

## **Feasibility and challenges of $^{22}\text{Na}$ based radioactive tracer dilution for mass measurement of molten salts**

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### **ABSTRACT**

Molten salts play a crucial role as electrolytes in the pyroprocessing of spent nuclear fuels, as well as being used as fuel salt in molten salt reactors (MSRs). These salts contain special nuclear materials that are dissolved within them, and accurate knowledge and monitoring of their inventory is necessary for nuclear materials accounting and safeguards purposes. However, determining the total mass of molten salts is a difficult task due to the complicated shapes of containers in pyroprocessing, and density variation caused by fission, on-line refueling, temperature differential, and changes in composition over time during an MSR operation. In recent years, an innovative technique called radioactive tracer dilution (RTD) coupled with gamma spectroscopy has been proposed and evaluated as a potential means of accurately measuring the total mass of molten salt for pyroprocessing of spent nuclear fuels. In this study,  $^{22}\text{Na}$  was used as a radioactive tracer, and LiCl-KCl based tracer salt that bears  $^{22}\text{NaCl}$  was prepared and spiked into the molten LiCl-KCl- $\text{UCl}_3$  salt for uranium electrorefining, a critical step for pyroprocessing. To evaluate the potential application of the  $^{22}\text{Na}$  based RTD for mass monitoring of the molten salt system in MSRs, a small amount of  $\text{MgCl}_2$ -KCl- $\text{UCl}_3$  (depleted uranium) fuel salt was irradiated in-core in a research reactor at The Ohio State University and then analyzed for the fission products' gamma spectrum. The primary objective of this irradiation was to evaluate the potential gamma spectrum interference at 1274.5 keV of  $^{22}\text{Na}$  peak as well as the low energy peaks from  $^{154}\text{Eu}$ . In this paper, the feasibility and challenges of  $^{22}\text{Na}$ -based radioactive tracer dilution for mass measurement of molten salt systems were summarized, and some approaches for addressing the challenges were proposed for future research.

### **INTRODUCTION AND BACKGROUND**

Molten salts, because of their unique properties in chemical and radiological stability, thermophysical properties (density, thermal conductivity, etc.), and solubility of fission products in them, have been increasingly used/ considered for different applications. Some typical applications include pyroprocessing of spent nuclear fuels where molten salts are used as electrolytes[1,2], molten salt reactors (MSRs) where molten salts are used as fuel salts or coolants

[3,4], and concentrated solar power systems where molten salts are used as thermal storage media [5,6].

Pyroprocessing is a high temperature electrochemical process in molten salts for recycling spent nuclear fuels (SNFs) including oxide fuels and metallic fuels. For oxide fuels such as uranium oxide fuels used in light water reactors, the uranium oxides are reduced to uranium metal in a LiCl-Li<sub>2</sub>O salt at around 650°C, and then the uranium metal is electrorefined in a LiCl-KCl-UCl<sub>3</sub> salt. Metallic fuels can be directly processed via electrorefining. More details on pyroprocessing in general, oxide reduction, and electrorefining can be found in relevant literature [7–10].

In both the oxide reduction and electrorefining processes, the fission products and other special nuclear materials will be accumulated in the molten salts. For safeguards purposes, it is necessary to accurately know the total mass of the nuclear materials in the salt including the isotopic compositions and the total mass of the salt as well. However, it is a challenging task to know the total mass because of the complicated shapes of the system, composition and density changes, materials losses due to different factors (e.g. vaporization, impurity induced oxidation of the salts, etc.) during the operations.

Similarly, in MSR, the fission products will be dissolved and accumulated in the fuel salt over the duration of the reactor operation. The composition of the fuel salt will change over time. The total mass determination of the molten salts in MSR is likely more challenging than that for pyroprocessing molten salt systems. It is needed to know the volume of the salt and the density as well, both of which are difficult to measure accurately. Particularly, the density measurement is inconvenient in terms of the facility requirements and lead time for the results.

In recent years, a radioactive tracer dilution (RTD) was proposed as a technique for determining the total mass of molten salts and evaluated in terms of its feasibility using the molten salt systems for processing the spent nuclear fuels [11–14]. The <sup>22</sup>Na was selected as the radioactive tracer, and the molten salt systems studied included 600g-scale LiCl-KCl salt with different amount of salt used for electrorefining and a 8kg scale electrorefiner. The scientific principle, features, and experimental results were detailed in recent publications [13,14]. With regards to the principle of RTD for mass measurement, briefly, the mass of the molten salt in the vessel can be determined based on the radioactivity conservation rule:

$$M \cdot a_0 + m \cdot A = (m + M) \cdot a \quad (1)$$

where  $M$  is the mass (in gram) of the unknown molten salt in the vessel,  $m$  is the mass (in gram) of the tracer salt added into the molten salt,  $a_0$  is the specific radioactivity of <sup>22</sup>Na isotope (in  $\mu\text{Ci/g}$ ) for the molten salt in the vessel before tracer salt addition,  $A$  and  $a$  are the specific radioactivity of <sup>22</sup>Na isotope (in  $\mu\text{Ci/g}$ ) for the tracer salt and for salt samples taken from the vessel after tracer salt addition, respectively. Therefore, the mass ( $M$ ) of the molten salt in the vessel is 
$$M = \frac{m \cdot (A - a)}{a - a_0}.$$

The potential application of the <sup>22</sup>Na RTD technique for the total mass determination of MSR, is complicated by the salt chemistry due to the addition of the fission products, online-refueling, and

fuel burn-up. Therefore, to understand how the irradiation would affect the  $^{22}\text{Na}$  radioactivity measurement, a small amount of  $\text{MgCl}_2\text{-KCl-UCl}_3$  (depleted uranium) salt was irradiated in the OSU research reactor under  $1.1 \times 10^{13}$  n/cm<sup>2</sup>/s for one hour. The irradiated salt with  $^{22}\text{Na}$  tracer addition was then analyzed by gamma spectroscopy.

In this paper, we summarized the findings on the gamma spectroscopy of fission-products-bearing salt samples with a primary emphasis on the feasibility and challenges associated with the RTD technique for molten salt mass determination.

## EXPERIMENTAL

For context, the experimental procedures for RTD typically include (1) preparation of tracer salt; (2) addition of a predetermined amount of tracer salt to the molten salt system; (3) salt sampling after the tracer salt after homogeneous mixing; and (4) gamma spectroscopy analysis of the salt samples. Table 1 lists the two typical RTD experiments performed using the molten salts systems for pyroprocessing spent nuclear fuels. The salt samples were analyzed with gamma spectroscopy using an HPGe detector and the data acquisition time being 4 hrs.

Table 1 The initial salt mass and  $^{22}\text{Na}$  activity added in two RTD experiments

Salt	Salt mass	Activity of $^{22}\text{Na}$ Tracer added
Baseline ER salt	N/A	0
LiCl-KCl-24wt% ER salt	688 g	1360 $\mu\text{Ci}$
ER salt	8000 g (estimated)	4214 $\mu\text{Ci}$

For the irradiation experiment in the OSU research reactor, a 6.065 g  $\text{MgCl}_2\text{-KCl-UCl}_3$  fuel salt with 1.21mg  $^{235}\text{U}$  was double encapsulated and irradiated for one hour to achieve a total fluence of  $3.96 \times 10^{16}$  n/cm<sup>2</sup>. The one-hour irradiation test was not enough to produce significant quantities of longer lived fission products such as  $^{154}\text{Eu}$  and  $^{137}\text{Cs}$ ,  $^{22}\text{Na}$  was still added to evaluate other possible energy peak interferences.

## RESULTS AND DISCUSSION

The RTD technique for mass measurement is based on the dilution of the tracer and gamma spectroscopy analysis. The dilution of tracer in the molten salt is a chemical process. The gamma spectroscopy is the critical factor in determining the accuracy of the total mass measurement by RTD. Figure 1 shows the typical gamma spectra of salt samples taken from the tracer salt, base line ER salt, 688g LiCl-KCl-24%ER salt with  $^{22}\text{Na}$  tracer salt addition, and 8000g ER salt with  $^{22}\text{Na}$  tracer salt addition. The radioactivity of the  $^{22}\text{Na}$  tracer and  $^{154}\text{Eu}$  in the salt samples were shown in Table 2. There are multiple isotopes in the ER salt, like  $^{241}\text{Am}$ ,  $^{137}\text{Cs}$ ,  $^{154}\text{Eu}$  etc. But only  $^{154}\text{Eu}$  was shown in the table here because it exhibits the same energy peak in the gamma spectra

as  $^{22}\text{Na}$  at energy level of around 1274.5keV, which is the major fission product of interest in this study that may affect the accuracy and uncertainty of the  $^{22}\text{Na}$  radioactivity measurement.

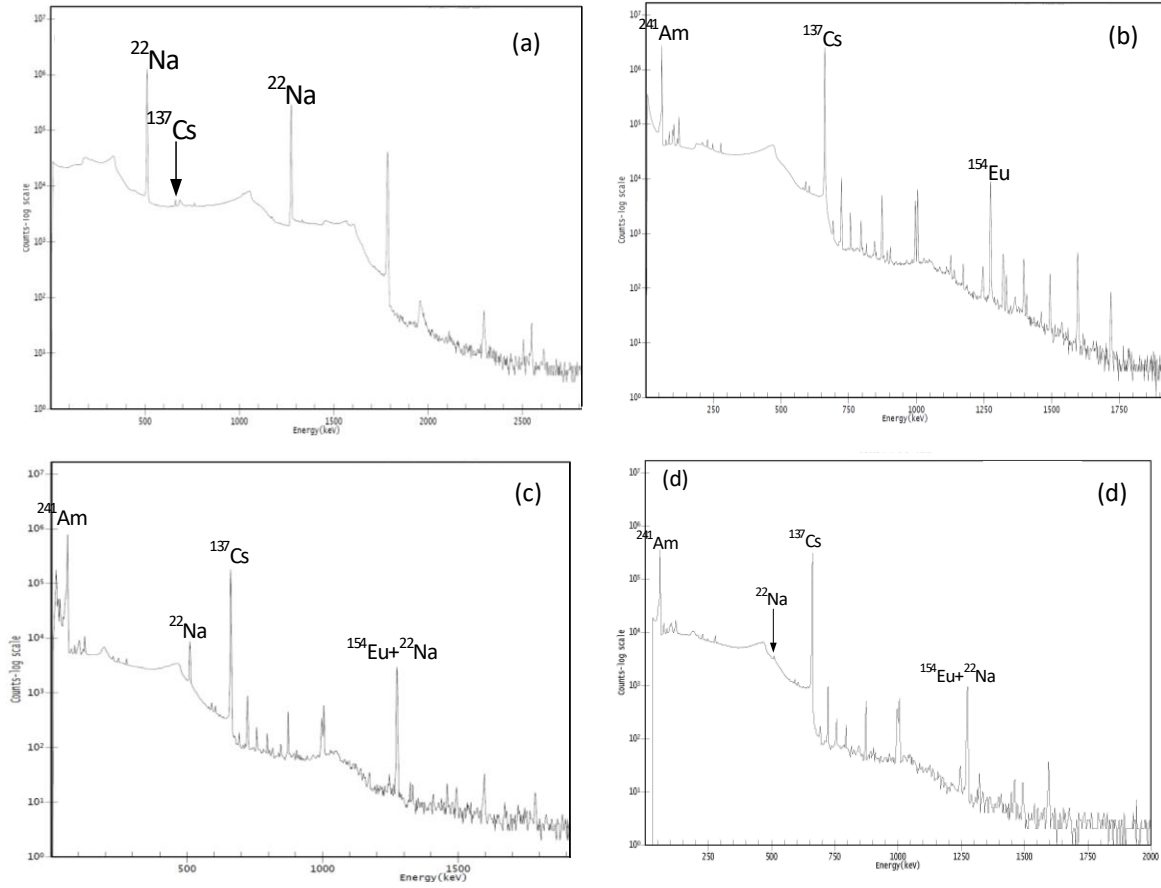


Figure 1 Typical gamma spectra of salt sample taken from the tracer salt (a), baseline ER salt (b), LiCl-KCl with 24% ER salt with  $^{22}\text{Na}$  spiking (c), and ER salt with  $^{22}\text{Na}$  spiking (d)

Table 2 Gamma radioactivity of the  $^{22}\text{Na}$  and  $^{154}\text{Eu}$  isotopes in the salt samples

	$^{154}\text{Eu}$ ( $\mu\text{Ci/g}$ )	Uncertainty of $^{154}\text{Eu}$ (in %)	$^{22}\text{Na}$ ( $\mu\text{Ci/g}$ )	Uncertainty of $^{22}\text{Na}$ (in %)
Tracer salt LiCl-KCl- $^{22}\text{NaCl}$	0	N/A	43.6	2
Baseline ER salt	5.8	2%	N/A	N/A
LiCl-KCl-24wt% ER salt	2.0	2%	2.1	2%
ER salt with $^{22}\text{Na}$ addition.	5.6	2%	0.55	13%

In the tracer salt sample, as expected, the gamma peak is predominantly from  $^{22}\text{Na}$ . The tiny  $^{137}\text{Cs}$  peak (which can be considered negligible) is mainly from the contamination during sampling in the hot cell. In the baseline ER salt without  $^{22}\text{Na}$  tracer addition, in addition to the  $^{241}\text{Am}$  and  $^{137}\text{Cs}$  peaks, there are multiple  $^{154}\text{Eu}$  peaks spanning from an energy range of 700–1700 keV. In Figure 2c (LiCl-KCl-24wt% ER salt), in addition to all the gamma peaks as shown in Figure 2b (for ER salt), the  $^{22}\text{Na}$  peak at 511keV was shown clearly, another  $^{22}\text{Na}$  peak coincides with that of  $^{154}\text{Eu}$ . In the 8000g ER salt with  $^{22}\text{Na}$  tracer addition, the peaks are similar to those in Figure 2b and 2c, and the  $^{22}\text{Na}$  peak at 511keV is just marginally visible in the spectrum, and another  $^{22}\text{Na}$  peak at 1274.5keV coincides with that of  $^{154}\text{Eu}$ .

From the radioactivity values for  $^{22}\text{Na}$  in Table 2, the uncertainty for the tracer salt and LiCl-KCl-24wt% ER salt is consistently low, at 2%. But the uncertainty for  $^{22}\text{Na}$  in the 8000g ER salt with  $^{22}\text{Na}$  addition is 13%, which is more than 6 times that for the LiCl-KCl-24wt% ER salt and is not acceptable for accurate molten salt mass measurement. The main reason for the significantly higher uncertainty is considered due to the fission product  $^{154}\text{Eu}$  affecting the  $^{22}\text{Na}$  measurement. In the ER salt with  $^{22}\text{Na}$  addition, the radioactivity ratio for  $^{22}\text{Na}/^{154}\text{Eu}$  is about 0.1, which means 90% of the total radioactivity at 1274.5keV is from  $^{154}\text{Eu}$ . This is expected to lead to higher uncertainty for  $^{22}\text{Na}$ . We have previously identified the techniques to improve the uncertainties such as increasing the  $^{22}\text{Na}/^{154}\text{Eu}$  ratio, using longer data acquisition time, etc. Note that the radioactivities of the  $^{22}\text{Na}$  and  $^{154}\text{Eu}$  were automatically analyzed by Apex Gamma software using standard parameters. Some more refined or tuned data analysis in gamma spectroscopy may also improve the uncertainty of the  $^{22}\text{Na}$  radioactivity in  $^{154}\text{Eu}$  bearing salt samples.

There is another type of fission product effect—the presence of the very high gamma radioactivity isotopes in the salt sample which can lead to the high dead time during the gamma spectroscopy measurement. The high dead time can affect the uncertainty of the gamma radioactivity. In the ER salt samples here, the main fission products with high gamma radioactivity is  $^{137}\text{Cs}$ , about  $460\mu\text{Ci/g}$ , which is not very high from the viewpoint of affecting dead time during measurements. We previously reported gamma spectroscopy of Mark-IV ER salt samples which contain  $2.4\times 10^5\mu\text{Ci/g}$   $^{137}\text{Cs}$ . For radiological safety reasons and to mitigate the dead time effect, the sample may need to be significantly diluted to reduce the radioactivity or use some shielding to reduce the radioactivity detected by the HPGe detector. But this will also significantly decrease the counts for the  $^{22}\text{Na}$  and increase the uncertainty. To address these challenges, a significantly longer data acquisition time is likely needed to generate enough counts for reliable measurements.

The detection limit is another challenge for the total mass measurement. Practically, for the purpose of accurately measuring the total mass, the detection limit can be defined as the minimum needed  $^{22}\text{Na}$  radioactivity in the salt samples that can be measured by the gamma spectroscopy system with good confidence, for example, 5% at  $1\sigma$ . Since the uncertainty is affected by multiple factors (fission products,  $^{154}\text{Eu}$ , dead time, etc.), the detection limit is also interlinked with the fission product effect. If the  $^{154}\text{Eu}$ , particularly when its gamma radioactivity is high, is present in the salt, the needed  $^{22}\text{Na}$  radioactivity is expected to be higher. Currently the detection limit of  $^{22}\text{Na}$  based RTD is still unknown, but it appears that when the  $^{22}\text{Na}$  radioactivity is about 30% that of  $^{154}\text{Eu}$ , an uncertainty of 5% for  $^{22}\text{Na}$  can be achieved.

The detection limit is particularly important for molten salt systems of large mass or volume since it will directly affect the amount the  $^{22}\text{Na}$  to be added. If the total mass of the system (for example, a commercial molten salt reactor) is high, a significantly large amount of  $^{22}\text{Na}$  is likely needed. Considering the high cost of the  $^{22}\text{Na}$ , such large amounts of  $^{22}\text{Na}$  may be not practical for the total mass measurement unless there are no other options.

Figure 2 depicts the gamma spectroscopy of irradiated  $\text{MgCl}_2\text{-KCl-UCl}_3$  salt with the addition of a  $^{22}\text{Na}$  tracer within an activated quartz and aluminum-6061 container. The gamma ray peaks from various fission products were identified post-irradiation, but no isotope was found to overlap or be in close proximity to 1274.5keV for  $^{22}\text{Na}$  at the specified concentration level. The  $^{59}\text{Fe}$  mainly comes from impurities in the outer encapsulation of the aluminum alloy. This suggests that  $^{22}\text{Na}$  RTD shows promise for total mass measurement of MSR from the perspective of fission products. However, the challenge of total mass uncertainty for MSRs remains to be analyzed. It is noteworthy that  $^{22}\text{Na}$  has a high neutron absorption cross-section (28,834 barn), and will burn off after a prolonged period following addition in the salt reactor. This feature is advantageous since the tracer eliminates itself, disallowing the activity of Na-22 in the system to build-up permanently.

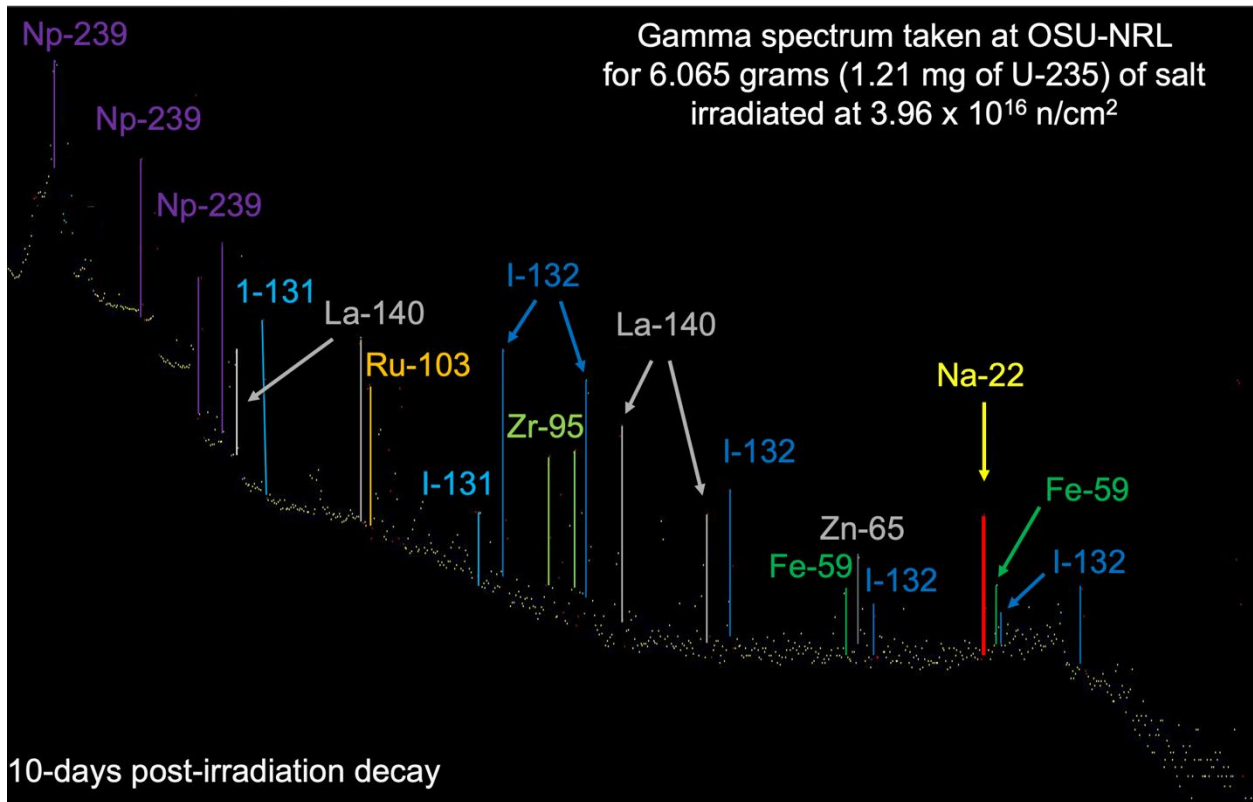


Figure 2 Gamma spectroscopy of  $\text{MgCl}_2\text{-KCl-UCl}_3$  salt irradiated in OSU research reactor

## SUMMARY

The feasibility and challenges of the  $^{22}\text{Na}$  based RTD technique for total mass determination of molten salt systems were summarized.

For the molten salt systems for pyroprocessing spent nuclear fuels, the presence of fission products particularly  $^{154}\text{Eu}$  in the salt samples, may affect the uncertainty of  $^{22}\text{Na}$  radioactivity during gamma spectroscopy. Detection limit of the  $^{22}\text{Na}$  based RTD for accurate mass measurement may also be affected by the fission products. Increasing the radioactivity ratio of  $^{22}\text{Na}/^{154}\text{Eu}$  is expected to improve the uncertainty for  $^{22}\text{Na}$  based RTD for molten salt mass measurement.

In addition, the one-hour irradiation test of  $\text{MgCl}_2\text{-KCl-UCl}_3$  salt at the OSU research reactor shows that although many radioactive isotopes were identified post-irradiation, no significant spectral interference with the  $^{22}\text{Na}$  peak at 1274.5 keV was found. This attests to the promising potential of using  $^{22}\text{Na}$  based RTD for mass monitoring in MSRs.

## ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy (DOE), Office of Nuclear Energy, under DOE Idaho Operations Office contract number DE-AC07-05ID14517 and Nuclear Energy University Program.

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