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Written Portion of Prelims Defense:

Do a critical reading of two journal articles and submit a brief report on your assessment

**“Isotopic Signatures of Weapon-Grade Plutonium from Dedicated Natural Uranium-Fueled Production Reactors and Their Relevance for Nuclear Forensic Analysis”**

1. Summary

The first article studied plutonium produced in three different Pu production reactors and determined that it is difficult to distinguish Pu from these reactors. The three reactors are listed below.

1. Hanford-type (graphite-moderated, light-water cooled) reactor [US]
2. Calder Hall-type (graphite-moderated, gas-cooled) reactor [United Kingdom – North Korea]
3. NRX-type heavy-water-moderated and light-water-cooled reactor [Canada – India, Pakistan]

It is alluded to that these reactors were chosen because of their Pu production status and their existence in states non P5 states (India, Pakistan, North Korea). Infinite lattice calculations were completed with MCNP and coupled to ORIGEN2 with another code called MCODE, which feeds results from one code to the other and uses a predictor corrector method for burnup calculations. The power density for all reactors were set at 40 W/cm3 and Pu isotopics were studied for these reactors under the conditions of natural uranium and recycled natural uranium loadings and a final 239Pu wt% of 93.8.

It is concluded that these three reactors cannot be distinguished from each other based on Pu isotopics in either uranium loading condition, the recycled uranium loading scenario having more 238Pu due to 236U. Two reasons for this are similar single group cross sections and uncertainties in reactor models and mode of operation. The author maintains that differences between fast reactors, LWRs with LEU, and these reactors can be distinguished with 238Pu/totPu and 242Pu/240Pu ratios. Further, the author states that the lack of actual sample data hinders the ability to distinguish between these productions reactors because, with these samples, specifics of irradiation are known and because there are differences in material properties. Finally the author concludes that a comprehensive database for nuclear forensic analysis, containing actual samples, should be created.

1. Criticism

In the first paragraph of the introduction, the purpose for this paper is to “understand the relative importance of predictive versus empirical isotopic signatures – both of which are relevant for nuclear forensic analysis.” In this paper predictive refers to simulation, and empirical refers to experimentally determined values of Pu. I think both are important and relevant for nuclear forensic analysis, because simulation should be validated, but not for the reason the author states later in the paper. As an aside, it almost sounds like there are two different isotopic signatures gathered from predictive and empirical methods, but in reality, the signature should be the same (ratio of certain isotopes).

In the second paragraph of the introduction, the author mentions that the age of the material and the time since last purification can be solved with chronometric methods. They provide an example of the 241Am/241Pu providing information about the time since last purification, but no support for the age of the material (time since being removed from the reactor). Presumably this should be done with Pu and its daughters because this study analyzes Pu isotope ratios. If it is not the intent to allude to being able to solve for both, then it should be made clearer.

In the second paragraph of the second section of the paper the author states that plutonium production is maximized in natural uranium-fueled reactors. Later in the paper the author repeatedly says that these three reactors are the most important types of production reactors. The first statement should be cited, because Fast reactors produce a lot of Pu with depleted uranium in the blanket region, and the second statement was supported historically, but could be false in light of fast reactor systems being built (PFBR in India).

When discussing the predictor-corrector method for solving for isotopics as a function of time steps, the author cites a reference to support that this method provides most accurate results for a given total number of MCNP calculations. This may or may not be true, but the source does not directly support this claim. The source compares three different methods for solving a function, with three different methods, with no discussion on the order accuracy (how error decreases as a function of number time steps) of each solution, which is needed to make such a definitive claim as the author states. Rather, the error is shown for a single time step. Predictor corrector calculations have been supported by big industry codes like CASMO because accuracy is increased, especially when burnable poison rods are involved. The case at hand does not have burnable absorber rods.

The author studies how the addition of neutron absorbers to the coolant to simulate control rods, when it actually simulates boron dissolved in water. If the author wants to simulate control rods, then they should simulate a larger portion of the core and include control rods. In the error analysis the author does not consider errors associated with: the 1-group assumption, effects of infinite lattice, or errors associated with experimental measurements. Also there are no error bars on any of the reported numbers.

The analysis of using reprocessed uranium to produce Pu utilized pure uranium output from the simulations, when in reality there would be some amount of impurities in the matrix. If these impurities are accounted for the author should mention how they were accounted for, if not, then the impurities effect on the neutron flux should be stated as negligible (especially at BOL).

Author says that actual samples would be more conclusive because the material caused by a priori unknown specifications are known, but the whole point of the forensic exercise is that you do not know. If the author is trying to state that we can model specific reactors, then you don’t need the material to be more conclusive (experiments do not have zero error), but to validate your simulation. I am not sure why they want actual samples or how they will help, they give a reason, but it doesn’t make sense to me.

Example:

“The Fact that countries generally produced weapon materials under strictly controlled and dissimilar operating conditions has created differences in material properties that nuclear forensics could exploit” (Do you need samples for that? Or the operating conditions)

1. Conclusion

This paper provided useful information about the Pu vector among several reactors, even beyond dedicated production reactors. I agree with the conclusion that the three reactors modeled would be difficult to distinguish based on the Pu vector, but I disagree with the conclusion that actual samples would provide definitive differences between reactors that could not be determined through simulation.

**“TRI-n-BUTYL Phosphate as an extracting solvent for inorganic nitrates - III”**

1. Summary

The second article explored D-values for the three different oxidation states of Pu, (III), (IV), and (VI), in nitric acid or sodium nitrate, with TBP diluted in kerosene. Samples were prepared from tetravalent Pu in 6 M HNO3. Pu(IV) was reduced with Fe(II) in order to run experiments for Pu(III) and Pu(VI) was prepared with anodic oxidation. Dependencies of nitric acid, TBP, Pu, and uranyl concentrations on D-values for Pu in its three oxidation states were explored. These dependencies were related to the power of the number of modules needed for reactions (equilibrium constant). Pu was measured with alpha spectrometry and nitric acid concentrations were determined through titration. Errors for this work were due to residual Pu(IV) during Pu(VI) experiments (up to 9%) and the reproducibility of final results was ±10%.

Pu(NO3)4, was most readily extracted by TBP in kerosene, followed by Pu(VI), and Pu(III), each with a D value less than the previous by an order, and two orders of magnitude, respectively. Increasing nitric acid concentrations increased extractability due to increased availability of nitrate ions. The D-value for these reactions should be related to the fourth power of the nitrate ion concentration, and this experiment yielded results something closer to a third power dependency because Pu(IV) could come complexed with a single nitrate.

Increasing TBP concentration for Pu(IV) had an showed a square law increase in D-values with constant nitric acid concentration because two TBP molecules are needed to form the extractable complex. The authors also tested sodium nitrate as the salting solution for extraction and found that, mole for mole, sodium nitrate was more effective at extracting across the board. This was compared with Al(NO3)3, which is even more effective than sodium nitrate.

Uranyl nitrate was shown to decrease D-values for Pu, simply because uranyl loads the organic phase, reducing the amount of free TBP, which lowers D-values for all other dissolved species. The author notes that plutonyl nitrate is less extractable than uranyl nitrate by a factor of approximately 10, which is unusual because increasing atomic number usually associates with increasing extractability for the lanthanides and actinides.

1. Criticism

In the opening paragraph the authors note that Pu(III) is less extractable than the other two Pu states. Throughout the paper it is never discussed why this is the case, namely, why the even oxidation states are more favorable extracted into the TBP, and why the (IV) oxidation state is more extractable than the (VI).

Experimental procedures for this paper were not described well for this paper. There is a blanket reference for the experimental procedures, but the publication should stand on its own. Specific instances of this are:

1. The experimental procedure for alpha samples and titration are not described at all and associated errors in the procedure are not highlighted
2. Poor description for the “back extraction technique” and “forward partitions.” This is especially difficult to understand when errors between solutions are described when the solutions being measured are specifically stated.
3. Titration measurements

Most experiments were run at trace concentrations of Pu, and disproportionation is discounted based on a reference at a much higher concentration. The author says, “our experiments at higher plutonium concentrations should be unaffected by disproportionation,” which is not in dispute, but they fail to mention effects at their lower concentrations.

Authors quote a 10% reproducibility error but fail to mention why this is the case and where these errors stem from. Also they state that their results are in general agreement with other published data, but in the paragraph where this is mentioned, no citation is provided.

The temperature coefficient for Pu was measured to be low by raising the temperature of a system already at equilibrium. The temperature change used was 15oC and probably not indicative of the temperature coefficient in general.

These scoping studies for Pu partition coefficients will probably be used in context of irradiated fuel. Adding fission products to solution, adds ions to the solution, which change the partition coefficient. This effect was not studied nor mentioned.

1. Conclusion

This paper provides useful partition coefficient constants for plutonium under varied circumstances. The experimental procedure was described poorly and errors were not quantified such that the reader is uncertain about procedures and sources of error in the experiment. The authors defend a point that would be useful for my dissertation, namely that the shape of D-value versus nitric acid concentration would remain the same for different concentrations of TBP. This is useful because my dissertation results could be extrapolated out to different TBP loadings.