that online reprocessing of the salt, or management of the salt, is preferable. It depends a lot on the approach taken by the reactor vendor. It's not a one-size-fits-all. When the reactor is a dissolved fuel reactor as opposed to, say, a TRISO fuel reactor, the off-gas management will certainly occur real time as the reactor is online.

Berta Oates
Thank you. Is there any cost estimate for the pursuit of these solutions? The questions in case, thousands of dollars, millions of dollars, billions of dollars, any…?

John Vienna
I think I can firmly say we don't have a cost estimate, even an order of magnitude estimate. It depends on which reactor, which salt, which processing scheme is going to be implemented. As Brian mentioned at the beginning, there are an awful lot of different salts, different processing schemes, and so until we narrow that down a little bit, it's hard to estimate the cost.

Berta Oates

Thank you. Would using thorium fuel simplify or complicate the MSR system?

John Vienna
Again, thorium fuel use assumes a breeder breeding uranium-233, so there will almost certainly be fuel processing and recycle so that the uranium-233 can be used as a fissile material. That can be done either after long burns with some other fissile material that is breeding U-233, or it can be done online real time, as the Oak Ridge design was done. It's one of many options. I am not entirely sure it's significantly more challenging than the last. Any operation where there is fuel reprocessing, that has the complication of the chemistry that has to be performed in order to reprocess the fuel.

Berta Oates
Thank you. What is the duration for mobilization of chloride-based salts?

John Vienna
I am not sure that I understand the question. Is there a way to reword that question?

Berta Oates
If you could add some more information to your question, we will circle back around and see if we can get you an answer.

Would the activation of the graphite, that is carbon-14, cause it to be GTCC without any fission products?

John Vienna
David, I am not entirely sure. There have been analyses of graphite from other reactors in Europe that some reactors that moderator graphite were sufficiently activated. I suppose it depends on the impurities and the carbon of the graphite. But the short answer is I don't know.

Berta Oates
Thank you. What areas of this research can a civil engineer going for his master's program in nuclear engineering could really fit in?

John Vienna
Oh, there are great opportunities there. I am glad for that question. There is, of course, the waste form fabrication and testing, the waste process design and testing, off-gas treatment method design and testing, and study of sort of geologic performance of waste forms are all great areas to study. I encourage the student to contact professors at schools that perform this sort of research, and there

really is some interesting and impactful areas of research going on right now.

Berta Oates
Great! Thank you. Is there a plan for environmental monitoring in the area surrounding an MSR? Is environmental monitoring necessary?

John Vienna
I don't know the answer to that. Patricia, do you?

Patricia Paviet
No, I don't know either.

Berta Oates
Thank you. Let's see. There are several here. From your point of view, what would be the best option to stabilize salts with high volume of chlorine-36 in terms of volume reduction?

John Vienna
If you wanted extreme volume reduction, then recycle of the chlorine would probably give you the highest volume reduction. There are waste forms that Brian discussed in the presentation that looked at that. If the primary objective was volume reduction, I would say use of chlorine recycle and mobilization of the associated cations.

Berta Oates
Great! Thanks. The next question deals with that is what is the cost of highly enriched chlorine-37 that has to be before it is recycled? What is the cost of highly enriched chlorine-37 that has to be before it's recycled?

John Vienna
I am sorry. Once again, I am not sure how to answer the cost question. Patricia, is that something you have information on?

Patricia Paviet
No, we don't know. Like, Brian said at the end of his talk, with the technology readiness level, MSR were a little bit earlier compared to SFR, for example. There's a lot of research that he has done right now, but in terms of costs, we simply do not know.

Berta Oates
Thank you. Chlorides are particularly water soluble and compose an issue from a transportation perspective. "Conventional wisdom" has to remove all salt and recycle it back. But if you are suggesting it's

okay from a regulatory perspective to maintain some in whatever waste form is selected.

John Vienna
Chloride can be immobilized in ways that avoid its dissolution into the environment. Typically, when we do immobilize it, as Brian said, leaving the chlorine intends to lower the waste loading of the resulting waste, but it is a viable option to develop a durable waste form that contains chlorine.

Berta Oates
Thank you. What is your opinion on batch reprocessing versus continual reprocessing? In the former, the spent salt from an MSR fleet of SMRs based on MSR technology would be shipped to a central reprocessing facility, perhaps co-located with a long-term storage facility or DGR.

John Vienna
That's a fine question, and a trade-off study is needed there. One option is to co-locate the process with the reactor; the other, as you pointed out, is to locate the processing system with the DGR. There are trade-offs there. Obviously, locating the processing away from the reactor requires salt transportation, which has an added cost because that transportation has to be performed in a way that's safe and secure, which is certainly possible but a challenge.

Berta Oates
Thank you. I think fluoride salt is not suitable for breeder MSR. Do you agree?

John Vienna
Well, it depends on what you are breeding. The breeder reactor at Oak Ridge, the design that Oak Ridge had for a breeder reactor was using a fluoride salt. That was a U-233 breeder from thorium as the fertile material.

Berta Oates
Thank you. At times, glass will no longer stay in their form. When glass form after time releases radioactive material in water, then this is dangerous. Question, how long will the glass keep radioactive substance?

John Vienna
We have analyzed the lifetimes of nuclear waste glasses. I am specifically talking about borosilicate glasses here for conventional nuclear waste from Pyrex process and the like. The lifetime of the glass can last on the order of millions of years and in deep geologic

disposal. It lasts sufficiently long for safe disposal to protect the environment.

Berta Oates
Thank you. Do you have a plan for fluoride-based salts?

John Vienna
A plan is maybe not the best term for it. It depends, again, on which salt and which reactor design, and which reactor vendor processing strategy. What I can say is there are viable options for fluoride salts that fit a whole range of different fluoride salts and reactor operation strategies. I don't think there's a showstopper there, but the exact plan would depend a lot on which specific salt and processing philosophy of the reactor designer and operator.

Berta Oates
Thank you. Does the waste form containing the molten salt reactor wastes, are they also destined for storage in geological repositories?

John Vienna
The most technologically advanced and publicly accepted management technique for high-level waste is to dispose of the waste form in deep geologic repository. I would say probably yes for the high-level waste. There are a number of other wastes that have other disposal routes available.

Berta Oates
Thank you. Have you estimated the different waste streams for specific MSR considering some of the options for waste management that you have presented?

John Vienna
We have made an estimate for a very limited range. As Brian mentioned at the beginning, there are a number of different MSR reactor flavors and different operating philosophies and separations processes. For one example of those, we have gone through and made estimates of waste volume. That one was the Oak Ridge designed breeder where U-233 was bred from thorium.

Berta Oates
Thank you. Is there a possibility of getting rid of the graphite and the core to reduce the graphite waste issue?

John Vienna
There are molten salt reactors that are planned for fast spectrum, and those reactors don't contain a graphite moderator. I think the answer is, yes, there are reactors without a graphite moderator.

Berta Oates
Thank you. I am not seeing any other questions. Patricia, have I overlooked anything? John, do you see anything in that list that we haven't discussed?

Patricia Paviet
No, I didn't see any other question, Berta.

Berta Oates
What's your view on heavy water as a moderator?

John Vienna
I have honestly not heard of heavy water being used as a moderator in a molten salt reactor, so I am surprised to hear it proposed, to be honest; but there may be somebody else out there that knows more about use of heavy water within the context of molten salt reactor. I have never heard that proposed before.

Berta Oates
I am not sure, Copenhagen Atomics, if that's who's doing that. Thank you, Christoph.

John Vienna
Somebody wrote there is a paper on D2O-moderated MSRs by Los Alamos. Thank you for that answer. I have not read that yet.

Berta Oates
Me neither. Has any consideration been given to converting spent molten salt fuel to an oxide form to be similar to current spent fuel waste?

John Vienna
That's an interesting question, and I am not sure I have heard of anybody considering doing it exactly that way. But it seems like a possibility, again, assuming that the current oxide fuel waste is primarily uranium oxide with minor concentrations of fission products and activation products. What we have looked at more closely is converting the waste into durable waste forms and recycling those components that are relatively high value. I don't know the answer.

Berta Oates
Thank you. Would rare earths produced by the reactor be economically significant compared to production from mining? That might be a…

John Vienna

Once again, I am not sure I can answer that. I would guess not, but I am not certain.

Berta Oates
Again, I apologize for the technical difficulties. John, I am very glad that you were able to be here to answer questions live, and I am glad that we were able to come up with a contingency to play the prerecorded video, even though my system didn't want to play it today. We will edit that portion, I think, so that in the recorded version that's posted online we won't have that significant delay. I appreciate people's perseverance and sticking with us while we worked through those issues.

I don't see new questions coming in, and so in the interest of your time, Dr. Vienna, I will bring this webinar to a close.

Patricia, do you have any closing thoughts or Dr. Vienna, either one of you?

Patricia Paviet
I would like to thank John and Brian for presenting today.

To reassure the people who could not hear very well at the beginning, all our webinars are archived on the GIF website, www.gen-4.org, so feel free to watch it again and to spread the word out.

Thank you so much again, John, for staying with us and answering to all these questions. That's the beauty of these webinars, and also the Q&A portion. Thank you, everyone.

John Vienna
I'd like to also add thank you for inviting us and thank you, everyone, for joining us and listening to our discussion on molten salt reactor waste.

Berta Oates
Thank you. Bye-bye.

Patricia Paviet
Thank you. Bye-bye.

END