Examining Reprocessing Waste to Help Estimate Past Plutonium Production

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ABSTRACT. Nuclear archaeology techniques are being developed to verify the completeness of declarations of initial fissile material holdings. Such a capability is important in the non-proliferation context when a state with past nuclear activities joins the Non-Proliferation Treaty, and in the arms control and disarmament contexts, if states declare their existing fissile material inventories. In cases where permanent structural or moderator materials exist inside a reactor core and are accessible to inspectors, forensic analysis of according samples could be useful to estimate plutonium production. As this may not always be the case, alternatives are required. This paper presents initial results of an examination to which extent measuring reprocessing waste can help verify declarations. In certain cases, it may serve either as a stand-alone capability, where other nuclear archaeology measures are not possible, or as a complementary consistency-check to increase confidence in the completeness of declarations. To assess the capabilities, we define several specific reactor operation histories, and simulate the fuel depletion, the separation process, and the decay of spent fuel and waste.

Background

While there is extensive experience in verifying both the correctness and completeness of nuclear material declarations issued by non-weapon states that are members of the Non-Proliferation Treaty (NPT), there is a lack of methods to verify nuclear material "baseline" declarations, i.e. the first verified declaration a state makes upon entering an agreement. This would be relevant for states that formerly possessed nuclear weapons wishing to join the NPT, and former or current weapon states joining the Nuclear Weapon Ban Treaty, which requires verifying the absence of undeclared nuclear materials. Additionally, baseline declarations will be important for achieving disarmament: A solid understanding of fissile-material holdings is needed to achieve a meaningful degree of predictability and irreversibility of future arms-control initiatives. Speculations about unaccounted fissile-material stockpiles, possibly equivalent to hundreds of nuclear weapons, could make progress in this area very difficult.

As was attempted after South Africa had joined the NPT in 1991,[1] the most promising approach to verify the completeness of baseline declarations is the reconstruction of the

state's fissile material production history.[2] This is called nuclear archaeology, a concept introduced in 1990.[3] Since then, however, there has only been limited research; there remains a research gap on applicable tools and methods, which must be developed for a systematic and effective nuclear archaeology approach.

While reconstructing the past production of highly enriched uranium also requires significantly more research, this paper discusses plutonium production. Here, one approach is to take samples from inside the cores of shut-down reactors, and deducing the neutron fluence from isotopic ratios of trace elements obtained from forensic analysis. From the fluence, the plutonium production can be deduced. One example of this approach is the Graphite Isotope Ratio Method, which is applicable for graphite-moderated reactors.[4,5] While this method has been tested, similar methods for heavy water reactors are in an early state of development. A concept has been proposed which can be used in reactors that use aluminum tubes, such as the Indian CIRUS reactor.[6]

These approaches are significant tools, but will be insufficient in two cases. First, a total plutonium production estimate for a reactor requires that the samples taken were present during the reactor's whole lifetime. For an accurate and relieable estimate, samples must be taken at various positions within the reactor core.[7] This is possible for graphite-moderated reactors, but, for example, not for all types of heavy water reactors, which do not necessarily have permanent structural elements (such as permanent aluminum tubes) inside the core. The reactors at the Savannah River Site, for instance, in the beginning used sleeves that were disposed of with the fuel, and later used semi-permanenent sleeves that could still be replaced.[8] Second, the current approach is only feasible as long as the cores of the reactors have not been dismantled or modified. It is, however, not clear that nuclear archaeology will always be possible before reactors have been at least partially dismantled. For these reasons, complementary approaches are required and should be developed.

Examining the radioactive reprocessing waste is one example of such a complementary signature, provided certain additional information is available such as reactor designs and reprocessing process documentation. Waste will remain accessible for many years, before it is permanently disposed of, and perhaps long after the fuel cycle facilities have been dismantled. This paper addresses information that could potentially be deduced specifically from high-level radioactive waste.

Potential Application

The high-level reprocessing waste contains nearly all fission products and minor actinides after dissolving the spent fuel. Amounts of plutonium and uranium that are sufficient for assay can also be found.[9] Accordingly, it contains a rich isotopic signature of past fuel cycle activities. Information could also be gathered from other waste streams, for example intermediate-level waste.

Radioactive waste could be used to estimate parameters such as fuel discharge burnup or cooling times.[10] This can help reconstruct the production history and be used to examine the consistency with a declaration. For instance, reprocessing waste measurements could point to incomplete declarations, perhaps undeclared plutonium production. Reprocessing waste can also be used to obtain an estimate of the total produced plutonium mass, as the plutonium mass correlates with the volume/mass or heat emission of the radionuclides in the total waste.

Which information can be deduced from the waste and how depends on the complexity of the fissile material production history of the state in question. In limited nuclear programs, it could possible to analytically deduce comprehensive information of the state's plutonium program, for example to determine whether all reactor campaigns have been declared by a state. A precedent is the IAEA verification in North Korea in the early 90s:[11] After having signed a safeguards agreement with the IAEA, North Korea issued its initial declaration in 1992. Therein, it stated that it had only conducted one reprocessing campaign of damaged spent fuel rods from the Yongbyon reactor in 1990, containing 84 grams of plutonium, while the other fuel rods of the first charge remained in the reactor. The separated plutonium was presented to IAEA inspectors, who found that it contained 2.4% Pu-240. Sampling the waste revealed, however, a Pu-240 fraction of about 2.25%. The IAEA concluded that North Korea had separated additional undeclared plutonium in kilogram-quantities, by discharging more spent fuel than declared from the Yongbyon reactor, and/or by having separated plutonium from a Soviet-supplied research reactor. Furthermore, evidence supported the hypothesis that reprocessing waste was kept at undeclared sites. The IAEA was, however, neither able to fully reconstruct the plutonium production history, nor to determine the exact produced plutonium mass.

In principle, an analysis of a larger number of radionuclides from waste could yield additional information, resulting in a more comprehensive understanding of past nuclear operations that what was published about the North Korean case. As scenarios where waste measurements become an important indicator are likely to re-occur, The North Korean example shows the importance of further research to optimize the capabilities of analyzing waste.

For large weapon states with extensive past plutonium production, an analytical approach alone will not be able to deduce the full complex plutonium production history from reprocessing waste. However, waste assay may still serve as a consistency-check of the declaration: All declared information can be used for forward-modelling of the fuel cycle history to calculate the expected waste compositions. Comparing the result to measurements would increase the risk for a state that inspectors could detect an incorrect or incomplete declaration.

Determining Burnup Values, Cooling Times, and Plutonium Production

In reprocessing plants, the dissolved high-level waste is stored in large monitored tanks. One waste tank can contain the waste of several or many reprocessing campaigns. Due to differences in reactor operations, the isotopic signatures of the spent fuel will vary, resulting in average values after mixing in the waste tanks. It can nevertheless be possible in certain cases to distinguish different campaigns to detect undeclared activities, even without prior knowledge of different burnup values or cooling times. The reason is that individual isotopic ratios are *different* functions of the sought parameters, here burnup and cooling time. Consequently, distinct functions for different isotopic ratios can be formulated, and the resulting system of equations can be solved for more than one parameter - depending on the number and nature of the equations.

The isotopic evolution as a function of burnup or time can only be determined if information on reactor design and operations are available, for example from inspection visits or credible documentation provided to inspectors. The exact isotopic composition depends on various secondary parameters, for example the initial fuel enrichment, the specific reactor power, intermittent down-times, the moderator and fuel density, and the reactor temperature.[12] For this paper, let us assume that the fresh fuel composition is known (e.g. natural uranium), as is the reactor design. Information on the reactor operations will be known, but likely be incomplete.

Based on the available information, depletion calculations provide data points of isotopic concentrations at various burnup points. Then, appropriate functions can be obtained by fitting these data points, as shown in an example below. Let us assume that fuel was discharged from a reactor at different burnups. One could solve the following system

$$\begin{aligned}
({}^{N_{1a}}\!/_{N_{1b}})_{meas} &= a * ({}^{N_{1a}}\!/_{N_{1b}})_{fit}(BU_1) + b * ({}^{N_{1a}}\!/_{N_{1b}})_{fit}(BU_2) + ... \\
({}^{N_{2a}}\!/_{N_{2b}})_{meas} &= a * ({}^{N_{2a}}\!/_{N_{2b}})_{fit}(BU_1) + b * ({}^{N_{2a}}\!/_{N_{2b}})_{fit}(BU_2) + ... \\
({}^{N_{3a}}\!/_{N_{3b}})_{meas} &= a * ({}^{N_{3a}}\!/_{N_{3b}})_{fit}(BU_1) + b * ({}^{N_{3a}}\!/_{N_{3b}})_{fit}(BU_2) + ... \\
&\vdots
\end{aligned} \tag{1}$$

where $({}^{N_{xy}}\!/_{N_{xz}})_{meas}$ are the measured isotopic ratios after mixing in the waste (assuming that decay is negligible), $({}^{N_{xy}}\!/_{N_{xz}})_{fit}(BU_i)$ are the fitted functions of burnup, and $a, b, ...$ are the relative fuel masses that were discharged at the specific burnup values ($a + b + ... = 1$).

An analoguous system can be used to calculate different cooling times of fuel, whereby no function fitting would be required, as decay $({}^{N_{xy}}\!/_{N_{xz}})_{decay}$ can be analytically calcu-

lated. This analysis requires the isotopic concentrations after discharge from the reactor ($N_{xx,0}$) to be known, for example from the burnup analysis above.

$$\begin{aligned} ({}^{N_{1a}}/_{N_{1b}})_{meas} = \quad & a * ({}^{N_{1a}}/_{N_{1b}})_{decay}(t_1, N_{1a,0}, N_{1b,0}) \\ & + b * ({}^{N_{1a}}/_{N_{1b}})_{decay}(t_2, N_{1a,0}, N_{1b,0}) + ... \\ & \vdots \end{aligned} \tag{2}$$

This approach is targeted at nuclear programs with limited fuel cycle histories. For complex fuel cycle histories, there would be too many unknown parameters. However, analyzing the waste can serve as a consistency-check by forward-modelling, as described above. Inspected states might provide forged documentation, while being consistent with one isotopic ratio. It will, however, be much more challenging to forge documentation, resulting in agreement with *many* assessed isotopic ratios, due to their different functional relationships.

Waste could be used to determine the total plutonium production, either as a consistency-check to determining the fluence from reactor samples, or as a stand-alone measure if reactor samples are not available. The plutonium production can be quantified if inspector access is given to all waste sites for the purpose of taking measurements, and if the cooling times are known from declarations that were checked for consistency with the waste sample analysis, or from the analytical approach for small nuclear programs. Inspectors would need to obtain the total masses of radionuclides. For waste stored in tanks, this could be achieved by measuring the waste volume, density, and composition. In the case of vitrified waste, if the isotopic composition is known, calorimetric methods may determine the mass of radionuclides inside the canisters or casks. An inspected party may try to hide waste. However, not only does it then risk that inspectors will discover it. Knowledge of when reactors operated and what the burnup values were hint at undeclared waste sites, if this knowledge (for instance obtained from open source information analysis) is not in agreement with the waste sampled from the declared waste site(s).

An Example

To demonstrate the described approach, let us assume that a state provides documentation on its past nuclear activities. It declares that it operated a test reactor only once and produced non-weapon-grade plutonium. In addition to information on operating records and reactor design, the state allows inspectors to take waste samples. The inspectors then examine whether the waste samples are consistent with the declared information.

To address this case study, we conducted infinite lattice depletion calculations using MCODE,[13] which couples MCNP and ORIGEN. We simulate a heavy water reactor using natural uranium slugs based on the Savannah River reactor designs and the Mark I fuel design,[14] operating at a specific power of 4.45 Watts per gram initial heavy metal.

To deduce burnup, we use three isotopic ratios that would be determined by mass spectrometry of waste samples: U-238/U-235, U-236/U-235 and Pu-240/Pu-239. All isotopes have very long half-lives, so the impact of an unknown cooling time is very low. Furthermore, the functional relationships of these ratios against burnup are all different, allowing to identify batches differing in burnup. We fit the MCODE results with functions describing the evolution of isotopic ratios over irradiation time at constant power, which is therefore proportional to burnup. These can be formulated based on the solution of the depletion equation. For example, we use the following fit function for U-238/U-238:

$$\frac{N_{U-238}}{N_{U-235}}(t) = \frac{N_{U-238}}{N_{U-235}}(t=0) \cdot exp((\overline{\sigma^{abs}_{U-235} - \sigma^{abs}_{U-238}})\overline{\phi} \cdot t) \tag{3}$$

where $\overline{\sigma^{abs}_{U-235} - \sigma^{abs}_{U-238}}$ and $\overline{\phi}$ are the parameters obtained from fitting. σ^{abs}_{U-xxx} are the total absorption cross-sections including fission. As the cross-sections and fluxes are not constant over time, we fit them to obtain average values. The other two functions are similar. In difference to U-238/U-235, for the U-236/U-235 and Pu-240/Pu-239 ratios, neutron absorption of one nuclide of the ratio forms the other. For the latter, the production of the parent Pu-239 from U-238 is also considered. All fitted functions are in good agreement with the MCODE data, see Fig. 1 for an example (the U-238/U-235 results).

In the case study, we assume that fuel of two different burnups has been reprocessed and mixed in the same waste tank (70% at 0.3 MWd/kg and 30% at 3.5 MWd/kg). This corresponds to the following ratios in the waste, that the inspectors would measure:

$$\frac{N_{U-238}}{N_{U-235}} = 162.1 \qquad \frac{N_{U-236}}{N_{U-235}} = 0.0383 \qquad \frac{N_{Pu-240}}{N_{Pu-239}} = 0.0637$$

Not knowing about this mixing, inspectors may first assume that only one batch has been reprocessed. Fig. 2 shows that the burnup values calculated for each ratio separately are, however, not in agreement. It is clear that waste of different burnup values has been mixed. To solve the system of three equations, we use the `fsolve` function of the Python library SciPy. Let us assume that the state declared it only discharged fuel at 3.5 MWd/kg. In (1), we specify $a = 1$, $BU_1 = 3.5$, and $BU_2 = 0.5$ as initial parameters for `fsolve` (to check whether a portion of the fuel had lower burnup). Using

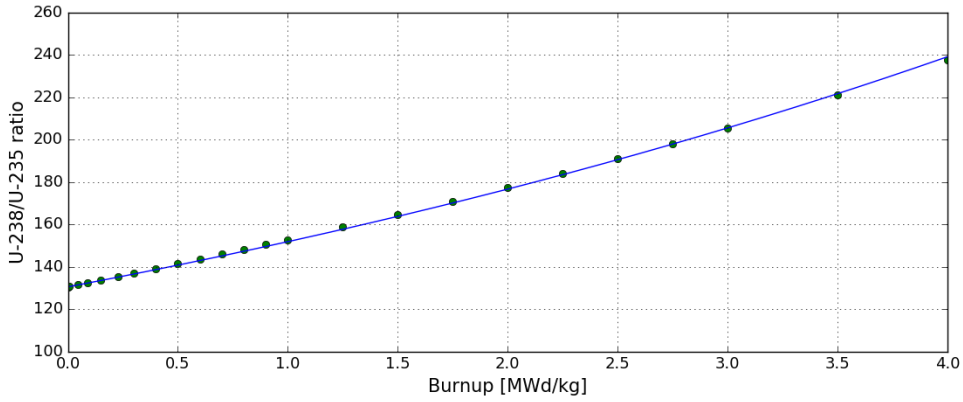

Figure 1: Comparison of data points obtained from MCODE simulations (green dots) and the function fit using the data points (blue line.

$b = 1 - a$ (assuming a maximum of two different burnup values), `fsolve` calculates the correct values $a = 0.3$, $BU_1 = 3.5$, and $BU_2 = 0.3$ based on the three isotopic ratio values. It is found that the state has produced undeclared weapon-grade plutonium.

Furthermore, it can be assessed when the weapon-grade plutonium had been produced. For this example, we use the isotopic ratios Cs-137/(Ba-137+Cs-137) and Cs-134/(Ba-134+Cs-134). Note that Ba-137 and Ba-134 are the respective stable daughter nuclides of the Cs isotopes, so that the denominator is constant over time, as Cs-137 and Cs-134 decay. The denominator would be obtained by mass spectrometry measurements, whereas Cs-137 and Cs-134 would need to be measured by gamma spectrometry under very controlled circumstances (good calibration, well known measurement geometry). The two nuclides have been chosen for their strong gamma emissions. The short Cs-134 half-life of 2.06 years limits, however, the range of cooling times that could be assessed. Another isotopic ratio would be required for longer cooling times.

In (2), according to the burnup results, we set $a = 0.3$, insert the values $N_{1a,0}, N_{1b,0}$ obtained by MCODE at $BU_1 = 3.5 MWd/kg$, set $b = 0.7$, and insert $N_{2a,0}, N_{2b,0}$ obtained by MCODE for $BU_2 = 0.3 MWd/kg$.

We succesffuly test that the system of equations is correctly solved for the case where the cooling time has been 6 years for the low burnup waste, and 7 years for the higher burnup waste (using $t_1 = t_2 = 7$ as initial parameters). This scenario would correspond to the following isotopic ratios:

$$\frac{N_{Cs-137}}{N_{Ba-137} + N_{Cs-137}} = 0.858 \qquad \frac{N_{Cs-134}}{N_{Ba-134} + N_{Cs-134}} = 0.114$$

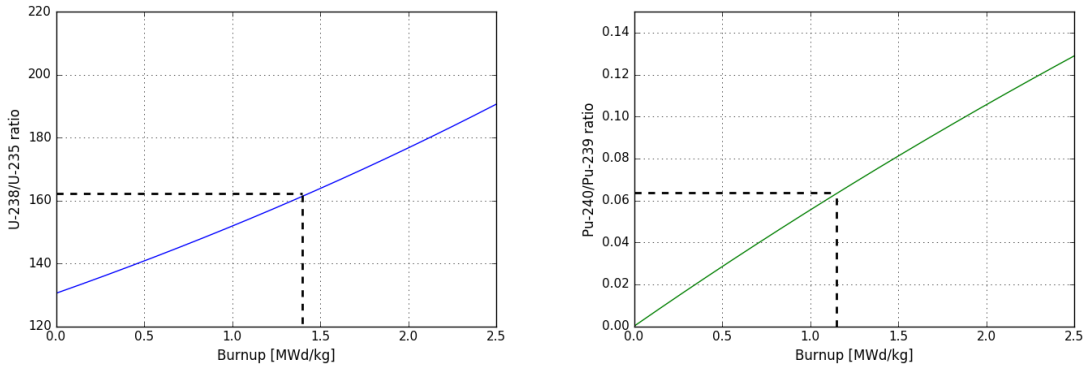

Figure 2: Isotopic ratios as a function of burnup. The horizontal dotted line shows the ratios after mixing waste of two different burnups. The vertical dotted line shows which burnup value it corresponded to, if there was only waste of one burnup. As these two burnup values are not in agreement, mxing waste of different burnup values must have occured.

The cooling times are the required information to deduce the total plutonium production from assessing the total masses of radionuclides in the reprocessing waste today.

Conclusion

This paper has introduced a method with an example of how reprocessing waste can help verify declarations of states on their fissile material production histories. It provides a unique signature of a state's past nuclear activities. By analyzing isotopics and waste mass, the produced plutonium can be estimated, and indications for potentially undeclared activities can be found. It is particularly important as there are cases, that cannot be effectively addressed by existing nuclear archaeology techniques. For example, reactor cores may already have been dismantled when nuclear archaeology is to occur, or permanent structural elements in still existing reactor cores may not be suited for accurate assessments of plutonium production.

This paper is purely conceptual in nature. Significant further study is required to examine how the presented concept could be applied in specific cases. Especially in more complicated fuel cycle histories, methods and algorithms to calculate the different burnup and cooling time values must be further studied. Due to uncertainties in the measurement of isotopic ratios, an exact solution of a system of equations may not be possible. Then, the task could be formulated as an optimization problem, that seeks to find the parameters that *best* fit to the isotopic ratios. As there may be more than one solution (minima of the optimization problem), it is also important to look for other,

ideally all possible solutions instead of finding only one of the local solutions depending on the choice of initial parameters. Only then can it be decided which of the solutions is the most plausible, given all prior knowledge of the inspected state's nuclear activities.

In future work, the uncertainties of measured isotopic ratios must be assessed, and the best-suited isotopic ratios must be identified. For example, uncertainties need to be examined that result from combining gamma spectrometry and mass spectrometry to obtain certain isotopic ratios, that cannot be obtained from one measurement technique alone.

The representativity of the acquired waste samples must be examined. If taken from waste tanks, it depends on the spatial homogeneity within the tank. If the waste remains acidic, it can be expected to be mostly homogenic. If, however, a waste tank contains waste in several different forms as a result of further processing, e.g. sludge, saltcake, and supernate, it will not be homogeneous, and a larger number of samples would need to be taken at different locations.

Lastly, while this paper's example is based on infinite lattice calculations, full-core simulations will be required to apply this concept, as differences in burnup throughout the core must be taken into account. Also core shuffling influences the precise isotopics of spent fuel.

The current uncertainties on fissile material stockpiles are high, and it will require a large and enduring effort to understand and reduce the current uncertainties. The complexity of past production activities requires an approach fusing various techniques into an overall nuclear archaeology concept to confirm future declarations. Examining reprocessing waste can be an important addition to the nuclear archaeology toolbox.

Acknowledgements

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Endnotes

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